POSEIDON'S PAINTBOX

HISTORICAL ARCHIVES OF OCEAN COLOUR IN GLOBAL-CHANGE PERSPECTIVE

POSEIDON'S VERFDOOS

HISTORISCHE ARCHIEVEN BETREFFENDE DE KLEUR VAN DE ZEE IN PERSPECTIEF VAN MONDIALE KLIMAATVERANDERING

(met een samenvatting in het Nederlands)

Proefschrift

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ABOUT THE COVER

The cover of this thesis was designed by myself and painted by Gerd Jan Roos,
a professional artist since 1979, who lives at the Island of Texel,
The Netherlands.

DIT PROEFSCHRIFT IS OPGEDRAGEN AAN MIJN VROUW IRENE WERNAND-GODEE
EN AAN MIJN MOEDER ADA WERNAND-SCHOOLEMAN

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SAMENVATTING

De titel van dit proefschrift verwijst naar de Griekse god van de zee Poseidon, die ongetwijfeld geen ’paintbox’ (verfdoos) heeft gehad, hoewel er genoeg aanwijzingen zijn dat dat wel degelijk het geval kan zijn geweest: de ‘Historical Archives of Ocean Colour’ die in de titel figureren spreken van vele kleuren van oceanen en zeeën. Dat deze ‘in Global-Change Perspective’ worden behandeld in deze dissertatie is nieuw: in de tijden dat de Grieken geloofden in vele goden was er nog geen sprake van ‘global change’ en opwarmen van de aarde door broeikasgassen. Het proefschrift is een compilatie van deels al gepubliceerde wetenschappelijke artikelen met het gemeenschappelijk thema ‘kleur van de zee’; in deze dissertatie worden gedachten, ideeën, bevindingen en theorieën behandeld die te maken hebben met observaties en analyses van de kleur van de zee (‘ocean colour’) over de periode 1600 tot 2000; dit is dan ook de prelude voor een discussie over moderne observatiemethodes ten behoeve van waarnemingen van ‘ocean colour’: met behulp van in satellieten gemonteerde sensoren waarmee de spectrale samenstelling van licht kan worden bepaald.

In de inleiding van dit proefschrift wordt ingegaan op de aan het bovengenoemde thema gerelateerde historische achtergrond van de mariene optica, en de instrumenten waarmee in de afgelopen eeuwen is waargenomen en gemeten; net als in alle exacte wetenschappen is er in de mariene optica sprake van een geleidelijke ontwikkeling: die van ‘meten’, dat vele eeuwen geleden begon, naar ‘weten’ en, sinds niet meer dan een eeuw, begrijpen van een verschijnsel dat nog steeds velen aanspreekt, niet alleen wetenschappers. Er worden achtereenvolgens zes thema’s behandeld.

Het eerste thema, *ontwikkelingen in de visie op de optica van de oceaan van 1600 (Hudson) tot 1930 (Raman) en de geleidelijke verschuiving in interpretatie van de kleuring van natuurlijk water*, gaat over de vraag hoe het te verklaren is dat er een lange tijd nodig was om het fenomeen ‘kleuring van de zee’ te verklaren, met name de typische blauwe kleur, terwijl dit fenomeen al eeuwen de interesse van zeevaarders had, voor praktische doeleinden van navigatie en opsporen van vis – waarover later meer.

Het tweede thema, *de geschiedenis van de Secchischijf*, betreft een beschrijving van de zoektocht naar een methode om helderheid van zeewater te bepalen voor de net genoemde navigatiedoeleinden (kleurveranderingen bij nadering van kusten, bij voorbeeld) en voor simpelweg het opsporen van voorwerpen op de zeebodem. De zoektocht naar het efficiënt bepalen van helderheid in meren en zeeën eindigt met een sinds de laatste decennia van de 19de eeuw en tot op de dag van vandaag gebruikte methode, die met de Secchischijf.

Het derde thema, *een spectrale analyse van de Forel-Ule 'zeekleurenvergelijkingsschaal'*, betreft de vraag hoe nauwkeurig met deze in het kader van oceanografisch en limnologisch onderzoek in 1890 voorgestelde schaal de kleur van een zeegebied is vast te leggen in het perspectief van hedendaagse metingen van en aan de kleur van de zee.

Het vierde thema, *veranderingen in kleur van de Noordelijke Stille Oceaan sinds 1930*, gaat over de vraag of er kleurveranderingen door middel van gearchiveerde historische Forel-Ule-observaties, in dit gedeelte van de oceaan zeer frequent gedaan, over langere termijn zijn vast te stellen in verband met 'global change': met name de opwarming van de aarde kan een geleidelijke verandering in kleur teweeg brengen vanwege het effect op biologische, chemische en fysische aspecten van de oceaan-oppervlakte.

Het vijfde thema, o*p de MERIS-satellietsensor gebaseerde classificatie van de kleur van de oceaan door middel van de Forel-Ule schaal*, behandelt de vraag of er een verband is te leggen is tussen de oude Forel-Ule methodiek, de classificatie van de zeekleur door vergelijk met één van de schaalkleuren, en de recente methode van het meten van deze kleur vanuit satellieten.

Het zesde thema, *trends in oceaankleur en chlorofyl vanaf 1889 tot heden*, behandelt kleurveranderingen per 10 jaar over de langst beschikbare Forel-Ule-reeks per oceaan en zee en gaat over de vraag of het mogelijk is deze kleurverandering om te zetten naar chlorofylconcentraties (indicatief voor de biomassa van marien microalgenplankton) om zodoende aansluiting te krijgen met de huidige tijd, nu chlorofylconcentraties worden bepaald door gebruik te maken van nieuwe technieken, zoals satelliet-remote sensing, die gekalibreerd wordt met hogedruk-vloeistof-chromatografie (HPLC) voor pigmentanalyse van microalgenpigmenten.

OPTICA VAN DE OCEAAN VAN 1600 (HUDSON) TOT 1930 (RAMAN); VERSCHUIVING IN INTERPRETATIE VAN DE KLEURING VAN NATUURLIJK WATER

Voor de beschrijving van de nomologische kennis, dus voor het ontdekken van beschreven wetmatigheden betreffende de kleuring van de zee, in het bijzonder de blauwkleuring van het zeewater, heb ik zowel wetenschappelijke publicaties als gerelateerde achtergrondinformatie geraadpleegd vanaf het begin van de 20^{e} eeuw, teruggaand in de tijd tot aan het begin van de 17de eeuw. Het doel was om de ontwikkeling van ideeën van ontdekkingsreizigers en wetenschappers ten aanzien van de kleur en de doorzichtigheid van natuurlijke wateren met hun oorzaak te beschrijven, en te toetsen aan huidige inzichten. De periode waarover de beschreven ontwikkelingen plaatsvinden, bevindt zich tussen de tijd van Henry Hudson de zeevaarder

(1565?-1611) en Chandrasekhara Raman (1888-1970), de wetenschapper die uiteindelijk de oorzaak van de blauwe kleur van water beschreef. Dit hoofdstuk wordt gekenmerkt door de beschrijving van waarnemingen door een verscheidenheid aan amateurs, maar ook beroemde wetenschappers die allen door het fenomeen ('de kleur van de zee') werden geïntrigeerd. Een aantal apparaten dat werd ontwikkeld om de kleur en de aan de kleur gekoppeld doorzichtigheid van zeewater te kwantificeren wordt besproken.

Twee van deze apparaten, in de 19de eeuw ontwikkeld, zijn nog steeds in gebruik; ze worden geanalyseerd en beschreven in de hoofdstukken 3 en 4. In de hierop volgende hoofdstukken wordt dieper ingegaan op data die met behulp van deze instrumenten over de afgelopen honderd jaar is verzameld.

De mechanismen verantwoordelijk voor de kleuring van zeewater werden pas echt blootgelegd aan het begin van de 20ste eeuw. Ik concludeer dat de relatief lange tijd, ongeveer 300 jaar, die nodig was om deze mechanismen te verklaren mede werd veroorzaakt doordat het specifieke onderwerp gedurende lange tijd in de marge van fysisch-biologisch onderzoek werd behandeld en de waterdistillatietechnieken, het maken van schoon helder water, pas aan het begin van de 20ste eeuw vervolmaakt werden. Dit hoofdstuk eindigt met Chandrasekhara Venkata Raman, die in 1922 bewees dat het de moleculaire verstrooiing van voornamelijk de kortere golflengten (blauw licht) en de absorptie van de langere golflengten (groen- tot rood licht) van het zonlicht in water de blauwe kleur veroorzaken. Voorbeelden van blauw water zijn de aan voedingsstoffen arme oceaan waarin de biomassa van microalgen en de hoeveelheid 'gilvin' en gesuspendeerd materiaal zeer laag is.

DE GESCHIEDENIS VAN DE SECCHISCHIJF

De wetenschappelijke vraagstelling voor dit hoofdstuk is mede bepaald na lezing van historische publicaties, die betrekking hadden op de interesse van toenmalige zeevaarders en wetenschapper om met behulp van een diversiteit aan voorwerpen en eenvoudige instrumenten de doorzichtigheid van zeewater vast te leggen. De belangstelling voor dit type van onderzoek kwam voort, zoals boven al aangeduid, uit basale overwegingen zoals het vergaren van kennis van bodemdiepte en helderheid van het kustwater voor navigatiedoeleinden, belangrijk voor een vroegtijdige herkenning van ondiepten en zandbanken. Pas veel later kwam het besef dat de helderheid van water een belangrijke ecologische waterkwaliteitsparameter is.

Een nu nog bestaande meetmethode om de doorzichtigheid van het water te meten is het gebruik van een in 1865, door de Italiaanse astronoom Secchi bedachte, witte schijf. Diverse verwijzingen naar deze meetmethode aan het eind van de 19de eeuw zouden de naamgeving

'Secchischijfmethode' opleveren, hoewel velen Secchi voorgingen ten aanzien van methoden voor de bepaling van de doorzichtigheid van meren en zeeën. Angelo Secchi startte zijn wetenschappelijke experimenten in 1864 voor de kust van de plaats Civitavecchia, noord van Rome. Dit hoofdstuk beschrijft de ontwikkeling van een nog steeds veelvuldig gebruikte methode om de helderheid van water te bepalen. Secchi was de eerste onderzoeker die uitgebreid onderzoek deed naar de grootte, de kleur en het te gebruiken materiaal van de schijf en beschreef zijn metingen in relatie tot de hoogte en positie van de zon en de meteorologische omstandigheden.

De eerste verslagen met tabellen met transparantiedata van natuurlijke wateren zijn die van de Duitse naturalist Adelbert von Chamisso. Tijdens de Russische "*Rurik*"-Expeditie 1815-1818, onder het bevel van Otto von Kotzebue, zijn tientallen experimenten uitgevoerd om de helderheid van het zeewater te meten. Theepotten, aardewerken en porseleinen borden, en zelfs een witte handdoek werden gebruikt voor het vaststellen van de helderheid van zeewater. Het zou dus tot het einde van de 19de eeuw duren voordat een gestandaardiseerde manier om de helderheid (transparantie) van zeewater te bepalen werd aangenomen.

De specifieke meting, waarbij de afstand van een, in het zeewater ondergedompelde en uit het zicht verdwenen, 30 cm in diameter wit geschilderde schijf, wordt genoteerd als de 'Secchidiepte'. Deze meting is, door zijn simpelheid, zeer algemeen geworden, ook tijdens hedendaagse oceanografisch expedities. De werkwijze om de doorzichtigheid van de zee te meten werd uitgebreid beschreven door de al eerder genoemde Vaticaanse priester en wetenschapper Pietro Angelo Secchi in 1865 in het wetenschappelijk tijdschrift '*Il Nuovo Cimento Giornale di fisica, chimica e storia naturale*'. De Oostenrijkse wetenschapper Josef Roman Lorenz Ritter von Liburnau experimenteerde met diverse voorwerpen om de doorzichtigheid van water te bepalen, waaronder witte schijven, in de Golf van Quarnero (Kroatië), jaren voordat de publicatie van Secchi uitkwam. Hij stelde in één van zijn publicaties vragen bij de naamstelling van deze manier van meten en koos er zelf voor om het 'de schijvenmethode' te noemen.

Concluderend, na het lezen van de tientallen pagina's tellende publicatie over de vele, nooit eerder uitgevoerde, experimenten van Secchi, geholpen door de commandant van het pauselijke stoomjacht en onderzoeksschip "*l' Immacolata Concezione*" Alessandro Cialdi in 1864, wordt deze methode vele jaren later nog steeds door zeegaande oceanografen geprezen. Sinds het eind van de 19de eeuw zijn wereldwijd honderdduizenden metingen volgens Secchi 's methode uitgevoerd en bewaard gebleven. Deze data behoren tot de oudste oceanografische data en ze geven inzicht in de veranderingen van oceaan, zee en meer over een termijn van vele decennia. Hierdoor is het tegenwoordig mogelijk om veranderingen in doorzicht in zeeën en oceanen aan klimaatonderzoek te koppelen, waarover later meer.

SPECTRALE ANALYSE VAN DE FOREL-ULE OCEAANKLEUREN VERGELIJKINGSSCHAAL

Eind 19e-begin 20e eeuw beschreef François Alphonse Forel (zie portret Figuur 1) een veelheid aan onderzoekingen in het Meer van Genève. In zijn 3-delige limnologische monografie '*Le Léman',* waarvan het eerste deel in 1892 en het derde en laatste deel in 1904 verscheen, beschrijft hij zijn onderzoek aan het ontstaan van de kleur van dit meer. Een van de simpelste manieren, maar niettemin effectief, om deze kleur vast te leggen is de uitvinding door hem, in 1890, van de Forelschaal om de kleurnuances tussen blauw en geelgroen in 11 stappen vast te leggen. Twee jaar later breidde de Duitser Willi Ule de schaal uit met de groen tot bruine kleuren in 10 extra stappen. De totale schaal, Forel-Ule-schaal (inzet Figuur 1) genoemd, bevat zodoende 21 met water van verschillende kleuren gevulde buisjes. In dit hoofdstuk wordt de constructie van de schaal met het originele recept van de vloeistofmengsels die Forel en Ule apart hadden beschreven gepresenteerd om een reconstructie van de schaal mogelijk te maken.

In de loop van de 20ste eeuw werden de processen die ten grondslag liggen aan de (ver-) kleuring van water steeds beter begrepen. Metingen met de Forel-Ule-schaal vonden deze gehele eeuw over de hele wereld plaats, zelfs na de intrede van de meest moderne spectrale radiometers (lichtmeters). Voor elke meting vergelijkt de waarnemer de kleur van het water boven een ondergedompelde witte schijf (Secchi-schijf) met de kleur van één van kleuren van de Forel-Ule-schaal. Vanaf de introductie tot eind jaren tachtig van de vorige eeuw werd deze kleurenvergelijkingsschaal intensief gebruikt door oceanografen en limnologen (wetenschappers die binnenwater onderzoeken) voor de classificatie en monitoring van alle mogelijke watertypen, die gedomineerd worden door bijvoorbeeld chlorofyl of door dood organisch materiaal of door beide.

De gearchiveerde Forel-Ule gegevens behoren tot de oudste oceanografische gegevensreeksen, naast zoutgehalte, temperatuur en doorzicht (zie boven: de metingen met de Secchischijf). Deze dataset bevat ver in de tijd teruggaande informatie over de kleur van het zeewater op vele plaatsen op aarde en daarmee informatie over bijvoorbeeld de toenmalige chlorofylconcentratie. Deze kennis verschaft inzicht in aspecten van zeeën en oceanen over langere termijn, over een periode van ver voor de komst van de satellieten die tegenwoordig worden ingezet; en 'ocean colour'-informatie van toen kan nu gekoppeld worden aan die van tegenwoordig, waardoor het bij voorbeeld mogelijk wordt over een periode van wel 100 jaar zeekleurdata te koppelen aan klimaat gerelateerde data (temperatuur, zeestroming en zonlicht en, gerelateerd daaraan, de planktonbiomassa aan de oppervlakte, die naar verwachting verandert met genoemde factoren).

Zijn de Forel-Ule-schaalkleuren receptmatig te reproduceren, hoe nauwkeurig is de schaal en hoe bruikbaar is de schaal voor de hedendaagse oceanografie, m.a.w. geeft deze schaal vandaag de dag een goed beeld van de kleuren van de zee? De uitkomst van deze analyse is in het bijzonder van belang ten aanzien van de wetenschappelijke waarde van de dataset beheerd door de Amerikaanse National Oceanic and Atmospheric Administration (NOAA) met daarin honderdduizenden van deze Forel-Ule-observaties, verzameld in alle wereldzeeën vanaf het begin van de 20ste eeuw. In het artikel, verschenen in 2010 in het 'Journal of the European Society' (JEOS), betreffende het hier beschreven onderzoek worden naast de optische eigenschappen en de bruikbaarheid van de schaal ook het recept en de reproductie van de schaal beschreven. De schaal is eenvoudig te reproduceren door middel van een samenstelling van kopersulfaat-, kaliumchromaat- en kobaltsulfaat oplossing. De spectrale transmissie per Forel-Ule-schaalkleur is gemeten met behulp van een moderne hyperspectrale radiometer (radiantiemeter) volgens het schema van Figuur 2.

Figuur 3 toont de resultaten van de door eigen spectrale analyse verkregen transmissiespectra. De zeer geleidelijke spectrale overgangen met een verschuiving van blauw via blauwgroen naar groen en bruin zijn eenvoudig waar te nemen. De Forel-Ule-observatie van de kleur van de zee levert een numerieke waarde tussen 1 en 21 op en een hedendaags meting van deze kleur geschiedt door middel van een hyperspectrale meting. Door middel van colorimetrische berekeningen kan een dergelijke hyperspectrale meting omgezet worden in één chromaticiteits coördinaten set met de kleurcoördinaten x, y. Dezelfde omzetting geld voor de hyperspectrale Forel-Ule-transmissiespectra van Figuur 3. Zodoende kunnen historische- met hedendaagse metingen worden vergeleken.

VERANDERINGEN IN DE KLEUR VAN DE NOORDELIJKE STILLE OCEAAN SINDS 1930

Het doel van dit aspect van mijn studie was het verkrijgen van inzicht in de stabiliteit van de kleur van de Noordelijke Stille Oceaan. Dit gebied wordt gekenschetst door de duizenden Forel-Ule (verder afgekort met *FU*) observaties die sinds 1930 plaatsvonden. Deze hoeveelheid observaties maakt het mogelijk data uitgebreid statistisch te analyseren. Zijn deze kleurenveranderingen gerelateerd aan natuurlijke cycli, zijn deze seizoensgebonden of zijn ze gebonden aan mondiale veranderingen? Bestudering van de kleur van het noordelijk gedeelte van 's werelds grootste oceaan kan wetenschappers inzicht verschaffen in het aan de zeekleur gerelateerde fytoplankton en dus het effect op het systeem Aarde, immers: deze plantaardige organismen kunnen dit systeem beïnvloeden, alleen al omdat ze de basis van de mariene voedselketen vormen.

De waardevolle Forel-Ule-dataset in dit gebied van de oceanen is gedigitaliseerd en wordt beheerd door het Nationale Oceanografisch Data Centrum (NODC/NOAA) in de Verenigde Staten. De verschillende seizoenen, maar ook eventuele lange-termijnveranderingen, kunnen als oorzaak voor een mogelijke verandering in de kleur van de oceaan worden gezien. Om menging van het rivier- en kustwater rond deze oceaan uit te sluiten zijn de observaties gefilterd. Alleen observaties van open zee, op meer dan 500 km van het vaste land, zijn voor deze analyse gebruikt. Na filtering bleven er 17000 observaties over, die de periode 1930 tot 1999 bestrijken. Voor een statistische analyse zijn de *FU* observaties ingedeeld per 5 jaar per seizoen en per 5 jaar onafhankelijk van het seizoen. In Figuur 4 zien we de resultaten van een seizoen onafhankelijke analyse.

De Noordelijke Stille Oceaan werd tussen de perioden 1930-34, met een gemiddelde *FU*=2, en 1950-54, met een gemiddelde *FU*=4.1, groener. Vervolgens werd de oceaan tot 1975-79 met een gemiddelde *FU*=2.1 weer blauwer. Gedurende de volgende 5 jaar werd de oceaan weer wat groener, gedurende de volgend 10 jaar weer blauwer en vanaf 1990-94 zien we dat het water weer groener nijgt te worden. De groenste periode van deze oceaan, met een gemiddelde *FU* waarde van 4.1, is gevonden tijdens het lustrum van 1950-54. Het blauwste oceaanwater, met een gemiddelde *FU*=1.7, treffen we aan in de periode 1990-94. Over de onderzochte periode verandert de kleur significant. Na deze vaststelling zou vervolgonderzoek zich kunnen richten op de mechanismen verantwoordelijk voor deze veranderingen. Kunnen deze verandering in zeekleur klimaat-gerelateerd kunnen zijn? De uitkomsten van mijn onderzoek zijn voor de periode 1960-1984 voor dit gedeelte van de oceaan in lijn met de resultaten, van op chlorofyl geanalyseerde watermonsters, van Venrick *et al*. (*'Science'*, 1987). Dit geeft vertrouwen in uitkomsten van de rest van de hier beschreven perioden. In een andere publicatie van Boyce *et al*. in Nature 2010 wordt een afwijkende conclusie gegeven; n.l. een geleidelijke afname van het fytoplankton in de Noordelijke Stille Oceaan sinds 1900. De conclusies van deze onderzoekers zijn gebaseerd op een omstreden methode door de chlorofylconcentratie uit de Secchidiepte te berekenen. Anders dan bij de hier gepresenteerde resultaten, hebben zij bij hun analyses ook data van het meer gekleurde kustwater meegenomen. Dit water heeft grote invloed op de kleur van de open zee en is in grote mate bepalend voor de uitkomsten van hun analyse.

Zoals al eerder werd opgemerkt wordt de oceaankleur deels bepaald door de aanwezigheid van fytoplankton; een toename in fytoplankton betekent een grotere opname van CO_2, één van de gassen dat het broeikaseffect en daarmee temperatuursverandering teweegbrengt. Fytoplankton is gerelateerd aan de *FU*-kleur, niet voor niets dus een door de Wereld Meteorologische Organisatie (WMO) vastgestelde essentiële klimaatvariabele. Toekomstig onderzoek zal zich moeten richten op het blootleggen van de mogelijke verbanden die er bestaan tussen factoren die het klimaat beïnvloeden en de kleur van de oceaan. Een eerste stap is de analyse van historische *FU*-observatiereeksen van andere oceanen en wereldzeeën en het koppelen van deze reeksen aan van de satelliet afgeleide oceaankleur. Dit komt ter sprake in het volgende hoofdstuk.

OP DE MERIS-SATELLIETSENSOR GEBASEERDE 'OCEAN COLOUR' CLASSIFICATIE MET BEHULP VAN DE FOREL-ULE SCHAAL

In dit hoofdstuk worden berekeningen (algoritmen) gepresenteerd om multispectrale Medium Resolution Imaging Spectrometer (MERIS) satellietsensordata om te zetten in Forel-Ule waarden 1 tot 21.

Omzetting van spectrale data naar Forel-Ule is tweeledig; de kleur van oceanen en kustwateren wordt vereenvoudigd geclassificeerd door een numerieke waarde tussen 1 en 21 in plaats van een meerkanaals of hyperspectrale classificatie; en satelliet-oceaankleuren data kunnen voor het eerst worden gekoppeld aan historisch gemeten oceaankleuren: die van de *FU*-schaal. MERIS is een meerkanaals radiometer met een spectraal bereik van 390 (blauw) tot 1040 (infrarood) nanometer, opgedeeld in vijftien programmeerbare spectrale banden. De onder auspiciën van de Europese ruimtevaart organisatie (European Space Agency, ESA) gebouwde ENVISAT satelliet, met hierop o.a. het MERIS instrument, is in maart 2002 de ruimte ingebracht voor het vastleggen van de kleur van zowel de atmosfeer, van kust- en oceaanwater en van land en poolijs. De missie van MERIS kan worden gezien in het kader van wetenschappelijk projecten met als doel het inzicht vergroten in de rol van de oceaan en oceaanproductiviteit ('primaire productie') op ons klimaat.

Met de komst van MERIS werd het voor het eerst mogelijk een koppeling te maken tussen de meerkanaals-spectrale satellietdata en Forel-Ule-data. Van de 15 aanwezige spectrale banden vallen er 9 banden goed verdeeld over het zichtbare spectrum en dit aantal banden is genoeg om via colorimetrische berekeningen de chromaticiteits coördinaten (x, y) te berekenen.

De in dit hoofdstuk gepresenteerde Forel-Ule-algoritme maakt het mogelijk de genormaliseerde MERIS spectrale band reflectie van 9 spectrale banden gemeten per pixel (beeldelement) om te zetten in een Forel-Ule waarde via colorimetrische berekeningen zoals beschreven in hoofdstuk 4. Zie Figuur 5, met hierin een 9-bands genormaliseerd reflectiespectrum van één pixel uit een MERIS satellietbeeld van de Gele Zee met een berekende Forel-Ule waarde van *FU*=9. 5 MERIS satellietbeelden van verschillende zeegebieden zijn, als voorbeeld, met behulp van het Forel-Ule-algoritme, omgezet naar Forel-Ule beelden.

Een voorbeeld van een naar Forel-Ule omgezet MERIS-satellietbeeld wordt gegeven in Figuur 6. Het betreft een beeld van de Gele Zee, waarvan in de linkerhelft van deze figuur de genormaliseerde bandreflectie van kanaal 5 (560 nm) te zien. De rechter helft toont het in Forel-Ule getransformeerde beeld. Door deze transformatie is het mogelijk een koppeling te maken met Forel-Ule-data van voor het satelliet tijdperk. Door een combinatie van geïnterpoleerde historische Forel-Ule-data en in Forel-Ule-data getransformeerde satelliet beelden kunnen door middel van ‘hindcasting’ virtuele satellietbeelden gecreëerd worden van een tijd van ver voor de komst van MERIS.

TRENDS IN DE KLEUR VAN DE OCEAAN EN IN CHLOROFYLCONCENTRATIE VANAF 1889 TOT HEDEN

In onderzoek aan de relatie tussen ‘klimaat’ en oceaan wordt veelal gebruikgemaakt van producten afgeleid van satellietgegevens, zoals de kleur van de zee en de hoeveelheid chlorofyl. In dit verband brengen analyses van lange-termijn-series ons informatie over een beperkt tijdperk, n.l. die van de operationele ocean-colour-satellieten; die dataset bestrijkt hooguit 30 jaar: sinds de lancering van Coastal Zone Color Scanner in 1978**.** Door terugkoppeling van satellietdata met historische Forel-Ule-data kunnen lange-termijn-series verlengd worden met vele decennia, zoals hierboven al opgemerkt.

In dit laatste hoofdstuk wordt een mondiale lange-termijn-serie van Forel-Ule statistisch geanalyseerd. Het betreft hier data over de periode 1889 tot 2000, met een overlapperiode van 20 jaar met ocean-colour-satellietdata. Uit de Forel-Ule-data zijn 10-jaarsgemiddelden van de kleur van oceanen en zeeën over de 20ste eeuw bepaald. Vervolgens zijn, voor alleen de oceanen, deze gemiddelde kleuren omgezet, via het Ecolight numeriek stralingstransportmodel, een biologisch-optisch model, naar chlorofyl concentraties. De verkregen resultaten kunnen een bijdrage leveren aan klimaatstudies, waarbij lange-termijn veranderingen in de oceaan van belang zijn.

Hoewel de Forel-Ule-schaal min of meer in onbruik is geraakt na de introductie van hyperspectrale optische sensoren, zijn de historische Forel-Ule observaties, hoewel indirect, de enige die ons iets kunnen vertellen over de in zee aanwezige hoeveelheid chlorofyl, een schatting voor de hoeveelheid fytoplankton, over langere termijn, dit dus gerelateerd aan de relatief korte periode waarover satellietsensoren operationeel zijn. De resultaten van de statistische analyse van de Forel-Ule-dataset worden gepresenteerd als gemiddelden per decade per oceaan en per wereldzee. Alleen data van de open oceaan en zee werden voor deze analyse gebruikt (>500 km of >100 km vanuit de kust) door observaties van de kleur van het kustwater uit te sluiten beperkte ik de invloed van rivieren, van grote invloed op de kleur vanwege sedimentlast en eutrofiëring, en van aangrenzende zeeën op de gemiddelde kleur van de onderzochte oceaan of zee.

Via het biologisch-optisch model Ecolight is een relatie vastgesteld tussen het Forel-Ule-schaalnummer en de hoeveelheid chlorofyl in de oceaan. In het model kunnen verschillende concentraties van in zee voorkomen opgeloste en zwevende stoffen worden ingevoerd, plus de instraling van de zon waarna het model, als output, het lichtspectrum, op van te voren vastgestelde diepten, plus het aan de waterkolom terug verstrooide lichtspectrum zowel net onder als net boven het wateroppervlak genereert. Uit bovenwater-lichtspectra, het remote sensing reflectiespectrum, berekent het model automatisch de *x, y* chromaticiteitscoördinaten. Naar aanleiding van de verkregen resultaten (zie hoofdstuk 4) is één nieuwe Ecolight-model-output-parameter toegevoegd n.l., het Forel-Ule-schaalnummer berekend uit *x, y* chromaticiteitscoördinaten afgeleid van het remote-sensing-reflectiespectrum. Een voorbeeld van het reflectiespectrum met het afgeleide Forel-Ule-schaalnummer (de outputs van het model) met als modelinput een chlorofylconcentratie van 8 mgm^{-3} is the zien in Figuur 7.

Resultaten van het gebruikte Ecolight bio-optisch model laten zien dat met behulp van de eerste 10 Forel-Ule-schaalnummers een goede schatting is te geven van de chlorofyl concentratie over een range van 0.1 tot 40mgm^{-3}.

Vervolgens is de gevoeligheid van de Forel-Ule-schaal getest, m.a.w. komt de naar chlorofyl omgezette Forel-Ule-waarde overeen met de in-situ gevonden chlorofyl waarde. Voor dit doel zijn alle beschikbare observaties van de Noord Atlantische Oceaan gebruikt voor de bepaling van de maandelijkse variabiliteit van oceaankleur en de hieruit berekende hoeveelheid chlorofyl. De resultaten van deze test zijn vergeleken met in de literatuur beschreven data van geanalyseerde watermonsters. Ze leveren na vergelijk met de in het laboratorium op chlorofyl geanalyseerde monsters reële maandelijkse chlorofylconcentraties op waarmee op inzichtelijke wijze de Noord-Atlantische planktonvoorjaarsbloei in kaart is gebracht.

Uit de resultaten van dit onderzoek kan geconcludeerd worden dat de hoeveelheid chlorofyl in de Indische Oceaan is verminderd en in de Atlantische oceaan omhoog is gegaan terwijl in de Stille Oceaan een op en neergaand chlorofyl concentratie beeld is te constateren. Uit de resultaten van dit dissertatiehoofdstuk blijkt dat er wereldwijd geen sprake is van een afname in oceanisch chlorofyl, zoals geconstateerd door Boyce, Lewis en Worm in een recent verschenen artikel in '*Nature*', met de titel '*Global phytoplankton decline over the past century*'. De Canadese onderzoekers hebben de transparantie van zeewater in plaats van de kleur van zeewater gerelateerd aan chlorofyl met als uitgangspunt dat de Secchidiepte een schatting geeft van het chlorofylgehalte in zee. Historische Secchidiepte-observaties werden omgezet naar chlorofylconcentraties. In de literatuur wordt terecht de omzetting van Secchi-data naar chlorofyl bekritiseerd, zeker wanneer één en dezelfde relatie wordt toegepast op data afkomstig uit verschillende zeegebieden.

In de open oceaan is het chlorofyl de sterkste licht verzwakkende component; in de overige zeeën en kustwateren wordt de kleur niet alleen bepaald wordt door het hierin aanwezige plankton maar ook door mineralen en opgeloste organisch materiaal. Plankton bevat bovendien niet alleen bladgroen, maar ook vele andere pigmenten.

Een bijkomende en storende tekortkoming, die bijdraagt tot de totstandkoming van de mijns inziens ongenuanceerde titel van de publicatie van Boyce *et al*., is de analyse van de data, waarbij geen onderscheid gemaakt werd tussen data verzameld in kustwater en data verzameld in open oceaan water. Zij selecteerden data van zeeën dieper dan 20 m of van meer dan 2 km uit de kust voor hun analyses. Men kan zich voorstellen dat zowel antropogene factoren als de uitstroom van rivieren na extreme regenval een grote invloed hebben op de kwaliteit van het kustwater en dus ook de meer open, aangrenzende oceaangebieden.

In Figuur 8 wordt het verloop van een over tien jaar gemiddelde chlorofyl concentratie tussen 1889 en 1999 getoond voor vijf oceanen. Van elf wereldzeeën wordt over dezelfde periode alleen de tienjaarlijks gemiddelde Forel-Ule-kleur berekend. Wat betreft de zeekleur tonen deze zeeën een wisselend beeld over de onderzochte periode.

De in dit hoofdstuk gepresenteerde resultaten geven over de gehele periode 1899 tot 1999 geen eenduidig beeld van een stijgende- of dalende chlorofylconcentratie, of het groener of blauwer worden van een onderzochte oceaan of zee. Deze conclusie maakt het onwaarschijnlijk dat er een oorzakelijk verband bestaat tussen een veronderstelde mondiale klimaatverandering en de kleur van de zee.

ALGEMENE CONCLUSIES EN VOORUITBLIK

Het in dit proefschrift opgetekende historische overzicht betreft de periode tussen 1600 tot heden en toont de lange weg, de zoektocht, van wetenschappers van alle tijden om ten aanzien van de verklaring voor het ontstaan van de specifieke kleuren van meren en zeeën tot consensus te komen. Nu nog steeds bekende wetenschappers bogen zich over het probleem 'waterkleuring' en met name de blauwkleuring, puur uit nieuwsgierigheid, naast hun dagelijks wetenschappelijk werk, dat meestal op een ander vlak lag. De in dit proefschrift beschreven zoektocht, in al haar facetten, schetst op inzichtelijke wijze het doorlopen onderzoekstraject. Ter sprake komen de tijden waarbij de kleur van de zee voornamelijk dichters en schilders fascineerde; en die fascinatie voorbij en gericht op praktische toepassingen van kennis volgde het inzicht in de relatie tussen zeekleur en bodemdiepte voor navigatiedoeleinden, en tussen zeekleur en het lokaliseren van visgronden. En toen eenmaal de wetenschappelijke interesse was gewekt voor het vinden van een verklaring van het probleem van de kleuring van natuurlijk water, kwam de instrumentele ontwikkeling in een stroomversnelling en werden vele hulpmiddelen voor de bepaling van kleur en helderheid van meer en zee in de 19de eeuw geconstrueerd. Uiteindelijk mondde de bemoeienis van nu alom bekende onderzoekers als Tyndall, Rayleigh, Einstein en Raman tot de wetenschappelijke vaststelling van de oorzaak van het probleem van de blauwkleuring van water, n.l.: de verstrooiing en absorptie van zonlicht aan watermoleculen.

Kort na deze vaststelling werden ook de oorzaken van het anders dan blauw gekleurde rivier, meer, zee en oceaanwater duidelijk.

Sinds het einde van de twintigste en het begin van de een-en-twintigste eeuw is er een verscheidenheid aan geavanceerde optische instrumenten beschikbaar om zowel de kleur als de transparantie van het zeewater langs elektronische weg te bepalen. Desondanks pleit ik voor een herinvoering van het gebruik van de, in dit proefschrift beschreven, Forel-Ule-schaal en de Secchischijf als standaard instrumenten tijdens toekomstige oceanografische expedities. Belangrijke reden voor deze aanbeveling is dat beide instrumenten eenvoudig te vervaardigen zijn. De simpele meetprotocollen maken het ook voor leken mogelijk een meting uit te voeren, zelfs daar waar met eenvoudige vaartuigen een zeegebied bemonsterd wordt en er geen alternatieven mogelijk zijn. Een grootscheepse herintroductie van deze twee klassieke meetmethoden maakt het mogelijk de, uit historische observaties opgebouwde, lange-termijn-series van helderheid en kleur van de zee te continueren. Een eenvoudig alternatief voor de bepaling van de Secchidiepte is om een Secchischijf standaard te monteren op een frame dat tijdens oceaan expedities gebruikt wordt om de Conductiviteit, Temperatuur en Diepte van de waterkolom te bepalen; het CTD frame. Zodoende kan men tijdens het zakken van het frame op een simpele en snelle manier de Secchidiepte bepalen, ter continuering van de lange-termijn serie van de transparantie van de zee. ‘CTD’s’ worden veelvuldig en op vele locaties geëffectueerd voor oceaanonderzoek.

Uit een analyse van resultaten van spectraalanalyse van de Forel-Ule-schaal blijkt dat, ten aanzien van de kleur, deze schaal voldoende onderscheidend vermogen oplevert voor een adequate kleurenclassificatie van natuurlijk oppervlaktewater. De methode is simpel, met als groot voordeel dat een Forel-Ule-observatie een numeriek getal oplevert dat, in tegenstelling tot een meerkanaalsspectrum, de interpretatie van kleurveranderingen van natuurlijk water sterk vereenvoudigt. Door omzetting van *in-situ* gemeten meerkanaals-kleurenspectra naar een Forel-Ule-schaalnummer, door middel van de in dit proefschrift beschreven colorimetrische berekeningen, wordt weer aansluiting verkregen met de *historische* Forel-Ule-dataset.

Een van de resultaten van dit onderzoek houdt verband met de techniek van het monitoren van zeekleur vanuit de ruimte en schept de mogelijkheid om via colorimetrische berekeningen MERIS-reflectiebeelden om te zetten naar de Forel-Ule beelden. De MERIS-sensor, beheerd door de Europese Ruimtevaart Organisatie ESA, is tot nu toe de enige operationele satelliet-sensor, die toegerust is met het minimum vereiste aantal spectrale banden nodig voor een dergelijke omzetting. Mijn advies aan de ESA is daarom: implementeren van de Forel-Ule-index als extra waterkwaliteitsproduct. Naast de MERIS-standaardproducten, zoals chlorofyl, totaal zwevende stof en CDOM-index (de mate van afwijking van de normaal aanwezige hoeveelheid gekleurd opgelost organische stof) die ESA nu aanlevert, zou ‘de kleur van de zee’ een welkome aanvulling zijn, waardoor het mogelijk wordt ook de eerste MERIS-satellietbeelden naar deze index om te zetten. Hierdoor kunnen ook deze waarnemingen toegevoegd worden aan de historische Forel-Ule-dataset en is er zodoende een overlappende reeks van gemeten en berekende data voorhanden voor intercalibratie of validatiedoeleinden. Forel-Ule remote sensing data geven tevens de mogelijkheid op lokale schaal kusterosie, sedimenttransport en eutrofiëring te monitoren.

Een belangrijke uitkomst van dit onderzoek naar de veranderingen in de kleur van de oceanen en wereldzeeën over de lange termijn, tussen 1900 en 1999, is dat trends in de vastgestelde kleurveranderingen per zeegebied verschillend zijn. Oceanen en zeeën worden blauw en vervolgens weer groen met een onderling verschillende periodiciteit. Indien we de oorzaken van de gevonden en gepresenteerde veranderingen in de kleur van het zee- en oceaanwater en/of chlorofylconcentraties willen benoemen zal op lokale schaal, niet op de schaal van ‘de oceanen’, gekeken moeten worden naar mogelijke verbanden tussen deze veranderingen en klimatologische of oceanologische veranderingen. Als katalysator van mogelijke lokale kleurveranderingen moeten we denken aan klimaat gerelateerde veranderingen, zoals sterkte en richting van zeestromingen, waardoor zelfs hele ‘upwellingsgebieden’ van positie kunnen veranderen, waardoor het plaatselijke groen gekleurde water (een upwellingsgebied is vaak rijk aan plankton) naar blauw kleurt (geen upwelling, weinig voedingsstoffen, minder plankton).

Bij dit alles moeten wij ons wel beseffen dat de bovenste laag van de oceaan, een laag van enkele tientallen meters diepte, het sterkst bijdraagt aan de kleur van de oceaan en dat deze bijdrage snel afneemt met de diepte. De intens gekleurde laag van het dieper gelegen chlorofylmaximum (80 tot 140 m diep) heeft zeker geen invloed op de kleur aan de oppervlakte.

> ‘*Ocean colour’ metingen in het algemeen, vanuit de ruimte of vanaf een schip, geven ons informatie van de kleur van de bovenste laag van de zee, niets meer en niets minder. De in dit proefschrift gepresenteerde conclusies gelden daarom alleen voor deze laag en niet voor de gehele waterkolom*.

De laatste opmerkingen betreffen de in dit proefschrift beschreven dataset, die uit ongeveer 220.000 Forel-Ule observaties bestaat. Ongeveer 60.000 observaties van open zee en oceaanwater (>100 km van de kust) zijn hiervan geanalyseerd. Het is belangrijk de niet geanalyseerde mondiale observaties in kustwater en in continentale zeeën (< 100 km van de kust) op de in dit proefschrift beschreven manier te analyseren om de mate van eutrofiëring op mondiale schaal vast te stellen en om vervolgens de invloed van deze chlorofyl- en CDOM rijke kustzeeën op de kleur van het oceaanwater vast te stellen. Door verfijning van het in dit proefschrift gebruikte biologisch-optische model moet het mogelijk zijn de zeeën waar CDOM niet co-varieert met chlorofyl te classificeren op zowel CDOM als op chlorofyl. Kan deze scheiding in de toekomst gemaakt worden, dan is het mogelijk ook van de resterende 160.000 Forel-Ule-observaties voor het continentaal plat chlorofyltrends over de afgelopen eeuw vast te stellen.

SUMMARY

The title of this thesis refers to Poseidon, the Greek God of the sea, who without doubt did not possess his own paint box, although the subtitle might suggest otherwise: 'Historical Archives of Ocean Colour' refers to the many colours the oceans and seas can adopt. This thesis is a compilation of partly published scientific material, all with a common theme 'the colour of the sea'. Its first part deals with the historical development of challenging thoughts, ideas and theories on observations and analysis of the colour of the sea ('ocean colour') in the period 1600 to 2000. This is a prelude to a discussion on modern ocean colour observation methods: using satellite-mounted sensors for the determination of the spectral composition of light.

In the thesis introduction issues are discussed on the historical background of marine optics and on marine optical devices that were used over the past centuries to observe and measure. As in all sciences, in marine optics we can see a steady development: that of 'measuring', beginning many centuries ago, to 'knowing' and since less than a century to the understanding of the phenomenon. Hereafter, six themes are treated successively.

The first theme, '*Ocean optics from 1600 (Hudson) to 1930 (Raman), shift in interpretation of natural water colouring'*, addresses the question of why it took so long a time to explain the phenomenon 'the colouring of the sea', especially the blue colour, despite the age-long interest of sailors, for practical purposes of navigation and detection of fish – of which more later.

The second theme '*On the history of the Secchi disc*', describes the search to establish methods for the determination of (sea) water clarity concerning purposes of navigation (near coast colour changes) just mentioned to detect shoals, and for a more basic purpose, tracing lost objects. The search to determine the clarity of lakes and seas culminated in the invention of the Secchi disc, used since the late 19^{th} century.

The third theme, '*Spectral analysis of the Forel-Ule ocean colour comparator scale*', addresses the accuracy of a colour scale proposed, used in limnology and oceanography. Scale observations are put into perspective with contemporary measurements on the colour of the sea.

The fourth theme, '*Ocean colour changes in the North Pacific since 1930*', handles the question whether long-term ocean colour changes using historic Forel-Ule observations, in this part of the ocean made very frequently over time, can be determined in relation to global change. In principle global warming may cause a gradual change in ocean colour due to the effect of biological, chemical and physical aspects on the water quality of the ocean-surface.

The fifth theme, '*MERIS-based ocean colour classification using the Forel-Ule scale'*, addresses the question whether a relation can be established between the old Forel-Ule methodology, the

classification of ocean colour by means of one of the scale colours, and the more recent satellite ocean colour methodology.

The sixth theme, '*Trends in ocean colour and chlorophyll concentration since 1889 to present*', addresses decadal colour changes per ocean and sea, using the longest available Forel-Ule dataset and it confirms the possibility to transform these colour changes into chlorophyll concentration (indicative of the biomass of marine planktonic microalgae) changes. Such a transformation is needed to provide a link to the present in which chlorophyll concentrations are determined by using new technologies such as satellite remote sensing calibrated with high-performance liquid chromatography (HPLC) pigment analysis to determine marine microalgae pigments.

OCEAN OPTICS FROM 1600 (HUDSON) TO 1930 (RAMAN); SHIFT IN INTERPRETATION OF NATURAL WATER COLOURING

For a description of nomological knowledge, I consulted scientific publications as well as related background material from the 20th century, going back in time to the beginning of the 17th century. The purpose was to reveal described laws related to empirical reality of, in this case, the (blue-) colouring of the sea.

The scientific aim is to describe the development of thought and ideas of explorers and scientists regarding the colour and transparency of natural waters with its cause, and compare them with current views. The period studied here concerns the time of Henry Hudson the seafarer (1565?-1611) to Chandrasekhara Raman (1888-1970), the scientist who ultimately explained the cause of the blue colouring of (pure) water.

This chapter describes a variety of amateurs but also famous scientists, all intrigued by the phenomenon of 'the colour of the sea'. A number of devices developed to quantify colour and associated water transparency are discussed here.

Two of these devices were developed in the 19th century and are still in use; they are discussed in chapters 3 and 4. A century of data collected with one of these instruments is discussed in more detail in chapters to follow.

The mechanisms responsible for the coloration of seawater were exposed only in the early 20th century. I conclude that the relative long period of 300 years necessary to clarify the underlying mechanisms was due to the fact that, in those days, the type of research took place in the margins of physical-biological research. Another reason for this delay is the difficulty of making pure water, which was not perfected until the beginning of the 20th century. This Chapter ends with Chandrasekhara Venkata Raman, who proved in 1922 that it was molecular scattering of mainly the shorter wavelengths (blue light) together with the absorption of the longer wavelengths (green- to red light) of sunlight penetrating the water that gives pure (sea-) water its blue colour. Examples of blue coloured waters are the nutrient-poor waters of the central oceans in which the micro-algae's biomass and the amount of 'gilvin' and suspended matter are very low.

ON THE HISTORY OF THE SECCHI DISC

This chapter traces historical publications pertaining to the interest of former sailors and scientists who were busy trying to determine the transparency of seawater with the help of a variety of objects and simple instruments.

Interest in this type of research came, as mentioned before, from basic considerations such as acquiring knowledge of the local bottom depth and water clarity of coastal water for navigation purposes, important for an early detection of shoals and sandbanks. Only much later did one realise the importance of water clarity as a valuable ecological water quality parameter.

A still existing method to determine water transparency of lakes and seas is the use of a submerged white disc, introduced in 1865 by Secchi. Several references to this method at the end of the 19^{th} century adopted the naming 'Secchi disc method', although many started the use of similar methods long before Secchi. Angelo Secchi began his scientific experiments in 1864 off the coast of the town Civitavecchia, north of Rome. Secchi was the first researcher who experimented with size, colour and texture of the disc and he described his observations in relation to the sun's position (elevation) and meteorological conditions.

The first reports with transparency tables of natural waters are those of the German naturalist Adelbert von Chamisso. During the Russian "*Rurik*" expedition 1815-1818, under the command of Otto von Kotzebue, dozens of experiments were performed to measure water clarity. Teapots, a variety of pottery and porcelain dishes and even white towels were used to determine it. It would be until the end of the 19^{th} century before a standardized way of water clarity (transparency) determination was assumed.

The specific measure of a 30 cm white-painted disc from the sea surface down submerged in seawater until out of sight is recorded as the so-called Secchi depth. This measurement, also because of its simplicity, has become very common, even during modern oceanographic expeditions. The method for measuring transparency of the sea was described in detail by the aforementioned scientist and Vatican priest Pietro Angelo Secchi in the journal '*Il Nuovo Cimento Giornale di fisica, chimica e storia naturale*' of 1865. During the experiments Secchi was assisted by the commander of the papal steam yacht and research vessel '*l'Immacolata Concezione*' by Commander Alessandro Cialdi.

The Austrian scientist Josef Roman Lorenz Ritter von Liburnau experimented with various objects to determine the transparency of water, including white discs in the Gulf of Quarnero (Croatia), years before Secchi's experiments. He questioned in one of his publications the naming of the method and found 'the disc approach' much better.

In conclusion, after reading the dozens of pages published on the many experiments Secchi performed to establish an adequate method to determine water transparency I understand the naming of the method. The Secchi disc method, many years later, is still greatly appreciated by limnologists and oceanographers.

Since the end of the 19th century, hundreds of thousands of measurements were performed according to Secchi's method and archived. These data are among the oldest oceanographic data and they provide insight into changes of oceans, seas, and lakes over many decades. As a result, it offers an opportunity to link transparency to climate research, to be discussed further on.

SPECTRAL ANALYSIS OF THE FOREL-ULE OCEAN COLOUR COMPARATOR SCALE

During the late 19th and the early 20th century, François Alphonse Forel (portrait Figure 1) described numerous research studies on Lake Geneva. In his three-volume limnological monograph 'Le Leman', from which the first part was published in 1892 and the third in 1904, he describes his search for the cause of the apparent colour of this lake. One of the simplest effective ways to capture this colour was his invention, in 1890, of the Forel scale which covered the colour shades of the lake between blue and yellow-green in 11 steps. Two years later, the German Willi Ule expanded the scale with green to brown colour shades in 10 additional steps. Combining both scales gave the Forel-Ule scale (inset Figure 1) its name and contains 21 glass tubes with mixtures of coloured chemical solutions. Included in this chapter is a description on how to manufacture the scale using the original recipes of the fluid mixtures described by Forel and Ule separately. In the cause of the 20th century, the processes underlying the (dis-) colouration of water were more and more understood. The entire past century, Forel-Ule scale observations were continued on a global scale and even after the entry of the most modern spectral radiometers. Concerning the old comparator scale, for each measurement, the observer compares the colour of the water above a submerged Secchi disc with one of the Forel-Ule tube colours. Since the introduction of this colour comparator scale until the late eighties of the past century, it has been extensively used by oceanographers and limnologists to classify all kinds of natural waters, *i.e.*, waters dominated by chlorophyll- or coloured dissolved organic or by both, on their colour.

Archived Forel-Ule data belong to the oldest oceanographic data series, in addition to salinity, temperature and water transparency. This dataset contains information on changes in water quality from all over the globe and from far back in time and hence indirect information on the chlorophyll concentrations of the past. This knowledge provides insight into aspects of oceans and seas over the longer term, well before the arrival of ocean colour satellites that are deployed today. This way ocean colour information from the past can be linked to the present with the opportunity to couple a century of ocean colour data to climate-related data (sea surface temperature, ocean currents and available sunlight with related surface phytoplankton biomass, which is expected to vary with the factors mentioned).

Can Forel-Ule scale colours be reproduced according to the old recipe, how accurate is the scale and how useful is the scale for contemporary oceanography, *i.e.*, does the Forel-Ule scale today represent the 'true' colours of the sea? The outcome of this analysis is particularly important with regard to the scientific value of a global dataset maintained by the U.S. National Oceanic and Atmospheric Administration (NOAA), which contains hundreds of thousands of these Forel-Ule observations, dating back to the end of the 19^{th} century. This chapter addresses the scale's reproduction, optical properties, spectral accuracy and its utility. We find that the scale colours are easy to reproduce by a mixture of copper-, potassium- and cobalt-sulphate solution. The spectral transmission per Forel-Ule scale colour are measured using a modern hyperspectral radiance-meter as outlined in Figure 2.

Figure 3 shows the results of the scale's transmission obtained through spectral analysis. The smooth and gradual spectral transitions with a shift from blue via blue-green to green and brown are easy to observe.

The colour of the sea can be classified through the use of the Forel-Ule scale which results in a numerical value between 1 and 21. However, a contemporary colour classification is established through the use of hyperspectral radiometers which results in a colour spectrum compiled of multiple bands. By means of colorimetric calculations, such an *in-situ* or remote sensing colour spectrum can be converted into one (*x, y*) chromaticity coordinate set. The same conversion can be applied on the hyperspectral Forel-Ule transmission spectra of Figure 3. This allows a comparison of historical and contemporary ocean colour data.

OCEAN COLOUR CHANGES IN THE NORTH PACIFIC SINCE 1930

The aim of this chapter is to gain insight into the long-term variation of the colour of the Northern Pacific. This area is characterized by the thousands of Forel-Ule (*FU*) observations performed since 1930. This amount of observations makes it possible to statistically analyse the data. Are these colour changes related to natural cycles like the season or are they subject of global change? Examining the colour of the northern part of the world's largest ocean will give scientists a better understanding of changes in sea colour related phytoplankton and the impact of such a change on the marine food chain.

The valuable Forel-Ule data set of this part of the oceans is digitized and managed by National Oceanographic Data Centre (NODC / NOAA) in the United States. River- and coastal data were filtered out in this analysis. Only observations of open sea, at more than 500 km from the mainland, are used for this analysis. After filtering, 17,000 observations remained over the period 1930 to 1999. For a statistical analysis the *FU* observations are classified per 5 years and per season and per 5 years regardless of the season. In Figure 4, we see the results of a season independent analysis. The figure shows a greening Northern Pacific Ocean between the periods 1930-34 and 1950-54. The mean *FU* rises with over a factor of two from 2 to 4.1. Then, during a twenty-five years period until 1975-79, the North Pacific gets bluer again until its colour reaches the 1930-43 value with an average *FU* = 2.1. During the period 1975-99 the ocean colour is varying with a high of *FU*=3 in 1975-79. The greenest ocean water, with a mean *FU* value of 4.1, was found during 1950-54. The bluest ocean water, with a mean *FU* of 1.7, was found for the period 1990-94. Over a period of seventy years of investigation the colour varies significantly. Therefore, further research is necessary to point out possible mechanisms responsible for the identified variation. For instance, could this change in ocean colour be climate related?

Venrick *et al*. (1987) mentioned that a significant increase of integrated chlorophyll-a in the water column during May-October could be observed during 1968–1985. Water samples analysed by them on chlorophyll are in line with here presented findings. This outcome gives confidence for the rest of the periods described here.

As previously noted, the ocean's colour is determined, partly, by the presence of phytoplankton. A change in phytoplankton abundance implies a change in the uptake of CO_2, so it is not out of the blue that ocean colour has been established as an essential climate variable by the World Meteorological Organization (WMO).

Future research will need to focus on revealing a possible link between factors that influence the climate and the colour of the ocean. A first step to identify these factors is the analysis of historical *FU*-observation series collected in the other oceans and seas and merge these with satellite derived ocean colour data. This is discussed in the next chapter.

MERIS-BASED OCEAN COLOUR CLASSIFICATION USING THE FOREL-ULE SCALE

In this chapter algorithms are presented to convert multispectral MEdium Resolution Imaging Spectrometer (MERIS) data into Forel-Ule values 1 to 21. We propose a reintroduction of the Forel-Ule method to classify oceans on their colour. This way, satellite ocean colour data can be linked to historical measured ocean colour in terms of the Forel-Ule index.

MERIS is a multi-channel radiometer with a spectral range between 390 (blue) and 1040 (infrared) nanometres spread over fifteen spectral bands. The ENVISAT satellite with MERIS on-board was built under auspices of the European Space Agency (ESA) and was launched into space March 2002 to provide colour information of the atmosphere, ocean and coastal water, land and ice. The global mission of MERIS can be seen in the context of scientific projects towards a better understanding of the role the ocean and oceanic primary production plays in our climate. With the arrival of MERIS, it became possible, for the first time, to create a link between multichannel spectral satellite data and Forel-Ule data. Of the 15 available spectral MERIS bands, 9 are well distributed over the visible spectrum and this number of bands is enough to establish the chromaticity coordinates (x, y) through colourimetric calculations.

The Forel-Ule algorithm proposed in this chapter facilitates a conversion of MERIS normalized band reflectance, *i.e.*, the colour information measured per pixel in nine spectral bands, into a Forel-Ule value through colourimetric calculations, as described in chapter 4. Figure 5 illustrates an example of a 9-bands normalised reflectance spectrum of a MERIS pixel from a satellite image of the Yellow Sea with a calculated Forel-Ule number of 9. An example of a converted MERIS satellite image is shown in Figure 6. It is an image of the Yellow Sea. The left panel of the figure shows the normalised band 5 reflectance (560 nm) and the right panel shows the transformed Forel-Ule index image. This transformation enables comparison with Forel-Ule data from before the satellite era.

TRENDS IN OCEAN COLOUR AND CHLOROPHYLL CONCENTRATION FROM 1889 TO PRESENT

Current investigations into the relationship climate and ocean make use of satellite data derived products, such as colour of the sea and the amount of chlorophyll. In this regard, analysis of long-term series, using satellite data will provide us with information about a limited period, namely the period for which ocean-colour satellites are operational. This dataset covers at most 30 years: since the launch of the Coastal Zone Colour Scanner (CZSC) in 1978. Feedback loops can now be established between satellite data and historical Forel-Ule data, through which an opportunity is created to extend long-term series by many decades, as mentioned already above.

In this last chapter, a globally established long-term series of Forel-Ule data is statistically analysed. It concerns data over the period 1889 to 2000 and overlaps 20 years of ocean-colour satellite data. From Forel-Ule data, decadal means were established over the 20th century. Next, for the oceans only, the decadal means were converted into chlorophyll concentrations using a bio-optical model. The results obtained can contribute to climate studies in which long-term changes in the ocean are of interest.

Although the Forel-Ule scale more or less fell into disuse after the introduction of hyperspectral optical sensors, we must realise the value of the data collected through the use of the scale. Historical observations of the colour of the sea are the only available data that can tell us something, although indirectly, about the amount of chlorophyll, an estimate of phytoplankton abundance, in the sea over the longer term. This of course in context of the relative short period over which satellite ocean colour has been collected.

Results of the statistical analysis of the Forel-Ule dataset are presented in this chapter as means per decade per ocean and sea. Only data from the open oceans/seas were selected (> 500 km for the oceans or >100 km off coast for the seas). By the exclusion of coastal colour observations we limited the influence of rivers and shelf seas, with their major impact on the colour of neighbouring seas and oceans, due to sediment load and eutrophication.

Through the biological-optical model Ecolight a relationship could be established between the Forel-Ule scale number and the amount of chlorophyll present in ocean water. In the model, different concentrations of marine dissolved and suspended solids are used as input including the sun's radiation. The model then calculates the underwater light spectrum over pre-defined depths in the water column plus the backscattered light spectrum, both just below and just above the surface. From the above water reflectance spectrum, *i.e.* the remote sensing reflectance spectrum, the *x, y* chromaticity coordinates are automatically generated. Following the results of chapter 4, another Ecolight modelled and new output parameter, the Forel-Ule scale number, could be generated and was calculated from *x, y* chromaticity coordinates derived from the modelled remote sensing reflectance spectrum. An example of a modelled remote sensing reflectance spectrum and the Forel-Ule scale number (two outputs of the Ecolight model) of seawater containing 8 mgm^{-3} chlorophyll (model input) is shown in Figure 7. Results of Ecolight bio-optical modelling show an exponential relation for the first 10 Forel-Ule scale numbers with a chlorophyll concentration ranging from 0.1 to 40mgm^{-3}.

Next the sensitivity of the Forel-Ule scale was tested to establish if chlorophyll converted Forel-Ule values meet reality. For this purpose, all available observations of the North Atlantic were

used to determine the monthly variability of ocean colour and into chlorophyll converted ocean colour. The results of this test were compared with data from the analyses of water samples described in literature. They show, after comparison with samples analysed in the laboratory on chlorophyll, real monthly chlorophyll values through which the North Atlantic spring plankton bloom could be visualised which resulted in a clear and comparable view on the matter.

Concerning established trends in chlorophyll, we found for the Indian Ocean a decline in the amount of chlorophyll and for the Atlantic Ocean an increase in the amount of chlorophyll, while the Pacific Ocean shows an undulating pattern.

From the results of this dissertation chapter a global decline in oceanic chlorophyll cannot be identified, as was established by Boyce, Lewis and Worm in a recently published article in '*Nature*' titled 'Global phytoplankton decline over the Past Century'. The Canadian researchers used water transparency instead of ocean colour as a proxy for chlorophyll driven by the principle that chlorophyll could be estimated using a Secchi depth proxy. Historical Secchi depth observations were converted into chlorophyll concentrations. In literature, this conversion is criticized, especially when one and the same relationship is applied to data derived from different sea areas. In the open ocean chlorophyll is the strongest light-attenuating component. In other seas and coastal waters the colour is not only determined by phytoplankton abundance but also by minerals and dissolved organic matter. Besides, plankton does not only contain chlorophyll but also many other pigments.

An additional and disturbing shortcoming that, in my opinion, contributes to the creation of the 'bold' title of the publication of Boyce *et al*. is their analysis of the data, where no distinction has been made between data collected in coastal waters and data collected in open ocean waters. They either selected data of seas deeper than 20 meters or data more than 2 km from the coast for their analysis. One can imagine that both anthropogenic factors, as well as river outflow following heavy rainfall, have a major impact on the quality of coastal waters and therefore affect more open, neighbouring ocean areas.

In Figure 8, trends are shown of decadal mean chlorophyll concentrations between 1889 and 1999 for five oceans. For eleven world seas, concerning the same period, only the decadal means in Forel-Ule colour are calculated. Concerning long-term variations in colour or chlorophyll content, the investigated seas and oceans show a mixed picture over the period examined. This conclusion makes it unlikely that a causal link exists between an assumed global climate change and the colour of the sea.

GENERAL CONCLUSIONS AND OUTLOOK

In this thesis, the chronicled historic overview covers the period between 1600 and the present and shows, regarding an explanation of the origin of the colour of the sea, the long research path of scientists of all time reaching final consensus. Famous scientists, still known at the time, approached the 'water colouring' issue, in particular the blue colouring, just out of curiosity and usually as a secondary activity in addition to their daily scientific work. The quest described in this thesis outlines all stages of research. Discussed are the times of mainly poets and painters, who documented the colour of the sea out of pure fascination. Past the fascination one became aware of the relationship between sea colour and bottom depth and between sea colour and the location of fishing grounds.

Once scientific interest awakened, the search for the explanation of the colouring of natural waters started. Hereafter, the instrumental development gained momentum and during the 19^{th} century many tools were constructed to determine the colour and clarity of lake and sea. Eventually, through the interference of researchers like Tyndall, Einstein, Rayleigh and Raman, the cause of the blue colouration of water was revealed and could be assigned to the scattering and absorption of sunlight by the water molecules. Shortly after this assessment, the causes of other natural colours of river, sea and ocean water could also be clarified.

Since the turn of the twentieth century, a variety of advanced optical instruments became available to determine electronically the colour and transparency of seawater. Nevertheless I advocate a reintroduction of the Forel-Ule scale and Secchi disc, described in this thesis, with the qualification becoming standard equipment on-board future oceanographic expeditions. A major reason for this recommendation is the simplicity in device manufacturing. Through simple measurement protocols, laymen also will be able to perform measurements, even in areas where only simple vessels are available for sampling, and in case no alternatives are possible to power the necessary electrical devices. An ambitious reintroduction of these two classic methods allows the continuation of historic long-term series of transparency and ocean colour observations. A simple alternative for the determination of the Secchi depth can easily be established by mounting the Secchi disc on a frame that is used during ocean expeditions to establish conductivity, temperature and depth of the water column; the CTD frame. In this way, the Secchi depth can be determined in a simple and quick way during the lowering of the frame. 'CTDs' are accomplished frequently and in many locations in oceanographic research.

By examining the results of a spectral analysis of the Forel-Ule scale, it could be concluded that the scale's distinctive colour discrimination capabilities are more than sufficient to classify natural waters regarding their colour. Water classification according to Forel-Ule is simple, a multi-spectral classification is not. Classifying seas according to Forel-Ule has one big advantage; an observation can be expressed in a numerical value, which will ease the interpretation of

ocean colour changes. By conversion of *in-situ* or remote sensed multi-channel colour spectra to a Forel-Ule scale number through colourimetric calculation, as described in the thesis, a reconnection with the historical Forel-Ule dataset can be obtained.

One result of this research is related to the technique of monitoring sea colour from space and creates the possibility, using colourimetric calculations, to convert MERIS reflectance images into Forel-Ule images. The MERIS sensor, managed by ESA, is so far the only operational satellite sensor equipped with the minimum number of spectral bands required for such conversion. Therefore, I advise ESA to implement the Forel-Ule index as an extra water quality product. Apart from the MERIS standard products such as chlorophyll, total suspended matter and CDOM index (the degree of deviation from the normal amount present coloured dissolved organic matter) that ESA now provide, 'the colour of the sea' would be a welcome addition, and allows the conversion of the first MERIS imagery to be converted into this index. Forel-Ule data obtained this way can again be added to the historic Fore-Ule dataset to realise an overlapping series of measured and calculated data which can be used for inter-calibration and validation purposes. Forel-Ule remote sensing facilitates the monitoring of local-scale coastal erosion, sediment transport and eutrophication.

An important outcome of this research, concerning the identification of long-term changes in ocean colour and chlorophyll, is the non-uniformity of the found trends. Within the investigated period, 1899 to 1999, decadal changes are different for each of the investigated sea areas. Oceans and seas are bluing and greening with different periodicity. To identify driving forces responsible for ocean colour and chlorophyll change, we should look first at local scales and not at ocean wide scales. As a catalyst of possible local colour changes, we must think of climate-related changes, such as strength and direction of ocean currents, which could even change the position of areas of upwelling, causing the local normally green-coloured water (areas of upwelling are rich in plankton mostly) to discolour to blue (no upwelling, lesser nutrients, therefore less plankton).

Concerning all, we must realise that the upper layer of the ocean, a layer of a few dozen meters depth, contributes strongest to the colour of the ocean and that this contribution decreases with depth. The layer of the deep chlorophyll maximum (80 to 140 m deep) is intensely coloured but has certainly no effect on the colour of the sea surface.

> *‘Ocean colour' measurements in general, either from space or from ships, will give us information on the colour of the top layer of the sea, nothing more and nothing less. In this thesis presented conclusions therefore apply only to this layer and cannot be applied to the entire water column.*

The last comments concern the dataset described in this thesis, which contains approximately 220,000 Forel-Ule observations. Approximately 60,000 observations of open sea and ocean (> 100 km from the coast) were analysed. To determine the degree of eutrophication of coastal waters and shelf seas it is important to analyse the remaining and unprocessed data (< 100 km of the coast) in the same way as presented in this thesis for a further determination of the influence of these chlorophyll- and CDOM rich coastal seas on the ocean's colour. Concerning these seas, where chlorophyll does not co-vary with CDOM, a refinement of the bio-optical model presented in this thesis should allow the classification for both CDOM and chlorophyll. In case such a separation can be made it becomes possible to determine chlorophyll trends for the continental shelf over the past century.

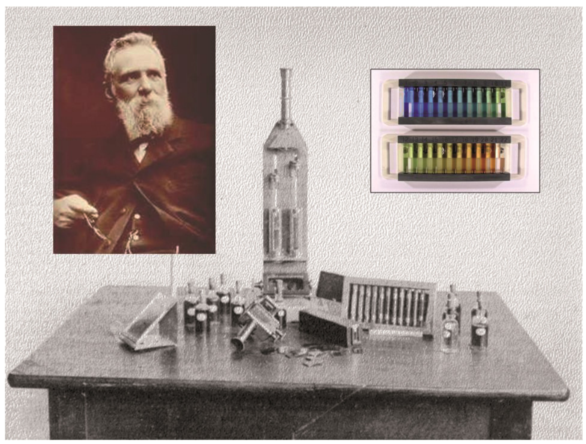

Figure 1 - Portrait: François-Alphonse Forel, the initiator of the colour comparator scale. On his laboratory table all ingredients to compose a new Forel scale (ca. 1905).
Figuur 1 - Portret: De initiator van de kleurenvergelijkingsschaal François-Alphonse Forel. Op zijn laboratoriumtafel alle ingrediënten voor de samenstelling van een nieuwe Forelschaal (ca. 1905). Source: Background; P. Roggero, Musée Océanographique de Monaco.

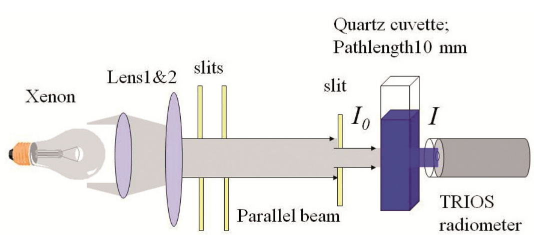

Figure 2 - Schematic drawing of the setup for the determination of the spectral transmission of 1 of the 21 coloured Forel-Ule liquids using a hyperspectral TRIOS radiance sensor.
Figuur 2 - De schematische opstelling voor de bepaling van de spectrale transmissie (lichtdoorlaatbaarheid) van 1 van de 21 gekleurde Forel-Ule vloeistoffen met behulp van een TRIOS hyperspectrale radiantiemeter (lichtmeter).

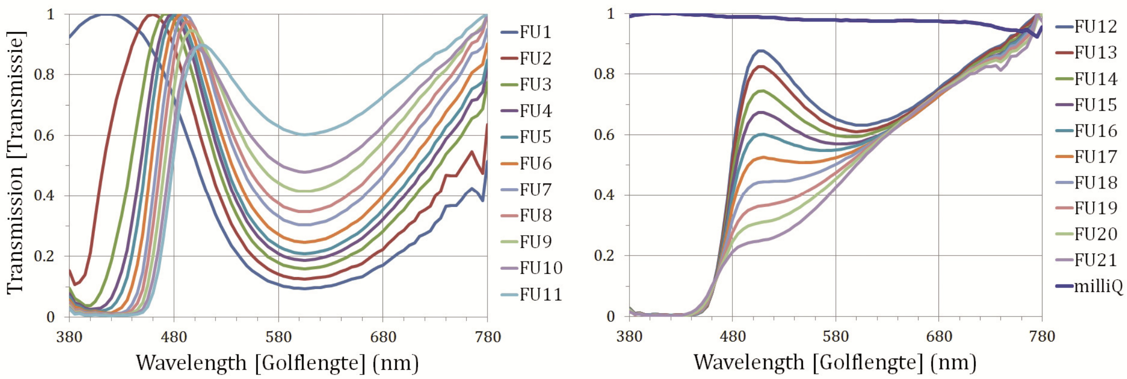

Figure 3 - Shown are the normalized transmission spectra of the 21 Forel-Ule scale colours. The blue line in the upper corner of the right panel is the transmission of purified water (Milli-Q water).

Figuur 3 - De door spectraalanalyse verkregen genormaliseerde transmissie van de 21 Forel-Ule-schaalkleuren (380nm=indigoblauw, 530nm=groen, 580nm=geeloranje, 680nm=rood en rond 780nm bevind zich het voor het menselijk oog onzichtbaar Infrarood. De blauwe lijn rechtsboven is de transmissie van gezuiverd water (Milli-Q water).

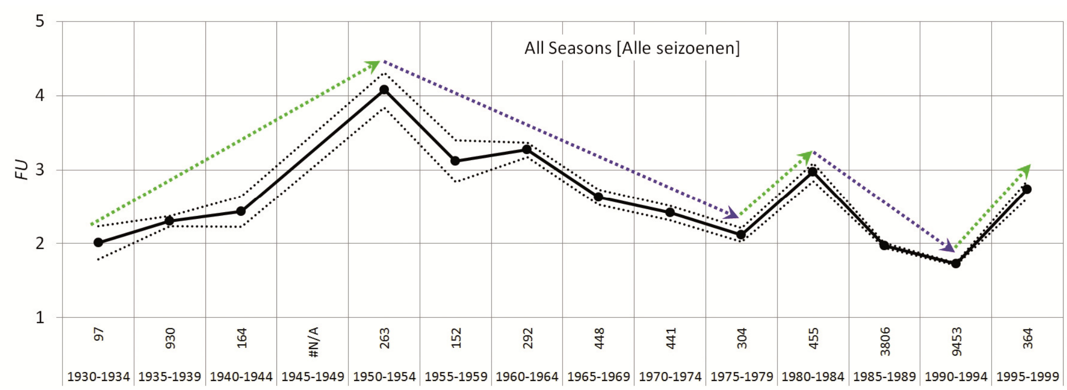

Figure 4 - The Forel-Ule colour changes of the North Pacific established per 5 years between 1930 and 1999 (black line and black dots with the error margin as dotted lines, below the horizontal axes; above the period is the number of available *FU* observations). Remarkable periods are 1930-1955 where the ocean is greening and 1950-1979 in which the ocean is bluing again.

Figuur 4 - De kleurverandering van de Noordelijke Stille Oceaan in Forel-Ule waarde vastgesteld per 5 jaar tussen 1930 en 1999 (zwarte punten met verbindingslijn, met de foutenmarge als gestippelde lijnen en onder de horizontale-as boven de periode het aantal beschikbare *FU* observaties). Opmerkelijke perioden zijn 1930-1955 waarin de oceaan groener wordt en 1950-1979 waarin de oceaan weer blauwer wordt.

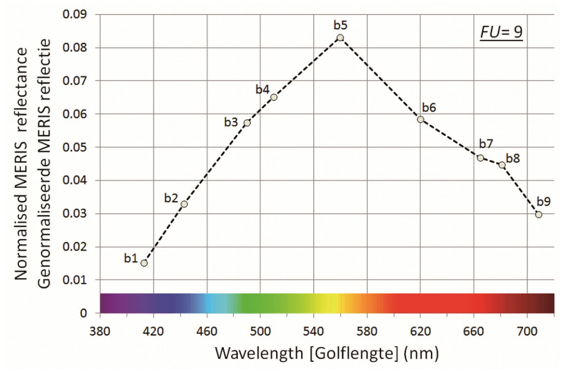

Figure 5 - Example of a 9-band (b1-b9) normalised reflection spectrum of a single pixel from a MERIS satellite image of the Yellow Sea with the calculated Forel-Ule value (*FU* = 9).
Figuur 5 - Voorbeeld van een 9-bands (b1-b9) genormaliseerd reflectiespectrum van één pixel uit een MERIS satellietbeeld van de Gele Zee en de hieruit berekende Forel-Ule waarde (*FU*=9).

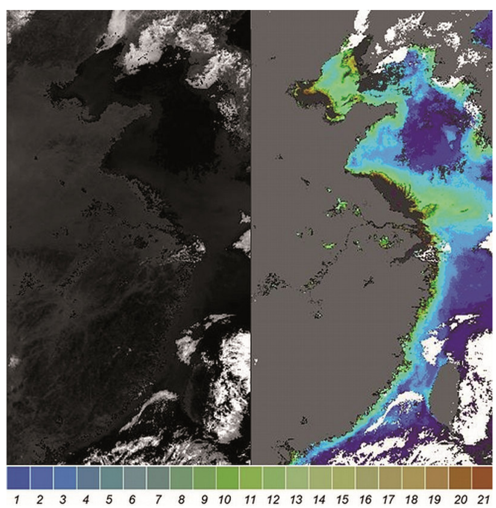

Figure 6 - An example of a MERIS satellite image (11 Feb. 2009) of the Yellow Sea. The left panel shows the remote sensing reflectance of MERIS-band 5 (560 nm) and the right panel shows into Forel-Ule converted spectral information contained in the 9 MERIS bands. In the right panel white indicates clouds, grey indicates land and black means ‘no data available’.
Figuur 6 - Een voorbeeld van een MERIS satellietbeeld (11 Feb. 2009) van de Gele Zee. Links de remote sensing reflectie in MERIS-band 5 (560 nanometer) en rechts het, met behulp van de spectrale informatie van alle 9 MERIS-banden, naar de Forel-Ule-schaal getransformeerde satellietbeeld. Voor het beeld rechts geldt: grijs is land, wit is wolken en zwart is ‘geen data beschikbaar’.

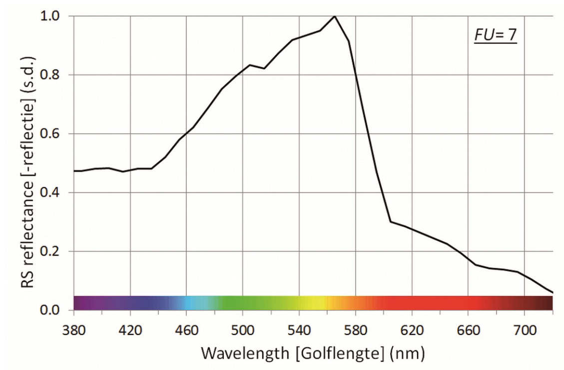

Figure 7 - The Remote Sensing reflectance spectrum modelled though Ecolight with corresponding calculated Forel-Ule-value (the model's outputs) with as model inputs clear ocean water (case 1) containing 8mgm^{-3} of chlorophyll.

Figuur 7 - Het met Ecolight gemodelleerde Remote Sensing reflectiespectrum met bijbehorende en berekende Forel-Ule-waarde (de outputs) met als model inputs een chlorofylconcentratie van 8 mgm^{-3} in helder oceaanwater.

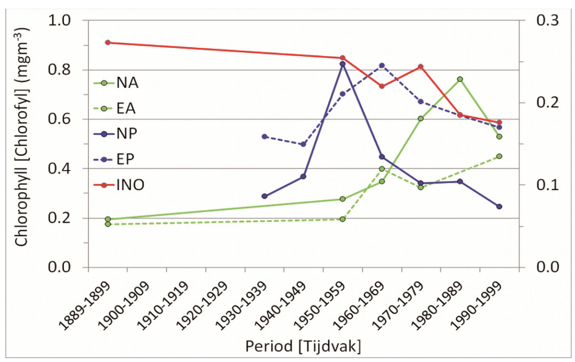

Figure 8 - The chlorophyll concentration in mgm^{-3}, averaged per decade, of respectively the North Atlantic- (NA), the Equatorial- (EA), Northern Pacific (NP), Equatorial Pacific (EP) and Indian Ocean (INO). The right y-axis belongs to EP and INO. The figure shows during the period 1889 to 1999 a greening Atlantic (increase of chlorophyll, green lines). However, the Indian Ocean (red line) is bluing (decline of chlorophyll) over the same period. Both the Northern- and Equatorial Pacific (blue lines) are greening over the periods 1930-1959 and 1930-1969 respectively and hereafter are bluing again until 1999.

Figuur 8 - De chlorofylconcentratie in mgm^{-3}, gemiddeld per tijdvak, van de Noord Atlantische- (NA), de Equatoriale- (EA), Noordelijke Stille- (NP), Equatoriale Stille- (EP) en Indische Oceaan (INO). EP en INO staan op de rechter y-as uit. De figuur laat tussen 1889 en 1999 een groener (meer chlorofyl) wordende Atlantische Oceaan (groene lijnen) zien. De Indische Oceaan (rode lijn) echter wordt blauwer (afnemend chlorofyl) over dezelfde periode. Zowel de Noordelijke als Equatoriale Stille Oceaan (blauwe lijnen) worden respectievelijk tussen 1930-1959 en 1930-1969 groener en worden hierna, tot 1999, weer blauwer.

CHAPTER 1 - GENERAL INTRODUCTION

"The foureteenth, in the morning, was calme with fogge. At nine, the wind at east, a small gale with thicke fogge ; wee steered south-east and by east, and running this course we found our greene sea againe, which by proofe we found to be freest from ice, and our azure blue sea to be our ice sea. At this time we had more birds then we usually found."

H. Hudson, First voyage, 1607

"For thence it may be gather'd, that the Sea-Water reflects back the violet and blue-Making Rays most easily, and lets the red-making Rays pass, most freely and copiously to great Depths. For thereby the Sun's direct Light at all great Depths, by reason of the predominating red-making Rays, must appear red; and the greater the Depth is, the fuller and in-tenser must that red be.
And at such Depths as the violet-making Rays scarce penetrate unto, the blue-making, green-making, and yellow making Rays being reflected from below more copiously than the red-making ones, must compound a green".

I. Newton, 1704

"Alles, was sich auf die Farbe des Wassers bezieht, ist ausnehmend problematisch".

A. Von Humboldt, 1815

"The colour of the Greenland Sea varies from ultramarine blue to olive green, and from the most pure transparency to striking opacity. These appearances are not transitory, but permanent; not depending on the state of the weather, but on the quality of the water. Hudson, when he visited this quarter in the year 1607, noticed the changes in the colour of the sea, and made-the observations, that the sea was blue where there was ice, and green where it was most open".

W. Scoresby, 1820

"Mit dem Spectroskop untersucht, zeigte sich in dem aus dem Wasser kommenden Licht das Roth ganz verschwunden, das Gelb sehr erheblich verblaßt, so daß die *D*-Linie kaum zu erkennen war, dagegen erschienen *Grün*, *Blau* und *Indigo* hell und die beiden Linien *E* und *b* flossen zu einem deutlichen dicken Absorptionsstreifen zusammen. Meine Absicht, auch das Licht der 'grünen' Grotte zu untersuchen, konnte ich leider wegen plötzlicher Erkrankung nicht ansführen; jedenfalls dürfte sich aber solches der Mühe verlohnen und möchte ich durch diese Notiz Veranlassung geben, das

Spectroskop bei Untersuchung der noch in vielen Stücken räthselhaften Wasserfärbung mehr als bisher zu benuntzen".

H. W. Vogel, 1875

"La question est depuis longtemps posée : à quoi tiennent ces différences de couleur? Pour étudier systématiquement la couleur des lacs, j'ai employé deux méthodes d'observation :
La première consiste à prendre la note de la nuance ou du ton avec des craies de pastel frottées sur un carton grisâtre. Aussi ai-je cherché une autre méthode. Je me suis fait une gamme de couleurs transparentes en adoptant la disposition suivante : Je fais deux solutions aqueuses, l'une bleue, de sulfate de cuivre ammoniacal, l'autre de chromate neutre de potassium, l'une et l'autre au 1 : 200^{e}".

F. A. Forel, 1895

"A sufficient deep layer of pure water exhibits by molecular scattering a deep blue colour more saturated than sky-light and of comparable intensity. The colour is primarily due to diffraction, the absorption only making it of a fuller hue. The theories hitherto advanced that the dark blue of the deep sea is reflected sky-light or that it is due to suspended matter are discussed and shown to be erroneous".

C. Raman, 1922

These quotes indicate that the colour of the sea has been an intriguing phenomenon since the days of Hudson, and probably much earlier. Through time the ever-changing colours of lakes and seas amazed travellers, and inspired painters and writers. At a later stage scientists interested in an explanation of the phenomenon became aware of the fact that the sea colour and its transparency could be related to "what's in the water", *i.e.* organic and inorganic material, which apparently determined its colour. Already William Hudson, explorer of the sea and navigator of the early 17th century, was aware of the fact that changing sea colours meant change in bottom topography; therewith the observation of 'colour' was useful for navigation purposes. Goethe described the colour of the sea during his crossing from Messina to Naples in 1739 in his book 'Voyage to Italy' (1786). For him, like many others, it was merely a joy to look at the variable colours of the sea. In figurative art that is inspired the sea we usually see beautiful, but most of all colourful seascapes. A painting of a realistically depicted sea, "*Bracing the Waves"* (1890) by the Armenian painter Aivazovsky Ivan Konstantinovich, is a good example (illustrated in Chapter 2).

During the attempts to explain the colour and transparency of the sea, scientists designed devices to measure and classify these water properties. The observations were considered useful in particular for navigation: the sea's colour indicates, it was realised, the presence of icebergs, shallow water, river discharge location, suspended matter, etc.

All explorers, writers, painters and scientists of the old days had one thing in common: their great ability of observing 'the undistinguished'; they wrote about or painted the blue in the ocean, the brown in the rivers, the black in the puddles and the transparency of raindrops. An example of the diversity in colour of natural waters is given in Figure 1.1. During the first quarter of the 19th century more and more theories on the colouring of natural waters were tested and explained. In the following, a modern view on the colours of the sea is sketched to clarify what was unknown a century ago. This colour, as we know now, is caused by a combination of scattering of the blue- and absorption of red to green sun rays by water molecules and by what is in the water. Besides, the colour can be influenced by the colours of surroundings like rocks, sky, trees and bottom. For this reason we refer to this phenomenon as the apparent colour of water and more generally as 'ocean colour' in the case of marine waters.

Figure 1.1 - An example of six differently coloured sea areas with from left to right top: Central Atlantic, Central North Sea, Coastal North Sea, left to right bottom; Coastal North Sea during algal bloom, Wadden Sea with lots of re- suspension of sediment and a coastal outlet dominated by coloured dissolved organic matter. Source: Photographs by B. Aggenbach (NIOZ) and A. Hommersom and by the author himself.

Next to seawater temperature, salinity and transparency, 'ocean colour' observations [1] belong to the oldest time series of climate-related data. Ocean colour is one of the Essential Climate Variables (ECV) for which sustained quality measurements are needed to track and analyse climate change [2]. This is nowadays considered an important aspect of the science of ocean optics; changes of climate, ocean circulation and mixing may well have effects on 'ocean colour' and *vice versa*, if only because the colour is influenced by phytoplankton presence and abundance, two biomass aspects that are closely related to temperature change and hydrographical variations (in currents; in density stratification, etc.) that go with such change; 'global change' and 'global warming' are phenomena widely discussed, even in the popular press and in politics because of the economic implications if humanity wishes to curb deleterious effects and consequences.

Insight in ocean optics has evolved gradually, from centuries ago, the time of mere observations of colour and transparency changes in time and space, to the period starting in the late 20th century when satellites were launched and ocean optics became a real science. In other words, an evolution from no more than human fascination for the colour of natural waters to the development of ideas, instrumentation, instrument validation and experimentation, the ingredients necessary to really understand the colouring of water. The intellectual path that emerges in this thesis is typical of the development in many disciplines of science.

LIGHT AND WATER

My work in the field of marine optics at the Royal Netherlands Institute for Sea Research began in the late seventies at the institute then known as NIOZ. In the beginning I was engaged to design state-of-the-art spectral radiometers. These instruments could measure both the transparency and colour of water, for the determination of the underwater light regime. With these optical measurements we were able to establish and model phytoplankton growth in seas and oceans ('primary production', the base of the marine food chain). These new instrumental designs replaced devices used at the time like the Secchi disc, to establish the water transparency and the penetration depth of sunlight in water and the Forel-Ule scale to establish the colour of the water. At the time I qualified these out-dated devices as primitive tools, but later I had to revise this opinion as simple but adequate relations could be established between Secchi depth, turbidity and particulate matter concentration; also, a validation experiment of the Forel-Ule-scale using modern optical equipment showed that the scale can be used with much success to classify natural waters on the basis of colour.

Classification of sea water can be achieved in various ways, e.g. by the concentration of dissolved or suspended matter in the sea, but also by its colour. Today, this colour (ocean colour) is determined through the use of multi-channel and hyperspectral radiometers. Resulting spectra are complicated. Until now it has been impossible to link these spectral data to available historical data as for instance Forel-Ule observations, which consist of simple numerical values between 1 and 21.

Spectral information, such as the colour of an object or the colour of the sea, may eventually be converted and simplified by colorimetric calculations (see paragraph on Colourimetry, page 15) to two numerical values, an *x* and *y* chromaticity coordinate. By converting the values 1 to 21 of the Forel-Ule scale to an *x* and *y* chromaticity coordinate we create a link between the old and the new way of determining ocean colour. By doing this, we can extend the times of modern ocean colour measurements (say, from the eighties of the past century) by many decades (to more than a century, so from the late 19th century).

This way, observations of the colour and transparency of the oceans available over 10 decades, may well be used to facilitate statements about effects of the influence of climate and global change under the influence of temperature rise of 'the oc ean' since 1850.

Confronted with all marine optics-related laws of science related to the interaction of light and seawater, my interest was more and more aroused by the ideas of the seafarers and scientists of far before my time concerning the phenomenon 'colouring of the sea'. However, were people centuries ago really interested to reveal the scientific truth in this respect, or did it never pass the stage of only a description of these colour changes during a stay at sea? It was known around 1600 that sea colour and bottom depth were somehow related and this knowledge was used for a safe navigation through shallow waters. Also it was known that the presence of ice was turbidity related, and even the occurrence of fish could more or less be established on the basis of the colour of water.

To obtain a more complete and reliable view of the philosophy of yesterday's scientists, I have tried to reveal the unrevealed, until now hidden in documents of the past. It is known now that, for at least hundred years, this branch of oceanography focuses on the study of the interaction of sunlight and seawater with only one purpose: to obtain insight in dynamic processes that are at the basis of this interaction, such as sediment transport and phytoplankton abundance and thus primary production. Seawater containing phytoplankton, as already observed above the basis of the food chain, needs the energy of light for growth. This energy comes from sunlight and is converted into carbohydrates through photosynthesis and then into plant material. Absorption of light in water however is not due solely by phytoplankton but also by water itself and by dissolved organic material called yellow substance or gilvin. Next to absorption of sunlight, (back) scattering takes place. Again, this scattering is caused by plankton (particularly light scatter by the calcareous skeleton of cells of the class *Coccolithophoridae*), but also by minerals and re-suspended sands. We now know that water molecules both absorb and scatter sunlight, a phenomenon discovered and described in the second decade of the past century.

OPTICAL OCEANOGRAPHY

Knowledge of the interactions between sunlight and the marine environment (optical oceanography) is essential for the understanding of photo-biological processes in the water (especially primary production) and at the same time these interactions generate information on the composition of seawater more generally referred to as 'water quality'. Different types of seawater can be recognised and classified by their colour.

The interdisciplinary field of optical oceanography started to develop over the twentieth century (See Spinrad 1988 [3]) and contributes to traditional oceanographic sciences as independent source of measurements and variables. Oceanographic research now takes place all around the world and is often accomplished through multidisciplinary projects with a joint problem. As an example of projects where the colour of the sea plays a central role, I mention the *Deep-Chlorophyll- Maximum* (DCM) Atlantic Ocean expedition of 1996, with the main objective to study the factors counteracting large fluctuations of microbial populations around the deep Chlorophyll Maximum. Another example is the *Integrated Network for Production and Loss Assessment in the Coastal Environment* (IN-PLACE) Wadden Sea project, which started in 2010 with the aim of describing and understanding the variability, both in space and in time, in primary productivity of phytoplankton and microphytobenthos in the western Wadden Sea. In both projects the key issue was the characterization of the vertical distribution of chlorophyll using optical measurement techniques. Marine-optical research, through the use of specific equipment such as underwater absorption-, scattering- and radiometers, can provide this insight.

The example of Figure 1.2 shows the result of one of the optical parameters, the light absorption at 676 nm (a chlorophyll absorption band), in the search to the deep chlorophyll maximum. By means of regularly taken depth profile measurements of the absorbed colour of the water, it became possible to study depth-related day and night rhythms of phytoplankton. Such a study can only be achieved through the use of optical techniques. Sampling at discrete depths, instead of profiling, in this case offers no alternative. Actually, this was, more than 30 years ago, the point made by Gieskes, Kraay and Tijssen, who measured vertical profiles of chlorophyll in the open central Atlantic Ocean in 1977 and observed rapid changes of the depth of the maximum chlorophyll layer within a day -- a depth that changed by tens of meters in a matter of hours. Gieskes and Kraay ascribed this phenomenon to internal waves, locally at a depth of around 100 m. Profiling was done with a fluorometer continuously recording chlorophyll concentration in *situ* (Gieskes *et al.*, 1978 [4]).

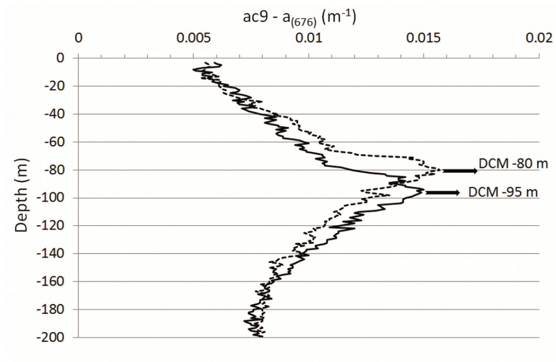

Figure 1.2 - Shown are 2 vertical profiles of the measured light absorption by chlorophyll of the open North Atlantic Ocean using a flow-through absorption meter. Through the many profiles, daily taken at one measuring station, the depth over which the deep chlorophyll maximum moves during day and night becomes visible. The example shows the deep chlorophyll maximum at noon located at 90 meters depth. At midnight it moved to 80 meters depth. Taking discrete water samples offers no alternative.

Optical oceanography in general facilitates climate related research through the water quality monitoring of sea and ocean to anticipate on possible changes in the ecological system using climate models. Changes in our climate are also associated with an increased carbon dioxide (CO_2) levels in the atmosphere. This increased carbon dioxide slowly penetrates the oceans, and leads to shifts in the chemistry of the sea with expected impacts on organisms with calcareous skeletons, such as corals and Coccolithophorids. Satellite ocean colour observations can be helpful here to observe changes. Indeed, ocean colour monitoring, especially from space, allows both local and global mapping of changes in the ecosystem. The information thus obtained can then be used as starting condition of ecological models to predict the development of ambient properties in ocean, coastal and estuarine systems.

INSTRUMENTAL DEVELOPMENT

Generally we can say that instrumental development runs parallel with an increase in both knowledge and scientific discernment, and so it is in the field of marine optics. In the 17th century there were no tools to classify phenomena such as water colour and transparency. This period and preceding periods can best be described as periods of just pure fascination for the colours and clarity of natural waters in all its aspects. Think of turquoise coloured alpine lakes, blue-green coloured glacial ice and of the differently coloured rivers and coastal seas, although we must bear in mind that sailors like Hudson used colour vision to navigate through the coastal zones. Shortly after 1791, the year in which the Swiss Horace-Bénédict de Saussure introduced his paper 'sky colour-comparator scale' (one new about a relation between air humidity and sky colour), named cyanometer, a start was made with the development of marine-optical instrumentation. It was at the beginning of the next century, on their way to South America, where Alexander von Humboldt and Aimé Bonpland used that paper scale to determine the colour, *i.e.* the blueness, of the sea. Von Humboldt tried to establish a relation between weather condition, bottom depth and the colour of the sea. That century, next to colour, numerous devices were tested to establish the water transparency, including teapots, white chinaware dinner plates and metal or wooden discs.

During the 19th century, developments in methodology and instrumentation are given first priority in the context of navigation and fisheries and even for the detection of lost cargo or the location of fishing grounds. More scientific interest in the colour of natural waters, especially in the blue colour and its transparency, produced a variety of optical devices for use in the laboratory. Two pieces of equipment are still in use: the first one being the Secchi disc (see Chapter 3), a white disc to measure the transparency of sea water, introduced in 1865 by the Jesuit Father Angelo Secchi. The second one being the Forel-Ule scale (see Chapter 4), a colour comparator scale to determine lake- and sea colour, introduced at the end of the same era by François Alphonse Forel and Willi Ule. The scale is based upon mixtures of coloured chemical fluids sealed in glass tubes. The Forel-Ule-scale will receive special attention in this dissertation as data collected with the scale can be used for hindcasting purposes (climate change reconstruction).

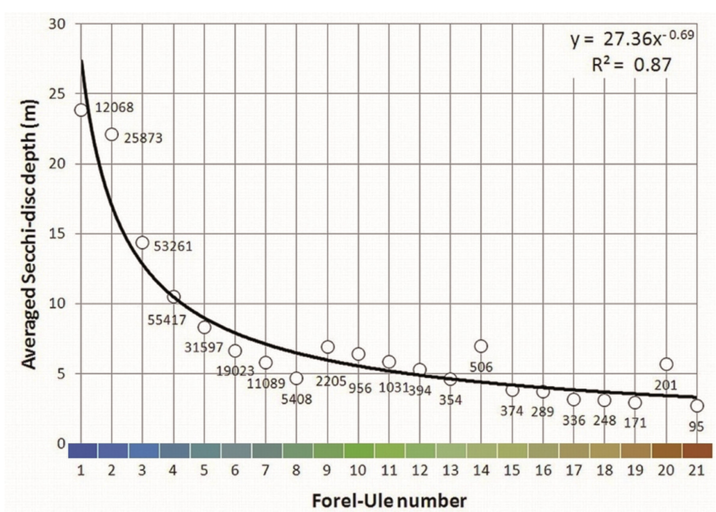

Figure 1.3 - The averaged Secchi-disc depth in meters as a function of the Forel-Ule number. The numbers of the data combinations are indicated. We see a simple relation, the bluer the more transparent the water becomes.

The natural colour of the sea (Forel-Ule number) and its transparency (Secchi disc depth) are inextricably related, as we can see from Figure 1.3. A blue sea (Forel-Ule-scale-numbers 1 to 4) has great transparency; a green sea (Forel-Ule-scale-numbers 8 to 12) has less transparency and a brownish coloured lake or tidal sea (Forel-Ule-scale-numbers 17 to 21) has the least transparency. The development of in-situ optical devices to establish the depth of the euphotic zone gained momentum after the introduction of light-sensitive materials, used in early photography, and the invention of the electric light bulb and the photovoltaic cell which can be dated round the turn of the century.

After the fifties of the last century, more and more optical instruments became available to measure the (angular) distribution of the underwater light field. The first optical instruments were equipped with so-called white light or PAR sensors to measure Photosynthetically Available Radiation. It would take another twenty-five years to develop more advanced radiometers which could accurately measure both the above- and the underwater light field per nanometre. Examples of modern radiometers, absorption- and scatterometers and transmissometers are shown in Figure 1.4.

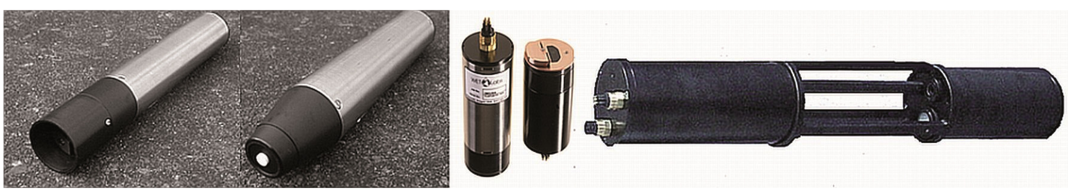

Figure 1.4 - From left to right; RAMSES hyperspectral radiometers for radiance and irradiance measurements by TriOS GMBH, Germany, a scatterometer (top- and bottom view) and the ac9 absorption- and transmissometer are both manufactured by WET Labs, USA.

These optical devices are actually used to monitor, in some cases autonomously, colour related phenomena, such as eutrophication or sediment transport in estuaries and tidal areas, to facilitate either eutrophication or sediment modelling and bottom morphology studies. Also, autonomous optical systems are used for early and rapid detection of toxic algae to benefit aquaculture and in broader sense to benefit tourist industry (bathing water quality). By placing radiometers on satellites (since 1978) it became possible to monitor ocean colour from space. Ocean colour satellite remote sensing is the only way to monitor the green colour of algae to derive (estimate) total and new primary production on an ocean large scale.

Optical properties

The optical properties of sea water can be divided into two classes, the Apparent (AOPs) and the Inherent (IOPs) Optical Properties. Apparent optical properties depend on the ambient light field and so they can be affected by the solar light conditions were historically seen the first to be described.

Inherent optical properties depend only on the constituents within the water and not on the ambient light field so they are not influenced by solar light conditions like the height of the sun. These properties can be established, tested and validated in a laboratory and became the focus of scientific studies in the second half of the 20th century.

Examples of inherent optical parameters are the absorption- (*a*), the scattering- (*b*) and the beam attenuation coefficient (*c*), all per meter (m^{-1}). The wavelength (λ) dependent beam attenuation coefficient c is defined as the sum of both wavelength dependent total absorption and total scattering

$$c(\lambda) = a(\lambda) + b(\lambda) \qquad (1.1)$$

Examples of apparent optical properties are the Secchi disc depth SD (m), the Forel-Ule index, the diffuse attenuation coefficient *k* (m^{-1}), the ratio of the upwelling- and downwelling sunlight, below or above the water surface. This ratio is called reflectance *R* (rel. units). An important and much used optical property is the remote sensing reflectance R_{RS} [5] and can be calculated according to

$$R_{\mathrm{RS}}(\lambda) = \frac{L_{\mathrm{sfc}}(\lambda) - \rho L_{\mathrm{sky}}(\lambda)}{E_{\mathrm{S}}(\lambda)} = \frac{L_{\mathrm{W}}(\lambda)}{E_{\mathrm{S}}(\lambda)} \qquad (1.\ 2)$$

where L_w is the water leaving radiance and E_s is the total downwelling irradiance from the sky and direct sunlight. L_{sfc} is the radiance measured above the sea surface. The term ρL_{sky} (L_{sky} is the sky radiance, ρ typically >0.02<0.03) corrects for the radiance coming from the sky that is reflected back at the air-water interface. All parameters are a function of wavelength (λ).

Optical properties of seawater are mainly determined (besides by the water itself) by three components: chlorophyll-containing algae, inorganic particles and (Coloured-) Dissolved Organic Matter (CDOM; also called Gilvin, yellow substance or Gelbstoff). Although the physical description of the 'blue' scattering of water was already known since 1922, provided by the Nobel prize winner Raman (Chapter 2 of this thesis), it took more sophisticated modern equipment to measure accurately the inherent optical properties, *a* and *b,* of pure-water (Pope and Fry in 1997 [6] and Buiteveld *et al*. in 1994 [7]. The spectral curves of these pure water optical properties are shown in Figure 1.5.

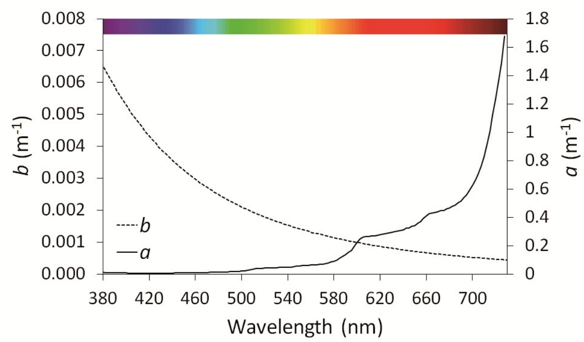

Figure 1.5 - The spectral absorption- (a) and scattering-coefficient (b) of pure water measured in the laboratory by respectively Pope and Fry in 1997 and by Buiteveld *et al*. in 1994. Note the difference in scale between the left and right axis.

The type and relative proportion of the different concentrations of main water constituents determines the water type or 'case'. Two extreme cases have been described by Morel and Prieur in 1977 [8]: case 1, introduced for oceanic waters (mainly dominated by small amounts of organic matter) and case 2 for coastal waters (dominated by highly variable concentrations of organic and inorganic matter).

Both the theoretical description of the underwater light field (radiative-transfer equation) and the determination of the inherent and apparent properties of seawater together is part of the marine-optical research field. In the blue ocean concentrations of dissolved and particulate matter are relatively low and therefore the optical path length of underwater sunlight, around 300 m, is relatively long compared to the optical path length of a few centimetres to meters in coastal waters such as the Dutch and German Wadden Sea with its high loads of sediment. Examples of optical measurements of the subsurface downwelling irradiance E_{d-} and the above water remote sensing reflectance R_{RS} are shown in Figure 1.6 (left and right panel respectively) where a full line refers to the blue ocean and the intermitted line refers to the olivine coloured Wadden Sea. Parameter R_{RS} is important in marine research as from this parameter chlorophyll concentration, mineral content and dissolved organic matter (CDOM) can be estimated. The R_{RS}-value in the bands 380, 520 and 685 nm can be correlated to respectively the CDOM absorption, the amount of suspended material and the chlorophyll concentration.

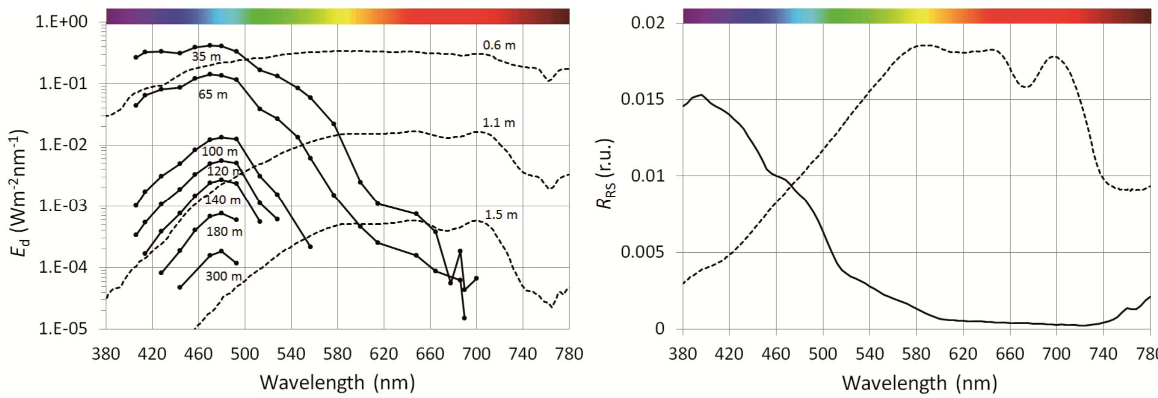

Figure 1.6 - The left panel shows the spectral downwelling irradiance Ed measured in the ocean (full line) and in the Wadden Sea (intermittent line). In the ocean we can still measure a fraction (blue) of the underwater sunlight at a penetration depth of 300 meters. The right panel shows the remote sensing reflectance for the blue ocean (full line) and for the turbid Wadden Sea (intermittent line) where blue light is strongly absorbed by CDOM.

Measurements to obtain optical seawater properties are usually performed from ships, measuring poles or buoys. However, we have to bear in mind that these types of measurements only provide spot information on the composition of the seawater. This is no problem for the slowly changing ocean, but it can be problematic for coastal waters with their strong temporal and spatial inhomogeneity, caused by tidal and other mixing processes that have a strong influence on temporal and spatial water quality and composition.

A synoptic determination of marine constituents through optical techniques can overcome this problem. Optical remote sensing from airplanes or satellites is the best synoptic determination technique. Optical remote sensing is a technique of measuring without having physical contact with the studied water body. The application of optical satellite remote sensing techniques to monitor the solar radiation scattered back from the water column became a major breakthrough in the seventies of the past century. The synoptically obtained impression from space made it possible to frequently (within days) monitor optical and other physical-oceanographic properties of oceans, seas and coastal areas, which resulted in an overwhelming amount of data revealing our blue planet’s health. Interestingly, and fully in line with the historic developments in colour measurements of natural waters (as described in Chapter 2), satellite-borne instruments that measure the reflection of the oceans in the visual spectral domain are generally known as ‘Ocean Colour’ sensors. ‘Ocean colour’ satellite remote sensing measurements by the Sea viewing Wide angle Field of view Sensor (SeaWiFS, launched in 1997 by the National Aeronautics and Space Administration NASA), the MEdium Resolution Imaging Spectrometer (MERIS on the

Envisat platform; launched in 2002 by the European Space Agency ESA) and the Moderate Resolution Imaging Spectroradiometer MODIS-aqua (launched in 2002 by NASA) have been proven to be the most valuable tools for studying changes in oceanic plankton and, more coastal-bound, sediment transport and anthropogenic pressure (changing sediment loads due to human activities along coasts and in bays). Further information on this subject is given by Ian Robinson [9] in his book '*Measuring the Oceans from Space'*.

WATER QUALITY PRODUCTS

At present, the focus of optical remote sensing research is the conversion of the measured colour to the composition of the water constituents (pigments in algae, coloured dissolved organic matter or 'CDOM', and suspended particulate matter) that are a major aspect of water quality. In other words, 'water quality' is a collective name for a number of bio-chemical parameters of natural waters. The bio-optical parameters are supplied to the ocean research community as water quality products that can be of organic origin, e.g., the chlorophyll and CDOM concentration, or of inorganic origin such as the suspended matter, or mineral concentration. Water quality can also be given as CDOM absorption or as an attenuation coefficient k (λ) at a specific wavelength, formerly as the inverse of the Secchi disc depth. In this thesis it is advocated that even the physiological colour of the sea, colour as we experience it, seen through the human eye expressed as a numerical value, can be called a water quality product. Most of these products are established from multi- or hyperspectral optical measurements, either from just above the sea surface or from space. Surface concentrations of Chlorophyll and total suspended matter plus CDOM absorption can be derived from the remote sensing reflectance R_{RS} (sr^{-1})

Relations to convert R_{RS} into a water quality product are called ocean or coastal colour algorithms. Algorithms might include a single wavelength range (called band) or a combination of multiple bands. As an example the SeaWiFS chlorophyll algorithm, also called OC4 switching algorithm, is shown. This empirical algorithm uses a single set of coefficients applied to the ratio R_{G} which is determined by the greatest ratio among three wavelength bands $R_{\mathrm{RS}}(443)/R_{\mathrm{RS}}(555)$, $R_{\mathrm{RS}}(490)/R_{\mathrm{RS}}(555)$, and $R_{\mathrm{RS}}(510)/R_{\mathrm{RS}}(555)$. For R equal to $\log_{10}$ (R_{G}) the chlorophyll algorithm [10] can be written as

$$Chla\ (\mathrm{mgm}^{-3}) = 10^{(0.366-3.067R+1.93R^2+2.649R^3-1.532R^4)} - 0.0414 \qquad (1.3)$$

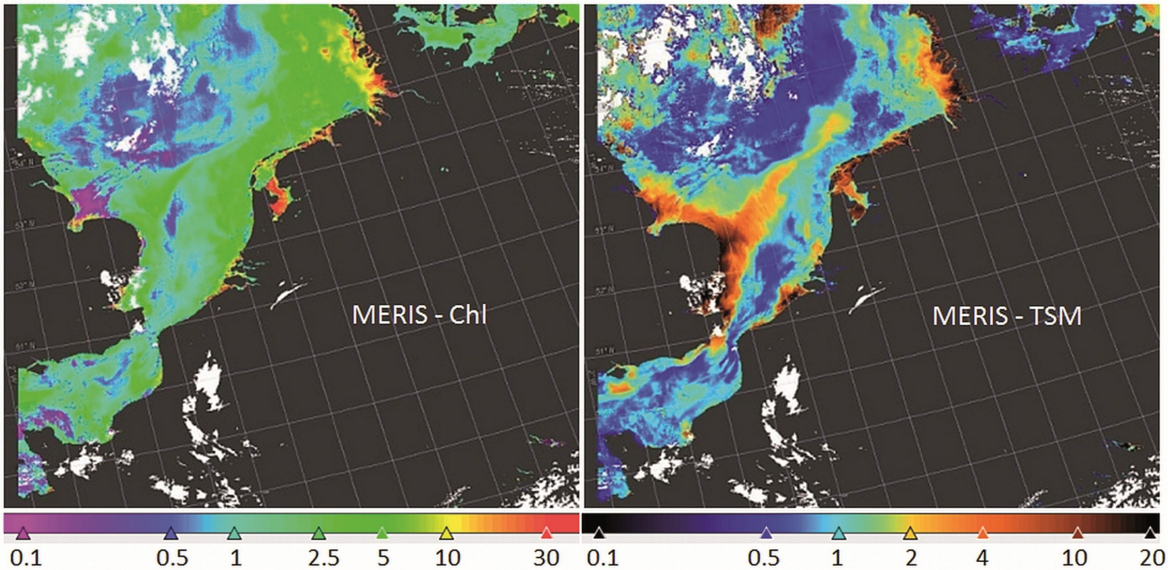

Figure 1.7 - Maps of the North Sea Chlorophyll-a (mg^{m-3}) and Total Suspended matter concentration (gm^{-3}), derived from a MERIS observation at the 4th of May 2006.

An ocean colour algorithm, such as presented in the equation above, can be applied to each picture element of a satellite image resulting in a chlorophyll distribution map. Two examples of MERIS water quality product maps of the North Sea are shown in Figure 1.7. The left image shows the spring Chlorophyll-a concentration in mgm^{-3} and the right image, same date, shows the Total Suspended Matter concentration in gm^{-3}.

Another example of the use of ocean colour from space is the identification and tracking of water masses called feature tracking (Quartly and Srokosz 2003 [11]). It is even possible to discriminate different plankton species in the ocean as was first described by Kirkpatrick *et al* in 2000 [12].

As a direct spin off from all the research on satellite-based 'ocean colour' measurements, many new instruments and knowledge have been developed that proves to be valuable for optically-based in situ measurements. At present, deployed by dedicated oceanographic research groups, more and more autonomous optical systems are placed on measuring poles or on board of ferries to monitor 'the health' of our coastal and oceanic waters. An example of such an optical system can be found at the Wadden Sea research jetty of the Royal Netherlands Institute for Sea Research at Texel, where in 2001 the newest generation of spectral radiometers was installed for the 'autonomous', self-supported monitoring of the Wadden Sea. A review on autonomous optical measurements from platforms was published in 2008 by Dickey *et al*. [13] where the authors describe the resulting recent advances in optical oceanography.

For unmanned autonomous optical systems it is necessary to simultaneously monitor conditions such as rain, white caps and sun glint, which can influence or even mask the colour of the water column**.**

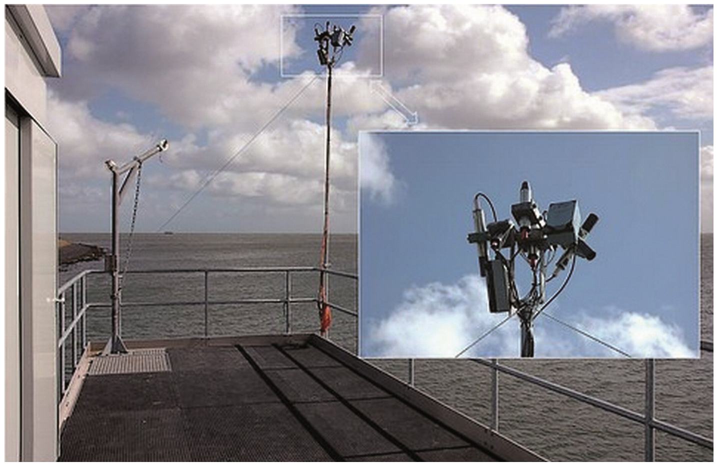

Figure 1.8 - The NIOZ jetty equipped with hyperspectral radiometers to monitor the Marsdiep inlet between North Sea and Wadden Sea. Chlorophyll and Suspended matter are the main derived water quality products which are monitored over a decade. Source: B. Aggenbach, NIOZ.

At the Royal Netherlands Institute for Sea Research such an automated optical system is operational since 2001. Every quarter hour colour measurements of the water, sun and the sky (including meteorological conditions) are acquired, from which the R_{RS}, chlorophyll and mineral concentration are calculated and stored in a database. This way the North Sea-Wadden Sea inlet, named Marsdiep, has been monitored for over a decade to detect possible changes in the ecosystem. The optical system mounted on a pole on the platform of the NIOZ jetty in the Wadden Sea, is shown in Figure 1.8. Guidelines to monitor coastal colour with this kind of automated systems are given by Wernand 2002 [14].

COLOURIMETRY

Before the invention of spectrometers that measure quantitatively the radiance in the visual wavelength domain, the human eye was the best instrument to determine the colour of the sea. Indeed, in a large part of this thesis an interpretation is presented of the Secchi disc depth and Forel-Ule measurements that are made by the human eye. However, also a significant part covers the hyperspectral characterization of the *FU* scale and the connection between the present multispectral observations by MERIS and the historic Forel-Ule measurements. Bridging the gap between the eye and spectrometers is provided by colourimetry. Colourimetry is the science that describes colours in numbers, or provides a physical colour match using spectral radiometers that simulate the spectral bandwidth of the human eye. One can express the colour of the sea by means of the spectral reflectance as shown before in Figure 1.6. However, one can also express this colour by one (*x, y)* set of chromaticity coordinates or even by a single numerical value. In the chapters 4 “Spectral analysis of the Forel-Ule Ocean Colour comparator scale” and 5 “MERIS-based ocean colour classification using the Forel-Ule scale” of this thesis colourimetry is at the basis of the described research.

Matthew Luckiesh wrote in 1921 on page 69 in his book ‘Color and its applications’ [15]:

> One of the greatest needs in the art and science of color is a standardization of the terms used in describing the quality of colors and an accurate system of color notation. The term ‘color', in its general sense, is really synonymous to the term light.

On the following page he wrote:

> The quality of any color can be accurately described by determining its hue, saturation or purity, and its brightness.

Colourimetry can best be described as the science of measuring colour or as ‘a system for colour measurements’, as it was introduced in 1931 by the Commission Internationale de l’Eclairage (CIE), or also known in its early days as International Commission on Illumination (ICI). An explanation of colourimetry, close to the matter discussed here, can be found in Curtis Mobley’s book ‘Light and water’ [16]. He explains colourimetry as the branch of science concerned with specifying numerically the colour of a sample of radiant power defined over the electromagnetic spectrum, *i.e.*, a technique by which an unknown colour is evaluated in terms of standard colours. Apel [17] explains the colour of the sea as the specification of the chromaticity (objective specification of the quality of a colour irrespective of its luminance) of the upward radiance and continues by saying:

> It is this intrinsic character that establishes the hue (colour) and the chroma, or strength of the colour of the sea.

The human eye

The human eye is sensitive to radiation reflected in the visible region of the electromagnetic spectrum, roughly between 380 and 780 nm. However, the eye is not equally responsive to all wavelengths within this visible region. Through the retina, a light-sensitive or photoreceptor layer at the back of the eye, incident light energy is converted into signals that are carried to the brain by the optic nerve. The retina consists of rods and cones (named after their shapes). There are about 100 million rods, highly sensitive low-light, not sensitive to colour, and around 5 million cones which provide, at high light levels, the eye's colour sensitivity. A small part in the middle of the retina, called *fovea centralis*, is the centre of the eye's sharpest vision and the location of most colour perception. There are three types of cones in the retina containing red, green and blue sensitive photo-pigments. So, the property of human colour vision can be referred to as trichromacy (based on perception of three primary colours). Detailed information on light vision and physiological colours can be found in Atchison and Smith 'Optics of the human eye' (2000) [18] and in Arne Valberg's book 'Light Vision Color' (2005) [19].

CIE XYZ SYSTEM

Experiments on how a standard human observer perceives colour started in the beginning of the 20th century. The most common type of human colour vision, trichromatism, can be demonstrated in a colour matching experiment by comparing the colour of two stimuli of different spectral radiant power. The two stimuli are viewed through the eye of an observer with 'normal colour vision', *i.e.*, the observer tries to match a patch of coloured light in the left half of the field of view with a combination of three adjustable patches of light in the right half of the field of view.

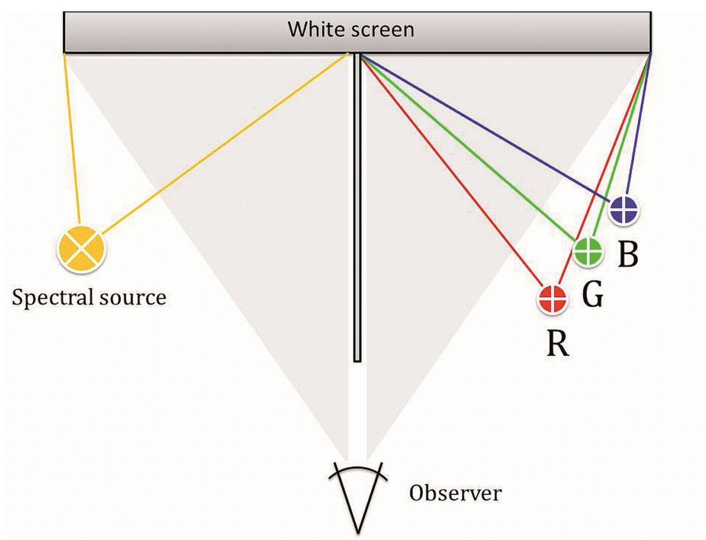

Figure 1.9 - To establish Colour Matching Functions the colour patch, falling at the left side of the screen, of a spectral source is compared to a composed colour patch falling at the right part of the screen. The composed colour is achieved by an observer by adjusting the relative intensities of the R, G and B light sources until the left and right part of the screen shows an identical colour.

The stimuli consist of a spectrally tuneable light source at one side of the vision field and at the opposite site a red (*R*), a green (*G*) and a blue (*B*) light source. The colour of the radiant power distribution of the single spectral light source can be matched by adjusting the relative intensities of the *R*, *G* and *B* lights (See Figure 1.9.) Results in the form of a so called Colour Matching Function (CMF, described in the next chapter) were accomplished under observing (viewing) angles of 2^0 and 10^0.

Generated response curves for the three different kinds of cones resulted in the colorimetric fundamentals proposed in 1931 by the Commission Internationale de l'Éclairage (CIE) [20]. In the commission's paper we find, concerning the study of colour perception, one of the first mathematically defined *XYZ* colour spaces derived from a series of experiments, according to the setup of Figure 1.9 using monochromatic stimuli (or real primaries) located at 700 nm, 546 nm and 436 nm performed around 1928 by William David Wright (1906-1997) [21] and around 1931 by John Guild (1889-1979) [22]. This set of real primaries, used in both positive and negative combinations, are named respectively *R*, *G*, and *B* and are related to the sensitivity of the human eye by the use of CMFs which match the later CIE 1931.

The CIE 1931 *XYZ* colour space can be defined as the first mathematically defined one. Any radiometric quantity measured spectrally or in a single band or colour can be assigned a unique set of chromaticity coordinates *x* and *y* (*z* can be omitted, see Eq. 1.6) and therefore a unique colour in the relevant *xy*-colour- space. The colour of the sea by means of its reflectance is such a radiometric quantity.

Basic terms and definitions used in colourimetry can be found in the International Lighting Vocabulary (CIE 1987) [23]. A more profound work on the matter by Wyszecki and Stiles 'Color science' has been published in 2000 [24].

COLOUR MATCHING FUNCTIONS

The CIE 1931 Colour Matching Functions (CMFs) for a 2^o standard observer form the basis for virtually all practical colourimetry. Colour as we experience it is produced by a combination of as already mentioned so called primary colours *R*ed, *G*reen and *B*lue. A visible colour *C* can be mapped in terms of three numbers *R*, *G* and *B* called tristimulus values and can be written as:

$$C = R\bar{r} + G\bar{g} + B\bar{b} \qquad (1.4)$$

where $\overline{r}$, $\overline{g}$ and $\overline{b}$ are the unit values or colour matching functions for red, green and blue. The CIE 1931 *XYZ* CMFs are graphically shown in Figure 1.10.

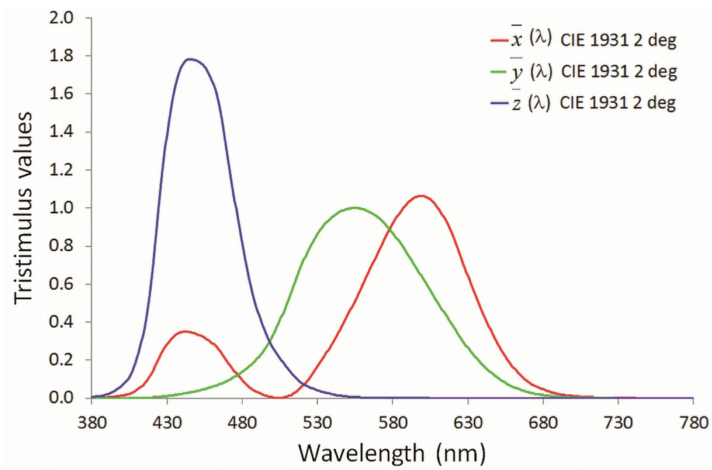

Figure 1.10 - CIE 1931 *x, y* and z colour matching functions for a 2o standard observer.

To eliminate negative tristimulus values the CIE established, through a linear relationship with the *RGB* tristimulus values a new reference system based upon the unreal primaries *X, Y* and Z. This way the CMFs could be represented as positive values over the whole visible spectrum.

How does the human eye interpret the colour of water? Basically, we can distinguish colours between dark blue (380 nm) to dark red (780 nm). A colour can be described as a mixture of three other colours or 'tristimuli'. The CIE 1931 tristimulus values called *X, Y*, and Z are 'derived' parameters from the RGB colours (Wyszecki and Stiles, pages 127-129) [24]. Tristimulus values can be calculated from the spectral reflectance, transmission or radiance scattered of an object, like from for instance seawater, to produce colour numerically and are determined by the following equations;

$$X = \int S(\lambda)\overline{x}(\lambda)d\lambda \quad Y = \int S(\lambda)\overline{y}(\lambda)d\lambda \qquad Z = \int S(\lambda)\overline{z}(\lambda)d\lambda \qquad (1.5)$$

where *S (λ)* stands for the spectral properties of any coloured light source, for instance spectral reflection or spectral transmission, and $\overline{x}$, $\overline{y}$ and $\overline{z}$ are the 1931 Colour Matching Functions (Stiles and Burch [25] and [26] and Speranskaya [27]). The chromaticity coordinates *x, y* and *z* can be calculated from the ratio of each of the tristimulus values and the sum of the values according to:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z} \tag{1.6}$$

As $x + y + z = 1$, and therefore $z = 1 - x - y$, the third coordinate offers no additional information and only two coordinates (by convention x and y) are used to represent the colour in a so-called chromaticity diagram as shown in Figure 1.11. The outer curved boundary is called spectral or monochromatic locus with the wavelength in nanometres.

The 'white point' W has the chromatic coordinates $x = y = z = 1/3$. If a line is drawn from the white point through a particular (x, y) chromaticity coordinate set F, then the ratio of the distance between this point to the white point, distance (a), and the distance from the locus to the white point, distance (a + b), gives us the colour saturation or colour 'purity' a / (a + b). As an example, imagine chalky water and clear water both with the same chlorophyll content. The colour of the water is determined by the amount of chlorophyll present in the water. In case of the chalky water, where the impact of the white calcite on its colour is nil, the (x, y) chromaticity coordinate set will be closer to the white point than in case of clear chlorophyll rich water. Therefore, the saturation of the colour will be less in case of chalky water but the actual colour of the water stays the same.

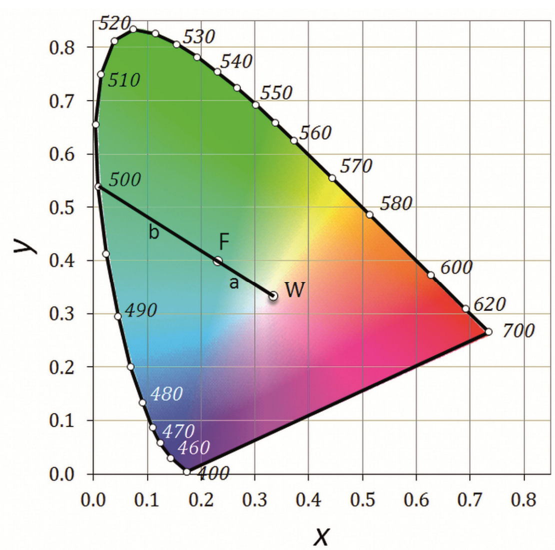

Figure 1.11 - The CIE1931 *x, y* chromaticity diagram for monochromatic colours. The outer curved boundary is the spectral or monochromatic locus, with wavelengths in nm. Each specific colour (F) is defined by its (*x, y*) chromaticity coordinate set. W is the white point. For example, the colour saturation or colour 'purity' of a specific colour on the black line is determined by the ratio between a and a+b.

Due to a possible underestimation of the sensitivity for wavelengths below 460 nm, Judd [28] derived a new set of CMF's in 1951 which were corrected again by Vos in 1978 [29] and are known as the Judd-Vos-modified CIE 2-deg colour matching functions. However, an evaluation of the CIE CMFs was carried out by the authors Shaw and Fairchild in 2002 [30]. They literally stated:

> Since 1931 the standard has withstood an onslaught of technical pressures and remained a useful international standard.

Therefore it was decided to use the CIE 1931 *xyz*-CMFs for a 2^o standard observer for all further chromaticity calculations in this thesis.

OUTLINE AND OBJECTIVES

This thesis is a compilation of scientific papers, most of them published, some recently submitted, but all with the common theme 'ocean colour'. The following questions prompted my project:

- ✓ In a search of the literature on the optical side of ocean science no historic overview was found of the work of those who laid the basis of modern 'ocean colour' research. How long did it take to understand and explain the phenomenon of the colouring of the sea, and why did it take so long? The time trajectory from observing a natural phenomenon to a full description and understanding is shorter or longer depending on the complicated nature of the phenomenon, but also the urgency to solve the problem**.** Were it only scientists who became intrigued by the colour of the sea, or was the colour of the sea something useful, to be applied for practical purposes of ship navigation, fish finding, and spotting icebergs and shallows? In other words, what was the purpose of the early and later observations? For this reason my literature search went back in time until the beginning of the 17^{th} century, the era of Sir Isaac Newton**,** to reveal all relevant material, observations and interpretations thereof available on 'the colour of the sea'.
- ✓ For many reasons sailors and explorers of the world were interested in the determination of water transparency, the simplest reasons concerning safety (no obstacles and shallows), fish finding, and navigation around icebergs by colour change monitoring from the ship's mast, even to allow the recovery of lost goods at sea. A truly scientific approach towards the subject was started by Angelo Secchi. He wanted to know to what depth sunlight could penetrate the water column, and whether or not, and where, sunrays lit the bottom of the sea [31], purely for scientific reasons, *i.e.*, out of curiosity. The Swiss François Alphonse Forel also experimented with different techniques with a white disc to establish the water clarity of Lake Geneva to study dependence of pelagic and benthic life in the lake on light. The 'Secchi' disc is still in use for

reasons of simple use, ideally for routine observations that can be integrated in ecosystem modelling, namely to determine primary productivity; but its history had never been documented fully.

✓ William Scoresby junior was amongst the first, at the beginning of the 19th century, to investigate the nature of sea colouring substances [32]. More research started at that time to identify the causes of the colours of the sea. Objects like dinner plates, coloured cloth, fruit, a white painted Six-thermometer, painted discs or semi-precious stones were used to classify these colours. With the passing of the century devices to identify the sea colours became more sophisticated. Even spectrographs designed for the laboratory were used. The development of these devices led to the Forel-Ule scale at the end of the 19th century. During my work at the Royal Netherland Institute for Sea Research over the past thirty years, I became interested in this simple instrument, so often used in the past to classify natural water on the basis of their colour. This colour comparator device (Forel-Ule-scale) was introduced around 1890, but it went out of use with the introduction, in the nineteen-seventies, of 'modern' radiometers. However, this old colour classifier had been used globally for over a century for which data, most unexploited, had been kept in the archives of the National Oceanic and Atmospheric Administration (NOAA) in the United States. The Forel-Ule dataset is in this thesis considered as a valuable element in climate-related observations of ocean change over time, as a matter of fact over decades. The dataset provides a direct measure of constituents contained within the ocean. Have these, notably phytoplankton pigments (a biomass indicator) changed over the last century, the period that 'global change' took place as a response to human interference with Earth? Could these historic 'ocean colour' data be coupled to newly gained 'ocean colour' data based upon completely different detection techniques: remote sensing by satellites, started three decades ago? If so, we can extend 'ocean colour' information back in time with almost one century (the reach back in time of the Secchi and Forel-Ule observations) and this would no doubt be a breakthrough in understanding our climate, in which the oceans play such an important role. However, to link old with more recent observations, the applicability of the Forel-Ule scale had to be established first by determining its spectral accuracy.

✓ The next question to be answered was if it is possible to identify and present any consistency or inconsistency over time of the colour of our main sea areas by exploring the historic dataset (reaching back to the late 19th century) in combination with satellite 'ocean colour' maps obtained only over the last 3 decades. The season, and more generally climate, can be considered as a forcing function of any possible change in 'ocean colour' over time since weather, temperature, light, and vertical mixing of the water column vary with the time of year, and over shorter and longer time spans. As examples of the effect of climate forcing altering the ocean's colour, I mention the publication of Fu *et al.* (2008) [33]. They concluded that abnormal weather, in this case snowstorms and low temperatures, influenced the open 'ocean colour' environment due to a rise in chlorophyll-*a***.** Venrick *et al.* (1987) [34] found a significant increase in total chlorophyll-*a,* during the summer, over a 20 year time span in the central North Pacific Ocean. They concluded that long-term fluctuations in atmospheric characteristics (decrease in sea surface temperature, increase in winter wind) changed the carrying capacity of the central Pacific's epipelagic ecosystem, a capacity that depends on primary production, that is in its turn related to the biomass of phytoplankton present.

To get an answer on the question above the historic dataset containing Forel-Ule observations has to be analysed per defined timespan to establish a mean Forel-Ule colour per sea area. Furthermore, possibilities should be investigated to transform Forel-Ule into chlorophyll biomass. This way an inter-comparison of already published chlorophyll-data can be established.

✓ Would it be feasible to transform a spectral reflectance based 'ocean colour' classification into a Forel-Ule based classification? In this way we could couple historic Forel-Ule observations to satellite 'ocean colour' observations with the benefit that we then can express 'ocean colour' into one numerical value, instead of the multiple information concealed in complete reflectance spectra.

The Chapters have the following titles, in the following order of the questions just raised:

Chapter 1. General introduction.

Chapter 2. Ocean optics from 1600 (Hudson) to 1930 (Raman); Shift in interpretation of natural water colouring: M.R. Wernand and W.W.C. Gieskes. Published as a book by Union des océanographes de France (UOF, July 2011). This chapter describes developments of ideas of explorers and scientists regarding both the colour and transparency of natural waters with their cause; insight is compared to current views.

Chapter 3. On the history of the Secchi disc. Published: M. R. Wernand, **"**On the history of the Secchi disc"**.** J. Europ. Opt. Soc. Rap. Public. 5, 10013s (2010). This chapter describes the evolution in methods and in instrumentation, developed by sailors and scientists, to determine the transparency of seawater.

Chapter 4. Spectral analysis of the Forel-Ule 'ocean colour' comparator scale. Published: M. R. Wernand, H. J. van der Woerd, "Spectral analysis of the Forel-Ule Ocean Colour comparator scale". J. Europ. Opt. Soc. Rap. Public. 5, 10014s (2010). This chapter describes a colour comparator scale from which the first 'ocean colour' observations date back to the end of the 19th century. The scale is spectrally analysed and we confirm that an 'ocean colour' classification according to Forel-Ule can be regarded as an objective method.

Chapter 5. Ocean colour changes in the North Pacific since 1930. Published: M. R. Wernand, and H. J. van der Woerd, "Ocean colour changes in the North Pacific since 1930" J. Europ. Opt. Soc. Rap. Public. 5, 10015s (2010). The North Pacific is characterized by the thousands of Forel-Ule observations that took place since 1930. The observations are analysed over a seventy year long period and results show a variation in the first four scale colours with a greenest ocean between 1950 and 1954 and a bluest ocean between 1990 and 1994.

Chapter 6. MERIS-based ocean colour classification using the Forel-Ule scale. In this chapter an algorithm is presented for the conversion of multispectral MERIS satellite data to Forel-Ule data. Satellite 'ocean colour' data can be linked to data from before the satellite era.

Chapter 7. Trends in ocean colour and chlorophyll concentration from 1889 to present. Submitted to 'Progress in Oceanography'. In this chapter, long-term trends in Forel-Ule data sets of the major ocean regions of Earth are analysed, the results suggesting no clear overall increase or decrease of 'ocean colour' and therewith of chlorophyll, in spite of 'global change'.

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CHAPTER 2 - OCEAN OPTICS FROM 1600 (HUDSON) TO 1930 (RAMAN)

SHIFT IN INTERPRETATION OF NATURAL WATER COLOURING

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ABSTRACT

In this essay, the gradual development of understanding of the transparency of natural waters and of insight in the cause of their various degrees of clarity and coloration is sketched from the times of Henry Hudson (1565? – 1611) to those of Chandrasekhara Raman (1888 – 1970). This historical overview highlights reports of explorers and scientists, many now quite famous, as well as observations of fishermen and other sailors intrigued by ocean and freshwater optics. A number of instruments, some of great simplicity, that were developed to quantify water transparency and colour , the latter gradually seen as an aspect of water quality and contents, is described. The Secchi disc (for transparency estimates) and the Forel-Ule scale (for colour), two pieces of equipment developed at the end of the nineteenth century, are still in use. The background of the colour of water remained a mystery until the beginning of the twentieth century. It is argued that this delay was caused by the fact that the subject was mostly treated as marginal. Moreover, aquatic optics is at the cross section of physics, chemistry and biology, and before the 20th century the understanding of all these disciplines was marginal, let alone grasped by one single person. In the third place, if proper pure-water distillation techniques had been available earlier the time span to understanding and theory development could have been shifted backwards by decades. The review ends with Raman, who showed in 1922 that water molecules scatter blue light and at the same time absorb the longer wavelengths in the visible part of the radiation spectrum, in this way explaining that the colour of the open ocean is blue, at least in the absence of particulate and dissolved matter that at times turn neritic and coastal seawater and lakes green and even brown. The history of insight into the cause of water colour can be considered as a metaphor of scientific progress in general: from observing a natural phenomenon without even trying to understand it, but instead using it for various purposes (in

this case: fish school localisation, and as an aid in ship navigation), to analysis of causes and if possible consequences, and the subsequent development of an encompassing theory.

Key-words*:* history of science, the colour of natural waters, water transparency, historic instrumentation, explorers of the world, Secchi disc, Forel-Ule, Raman

PREFACE

« L'eau est une substance incolore, inodore et sans saveur » (water is a colourless, odourless, and tasteless substance), as we have been taught since kindergarten, so why can a water body, such as a lake or the ocean for instance, have a colour, and even may have various colourings? Dating back to ancient mythology, fishermen and navigators have not waited for an answer before empirically using this visual information for their own purposes. An immediate answer to the initial question is, obviously, "there is something in the water that produces its tinge" which is somehow correct, even if the "something" was rather enigmatic. The mystery deepens when contemplating the open ocean; indeed, what can be said about the deep blue tint of such clear waters, *a priori* deprived from any discernible material? If most of the people were just noting the facts, those with inquiring minds were keen to find some reasonable causes for their visual impression.

The detailed history, over the last four centuries, of the many attempts to find satisfying explanations is proposed to our curiosity in the present monograph. It has been written by Marcel R. Wernand and Winfried W.C. Gieskes, distinguished marine biologists and opticists, and in the present case, meticulous historians as well as pleasant narrators.

The story, indeed, triggers off a whole series of genial intuitions and amusing mistakes, and a mixture of ingenious experiments and misinterpretations. In some sense, painters of the 19th century were better, at least in reproducing, if not explaining, what was offered by nature. The paintings, selected by the authors, nicely show the capacity of these artists in capturing the changing natural hues of the skies, waters, and also ice. When we know the solution of the problem of the colouring of a water body, as a modern student can now easily learn, it is difficult to imagine the length of the journey to reach this solution from the knowledge currently existing at the end of the 16th century, when the present account begins. It was necessary to know that white light is composed of all colours mixed together (a property unknown before Newton). It was also necessary to make a clear distinction between a transmitted colour and a reflected colour (we would say now a backscattered radiation); such discrimination supposes that the phenomena of absorption and of scattering are properly understood and separated, and that their spectral behaviours are at least roughly known. It was also necessary to realise that the sky reflection at the surface of the sea disguises the true colour of a water body. Even today, the confusion remains; ask people about what they think about the colour of the sea: “today it is grey for the sky is overcast; tomorrow, if the weather is fine, it will be blue”, which is a correct answer in terms of “apparent” colour, but not for the “intrinsic” colour the scientists are trying to explain. The readers will not be surprised to encounter through the whole story some well-known explorers, like Cook or von Humboldt, and to find again the names of the great physicists and opticists of the past centuries, like Newton and Arago, or Soret and Tyndall, amongst many others. The enigmatic phenomena of the sky and the sea colouring, and perhaps of their hypothesised interactions, have intrigued many scientists. Those readers with knowledge of Oceanography and Marine Biology will not be surprised to (inevitably) encounter Reverend Father Angelo Secchi, the papal astronomer with his white disc, and the limnologist François Alphonse Forel comparing the colour of the Lake of Geneva with his colour scale. Readers will certainly be more astonished in meeting poets and writers as well as alpinists and balloonists. The abundant iconography reflects the great diversity of the actors; it is a vivid miscellany of experimental designs, sketches, engravings, facsimile of writings, diaries, ship logs, and obviously solemn portraits.

The authors have made a thorough inquiry within the available literature, with many unexpected discoveries regarding the people who have contributed to the progressive building of a scientifically sound explanation. We are thus presented with an original account of a full history which ends in 1922 with Raman, who selected this topic for his Nobel lecture (in 1930). Actually, if the blue colour of the sky due to light scattering by air molecules was explained at the end of the 19th century, thanks to the theoretical work by L.W. Strutt (Lord Rayleigh), the blue colour of pure water bodies was still unexplained. Another step was needed, as the Rayleigh electromagnetic scattering theory for molecules comprising a gas does not apply to a liquid, such as water. In the first years of the last century, Einstein and Smoluchowski independently developed the adequate theory for the condensed state, soon experimentally verified for water by Ramanathan and Raman. The missing clue was at last found, and the deep blue hue was explained.

The colour of the sea was initially and for centuries a subject of pure scientific curiosity. Unexpectedly, this status will change; indeed, about fifty years after the first correct interpretation was given, the colour became a tool to investigate the content of the water, by interpreting its shift from a deep blue hue to various green shades. In particular, it is now possible to detect and quantify the chlorophyll concentration, and to do so from space, with the incredible spatial and temporal coverage that the satellite-borne radiometric sensors (called “ocean color sensors”) can now offer. This, however, is another story…

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INTRODUCTION

It was in the beginning of July 1608 that Henry Hudson, looking for a Northeast Passage to China and Japan and therefore sailing from one sea into another, noted in his ship’s log that a sea full of ice had a black-blue colour (Hudson, 1608, p. 99). Similar observations can be found in other old ship’s journals. In order to navigate their ships safely across the ocean, sailors used distinctions between the various colours of the sea. For the convenience of their successors, they often logged these observations.

In this article, we present an account of the attempts of explorers and scientists who tried to explain the mechanisms responsible for the transparency and the colouring of natural waters, to them a mysterious phenomenon. We describe the development of the concepts, issues and tools in a struggle of over three centuries by explorers of the sea and scientists in their search for the causes of the various colours and shades of natural waters, both marine and fresh. The essay, assembled in a chronological sense, starts at the time of Henry Hudson the seafarer (1600) and ends at the time of the Nobel Prize winner Chandrasekhara Venkata Raman (1930). Topics of a specific timeframe, such as the modern devices to determine and quantify the transparency and the colour of the sea, are explained in subsections.

In this overview, we also hope to give answers to questions such as: what was their motivation to report on the transparency and colour of seas and oceans? Was it fashion? Was it to impress others? Were researchers committed to this topic for practical reasons, or was it just a step towards other developments in their thinking?

Furthermore, this manuscript is written out of admiration for the surprising versatility, depth of thought and broad interest of early scientists. To quote Goethe, interviewed by Eckermann, talking about Alexander von Humboldt (Eckermann, 1827, p.188):

> He resembles a fountain with many pipes, at each side you only need to place a vessel to catch the refreshing streams, which flow endlessly[1].

This citation can be applied to many scientists living in the era before the twentieth century. However, for most of the men (no women, we have to notice) mentioned here, the efforts to explain the colour of water, with an emphasis on understanding why ocean waters are often blue, were no more than marginal science, just a mind exercise before they continued with subjects they considered of more importance. The absence of unified research has more often than not delayed the arrival of modern views on nature at the beginning of the twentieth century.

Recording seawater transparency and colour started during the first decades of the eighteenth century with observations of the founder of scientific oceanography (Vai & Caldwell, 2006), the Italian Louis Ferdinand Comte de Marsilli (Luigi Ferdinando Marsigli in Italian – 1658-1730). From the last decade of the nineteenth century until the present day, water transparency and colour has been quantified by means of a white disc designed by Angelo Secchi (1818-1878) while a colour scale was invented by François Alphonse Forel **(**1841-1912) and extended in colours by Willi Ule (1861-1949). Of course, nowadays more sophisticated electronic equipment, like the transmissometer and radiometer, is used, but the two historical devices are still the basis of ocean colour research.

Chandrasekhara Venkata Raman claimed, and later proved in 1922, that it was the molecular scattering of light in water that caused the blue colour of the sea, as well as the absorption of the longer wavelengths; water colour had in his view nothing to do with the reflection of the sky in water, as most people before him had proposed. In his Nobel lecture of December 11th 1930, he explained his reasoning to the world. This explanation ended the search for the mechanisms responsible for the colouring of natural waters that had eluded scientists for more than three centuries; indeed, to them it was just a mystery.

Throughout history the colours of rivers, lakes and seas, changing from place to place and from season to season, have amazed travellers and sailors alike; they inspired painters, and confused scientists. It was in the summer of 1826 when August Kopisch (1799-1853) and his friend Ernst Fries (1801-1833), both painters, (re-) discovered the '*GrottaAzzurra*' ('Blue grotto') at Capri, Italy and once inside were overwhelmed by the splendour of the colour of the seawater and its reflection on the ceiling (Kopich, 1838, pp. 9-59). Johann Wolfgang Goethe (1749-1832) described his physiological sensation of the colour of the sea during his crossing from Messina to

[1] *Ergleicht einem Brunnen mit vielen Röhren,woman überall nur Gefäße unterzuhalten braucht und wo es uns immer erquicklich und unerschöpflich entgegenströmt*.

Naples in his book *VoyagetoItaly*(Goethe, 17861788) and François Alphonse Forel published his findings concerning the transparency and colour of lake water in his monograph *Le Léman* (Lake Geneva, Forel, 1895). Goethe, the German writer, poet and scientist, and Forel, the Swiss multi-disciplined scientist and inventor of the word 'limnology', both had in common their great ability of observing the normal, the undistinguished, and trying at the same time to explain it. Transparency according to Goethe is the first grade of turbidity – a remark as trivial as Eugène Ionesco's (1912-1994), the Romanian-French playwright, who wrote in his 1949 play 'La Cantatrice Chauve' [The bold soprano]:

> The ceiling is above, the floor is below.

Everyone knows, but the trick is to wonder, as a good scientist should always do, and the colour of natural water is such an phenomenon: 'normal' people just take it for granted. Goethe, Forel and all the pioneers, in their search to explain the mysterious colouring of natural water, wrote about it, unlike others, who simply saw the blue in the ocean, the brown in the rivers, the black in the puddles and the transparency of a raindrop. This colour, influenced by its surroundings like the sky, the mountains, the trees, and the bottom and by "what is in the water", became known as the perceptible or 'apparent' colour of water.

Earlier names for these empirical facts or colour sensations were *'colores adventicii'* by Robert Boyle (1627-1691) (Boyle, 1664, p. 8) *'couleurs accidentelles'* (de Buffon, 1746, by Georges-Louis Leclerc Comte de Buffon (1707-1788), p. 151), *'imaginarii and phantastici'* (Rizzetti, 1675-1751, quoted in Goethe), or *'vitia fugitiva'* by Georg Erhardt Hamberger (1697-1755), quoted in Goethe (Goethe, 1810, p. 12) and last but not least to Robert Darwin's (1766-1848, Charles father) *'occular spectra'* (Darwin, 1786, p. 313). De Buffon's phrase *'couleurs accidentelles'* is very appealing, since it points out the ever-changing colour of the sea (and of lakes), seen through the human eye, depending on the place and time of observation.

In the following paragraphs, the development over the centuries is shown of the knowledge concerning the origin of the colour of natural waters. Systematically, results are shown of the observations and measurements by scientists who contributed to the understanding of the mechanisms behind this colouring, starting with the description of an observation to a full understanding of natural water colouring. The cause of the blue of the ocean has received most attention.

THE 17TH CENTURY

During the 17th century, one can find more and more written evidence of people interested in the colour of the sea. Seafarers wrote down their sea colour observations in ship's logs, as they understood the importance of this information while sailing unknown regions of the globe. A green sea meant fish and dark blue meant a sea with great depth. Although far from any explanation, people recognised the differences in water colours and how to use this information. In his attempt to find a northern passage to the Orient Henry Hudson had a great eye for detail. During his first voyage he not only wrote about the winds and the state of the sea but also kept track of the colour of the sea. On the 6th of July 1607, sailing in the Greenland Sea, he wrote (Hudson, 1607, p. 70):

> The sixth, in the morning, the wind was as before, and the sea growne. This morning we came into a very green sea; we had our observation 77 degrees, 30 minutes.

Hudson was of course aware of the danger of colliding into icebergs and knew that the water always changed colour near the ice. In these northern areas, his crew constantly watched for such changes. On July 11th 1608, during his second voyage a year later looking for a Northeast Passage Hudson, he again noted in the ship's log (Hudson, 1608,

p. 99):

> This fore-noone we were come into a greene Sea, of the colour of the mayne Ocean, which we first lost the eighth of June: since which time wee haue had a Sea of a blacke blue colour, which (both by the last and this yeeres experience) is a Sea pestered with Ice.

Hudson was aware of the fact that sea colour changes may also indicate bottom depth changes (Hudson, 1609, p. 120):

> The afternoon was reasonable clear. We found a rustling tide or current, with many over-fals to continue still, and our water to change colour, and our sea to bee very deepe, for wee found no ground in one hundred fathomes.

Even 'landlubbers' like Sir Francis Bacon, father of modern science (Spedding *et al.*, 1863, p. 434), tried to explain the phenomenon of different coloured waters. In 1631, a few years after his death, his majesty's chaplain Dr. Rawley (1590-1667) published Bacon's findings (see Figure 2.1) in the *Sylva Sylvarum or a Natural History* (Bacon, 1631, pp. 286-287).

Figure 2.1 – Sir Francis Bacon's findings in his *Sylva Sylvarum or a Naturall History* published in 1631 by his majesties chaplain Dr. Rawley.

In a small chapter on observations relating to the colour of the sea and other kinds of water Bacon states:

> The water of the sea and also other waters become blackish during movement and much whiter when at rest. Originated by different causes, easy to understand. When sunrays are penetrating this water surface they not longer will follow straight lines but by this constant moving surface progress along a much more obscure way. The opposite takes place when the water is in rest. Here transparency is always accompanied by a sort of whiteness.

Bacon at this point compares flat and rough water surface with respectively a mirror made of glass with a tinfoil or mercury inlay (whiter) against a simple mirror made of tin (darker). Furthermore, two small chapters in the works of the printer of the Royal Society John Martyn (Martyn, 1667, p. 485 and p. 496; Martyn, 1669, p. 700) contain findings, in old English, on the colour of some seas and rivers. From the 1667 issue of the philosophical transactions about *i.* the river colour in China and *ii.* the observations from a ship to and from New-England and near Barbados and from the 1669 issue of the philosophical transactions about *iii.* the change of sea colours under different illumination conditions:

> *i)*: "Rivers whereof one is faid to be of a Blew colour in Autumn, and for the rest of the year limpid. Another to be cold at the top, and very hot beneath". *ii)*: And as the Sea coloureth from green to dark, and so to blue, so in our return it colour'd from blue to

> dark, and so to green. When we were in the Latitude of Barbadoes, and had sailed so for two daies, and apprehended our selves to be within 70 or 80 Leagues, I observed the Sea was black and thick, not transparently blue, as before, and the foam against the Ship-sides was turbid, and of another consistence, than before. I had never seen the like before, yet was I willing to think the Sun not high enough, to give the water its due colour. I attended the suns progress, but behold, it turn’d Green; whereupon I asked the Master, who told me, we were within 60 leagues of Barbadoes, and that the Sea was there soundable, whereas before it was not so. But at Barbadoes in the anchoring places, it was Blue; and as we row’d ashore, in the shallow it was Whitish: and so at Jamaica near the shore it is transparently White, but within three yards more, transparently Blue. *iii)*: “About the colour of the sea, I have to add, That as we went, and passed from a Green Sea to an Azure, in the way when it was dark colour’d (which we formerly have spoken of) the top of each wave, as it was cast up before the Sun, shew’d it self to be Azure, the rest of the wave being dark-colour’d, approaching to black. And the like I observed coming home; for, though the Sea in its dark-colour resembled exactly what we saw before, as we went out; yet did the tops of the wave break and appear to be green, long before the great Waves or body of the Sea became green. I observ’d, that the Sea, which was Azure, and transparent in Sun-shinny dayes, was black and dark-colour’d, and much less transparent, when the Sun did not shine. But in the Green Sea there happens not the like Difference”.

In this matter, the colour sensation of natural waters, Isaac Barrow (1630-1677) cannot be forgotten, as he had an outspoken opinion on the blue colouring of seawater (Brewster, 1833, p. 29):

> The blue colour of the sea arises from the whiteness of the salt, which it contains, mixed with the blackness of pure water in which the salt is dissolved.

The opinion of Isaac Barrow (1630-1677) contained so little genuine philosophy that it must have attracted the observation of his former pupil and friend Isaac Newton (16421727). Concerning the ever-changing colour (*couleurs accidentelles*) of the sea Newton remarks on the colours of foam of the sea (Brewster, 1855, pp. 183-184):

> Now, it is obvious that froth, when seen under a clear blue sky, must have the colour of the sky itself, as it is nothing more than an accumulation of images of the sky reflected from the innumerable aqueous vesicles which compose it. The colour of froth, wherever it is place, must be the average tint of all the differently coloured rays, which fall upon it and are reflected to the eye.

Concerning Newton, Goethe however remarked in his ‘chromatics’ (Goethe, 1810, p. 35):

At this moment people prefer a more common theoretical consent, turning it off with either one or the other explanation of phenomena without taking the trouble to learn about the discrete and from there on building towards such a theory.[2]

With this remark he obviously criticized Newton's approach whom in fact first developed a theory and accordingly checked it by experimentation**.**

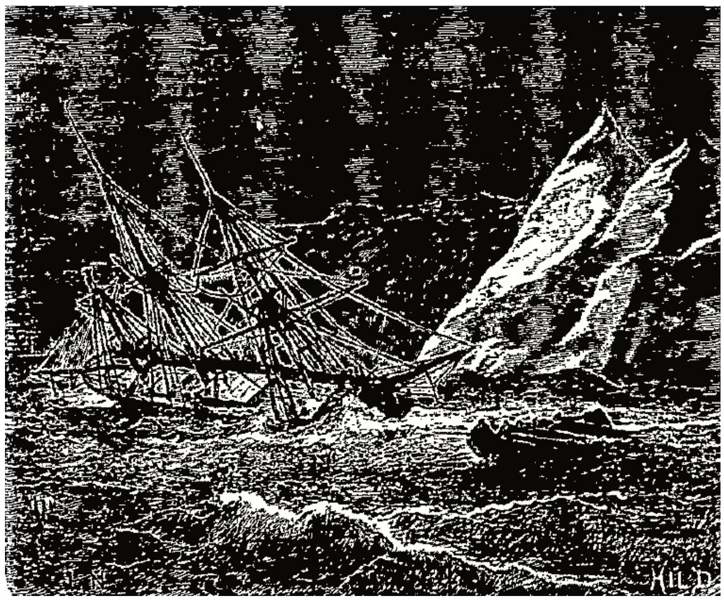


Figure 2.2 – The frigate *Speedwell* shipwrecked on the morning of 29 June 1676. Source: Les naufrages célèbres par Zurcher et Margollé, 1877.

Just before he was shipwrecked in 1676 Captain John Wood Jr. (1620-1704), member of the Royal Society and leader of an expedition in search of the Northeast Passage, described one of the oldest records concerning the transparency of the ocean water (directly connected with its colour) near Novaya Zemlya. Years later, a narrative of the expedition was published in collaboration with the English naval commander Sir John Narborough (1637-1688). This observation (Narborough *et al*., 1694, p. 307), made while looking overboard into the sea and noticing the ocean floor, has been quoted frequently over the past centuries:

We sounded and had 80 Fathoms of Water green Oar, at which time we saw the Ground plain, being very smooth water. The Sea Water, about the Ice and the Land, is very salt, and much saltier than any I ever tasted, and a great deal heavier and I may say the clearest in the World, for I could see the ground very plain in 80 Fathoms

[2] "*Deswegen finden wir, daß die Menschen lieber durch eine allgemeine theoretische Ansicht, durch irgendeine ErklärungsartdiePhänomene beiseite bringen, anstatt sich die Mühe zu geben, das Einzelne kennen zu lernen und ein Ganzes zu erbauen*".

> water, which is 480 Feet, and I could see the shells at the bottom very plain.

From his frigate *Speedwell* (see Figure 2.2), Wood could see shells at the bottom of the sea at a depth of eighty fathoms or one hundred and forty meters! What he saw were probably *Mya truncata* shells (first described by taxonomist Carl Linnaeus, 1707-1778, in 1758) on a dark coloured bottom.

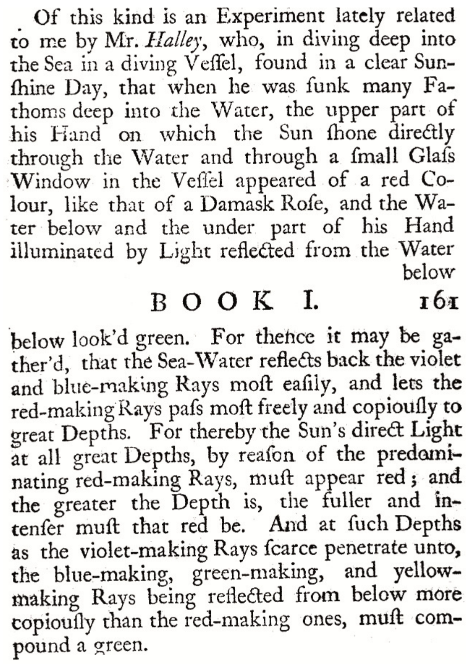
It is disappointing that until now Wood's direct observation has never been confirmed by other oceanographers, although Secchi disc measurements and theoretical considerations indicate that the ocean may well be even clearer in the absence of particulate and dissolved organic matter (see Gieskes, 1987, and Dirks, 1990). Apart from the original paper of Narborough, the observation of John Wood can be found in *Histoire Générale Des Voyages* (Jacques Philibert Rousselot de Surgy, 1737-1791, 1759, p. 168) and *Histoire des Naufrages* (Anonymous, 1789, p. 216). More than a century later the German geographer Otto Krümmel (1854-1912) mistook Wood with Hood and accidentally converts Faden (German) to feet and therefore comes up with a less astonishing figure of twenty-five meters depth (1 Faden = 1 Brasse = 1 fathom = 1.83 meters, so 80 fathoms equals 146.4 meters). The notes can be found in *Der Ozean* (Krümmel, 1902, p. 125) and in a re-edited version (Krümmel, 1902, pp. 250-279) of Georg Heinrich von Boguslawski's (1827-1884) oceanographic handbook (Boguslawski, 1884, p. 183). Wolf & Cadée (1994, p. 99) concluded in a paper on water visibility records:

> We have to consider this phenomenal depth of a hundred-forty-six meters as a water visibility record, knowing that the deepest lowered Secchi-disc ever, observed by Gieskes *et al.* in 1987 (p. 123), disappeared from sight at around seventy-nine meters.

Krümmel doubted the observation of Wood and even found twenty-five meters astonishing. However, Dirks in his thesis (Dirks, 1990, p. 153) calculates the maximum possible Secchi disc to be between hundred-fifty and hundred-seventy meters depending on the background light level – much more than the record-90 meters of Gieskes *et al*. (1987) seen in the Southern Ocean. Wood's observation cannot be considered simply as an optical illusion.

Concerning the explanation of sea colouring, at the end of the seventeenth century still a mystery, it can be concluded that it was mostly out of curiosity that accounts of this phenomenon were recorded and published, while at the same time less intellectual persons such as sailors and fishermen were already well aware of the meaning of the different colours of the sea in terms of sea-state, water depth, and presence of ice and icebergs.

THE 18TH CENTURY



Of this kind is an Experiment lately related to me by Mr. *Halley*, who, in diving deep into the Sea in a diving Veſſel, found in a clear Sun-ſhine Day, that when he was ſunk many Fathoms deep into the Water, the upper part of his Hand on which the Sun ſhone directly through the Water and through a ſmall Glaſs Window in the Veſſel appeared of a red Colour, like that of a Damask Roſe, and the Water below and the under part of his Hand illuminated by Light reflected from the Water below

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below look'd green. For thence it may be gather'd, that the Sea-Water reflects back the violet and blue-making Rays moſt eaſily, and lets the red-making Rays paſs moſt freely and copiouſly to great Depths. For thereby the Sun's direct Light at all great Depths, by reaſon of the predominating red-making Rays, muſt appear red; and the greater the Depth is, the fuller and intenſer muſt that red be. And at ſuch Depths as the violet-making Rays ſcarce penetrate unto, the blue-making, green-making, and yellow-making Rays being reflected from below more copiouſly than the red-making ones, muſt compound a green.

Figure 2.3 – A facsimile from Newton's notes in his "*Opticks*" after the experience of Halley. One Fathom is 1.82 meters.

Until well into this century, recorded sea colour observations were numerous, but no real effort had been made to explain the differently coloured sea and ocean regions visited. However, on page 139 in his *Opticks* Newton (1704, p. 139) describes an observation, shown in Figure 2.3, made by Edmund Halley (1656-1742). Here, we find an early explanation of vanishing colours of the sun through water. From the inside of his diving-bell (Figure 2.4) Halley looked at the top of his hand, that was coloured 'crimson' (red) as it was illuminated by sunlight travelling through the water and a small window : the opposite side of his hand was illuminated by bottom reflected sunlight, which according to Newton showed up as green.

A century later, the Italian physicist Macedonio Melloni (1798-1854) criticized this observation by saying that the high pressure in the diving bell must have had an influence on Halley's observation (Melloni, 1847, p. 321). Nevertheless, from Halley's observations Newton drew his conclusions in saying that seawater reflects the violet and the blue and transmits the red rays. The latter remark is obviously wrong: we now know that the red rays are the wavelengths first absorbed in water.

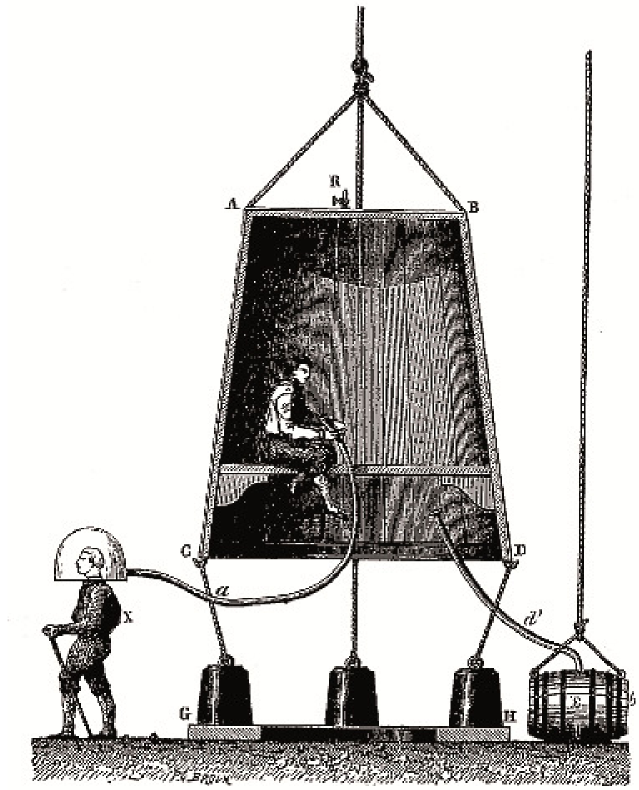

Fig. 397. — Cloche de Halley.

Figure 2.4 – In 1721, Edmund Halley experimented with his own renewed diving bell design. This was a sort like device as he used around 1690 in which he did his remarkable observation. The sunlight entered the bell through a glass window situated at the top of the device between A and B.

In 1706, Louis-Ferdinand Comte de Marsilli started to investigate, next to other physical parameters, the natural colour of water of the Gulf of Lions (see Figure 2.5). De Marsilli mentions in the chapter “Of its water” of his 1711 Italian dissertation on *‘The Natural History of the sea’* that transparency and colour are intrinsically coupled. He stated (Marsilli, 1711, p. 18):

> The colours are essential, permanent, occasionally and apparent by various reflections. To see its transparency, it must be put in a glass vase without receiving any reflection for it is that which causes all its supposed colours.

The latter is a brilliant remark for its time and it was only fully understood much later. Marsilli has written one of the first great scientific works with a focuss on the physical aspects of the sea, one of them being the colour. In Marsilli’s thesis, we find a table (see Figure 2.6) containing the colour of (sea) water for the first time.

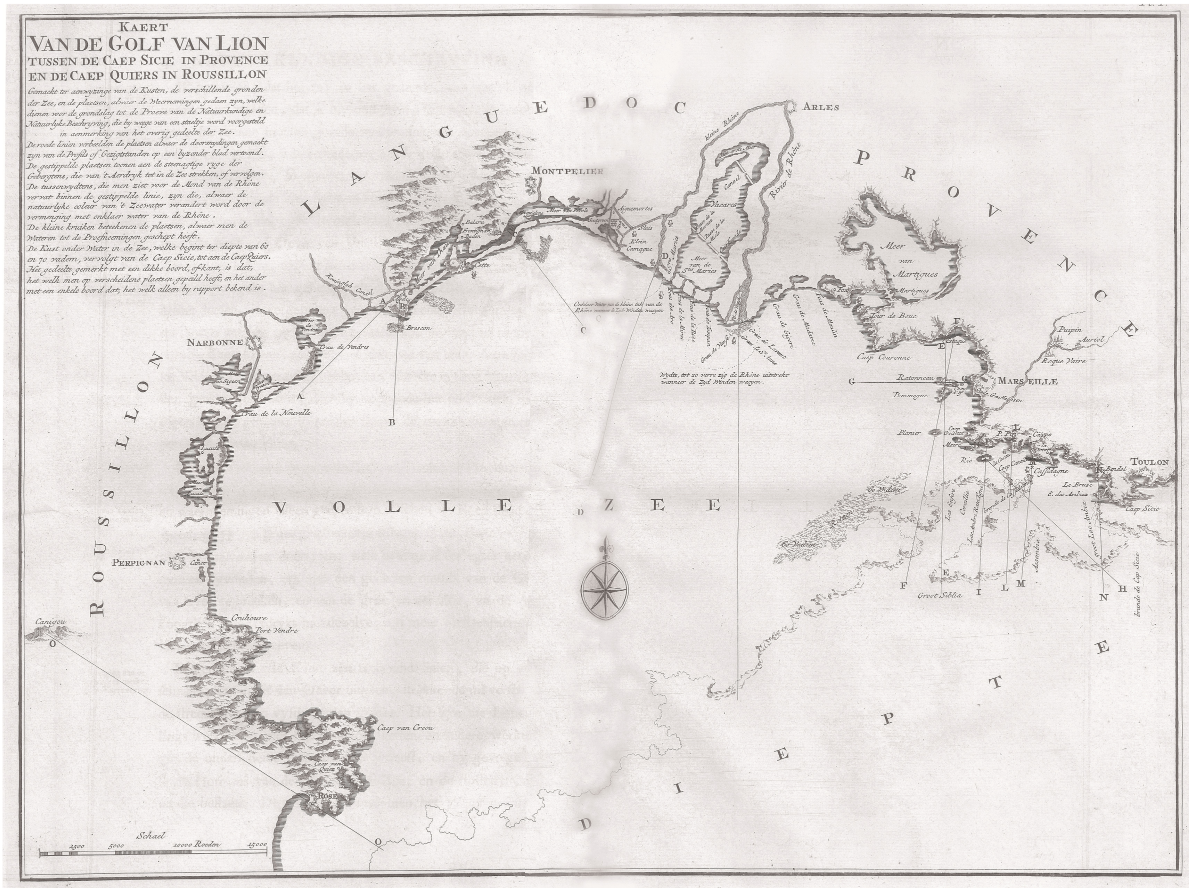

Figure 2.5 – The Gulf of Lions where Marsilli started his investigations in 1706 for his thesis *"The Natural History of the sea"*. Source: Dutch translated version of 1786, NIOZ.

The table contains three columns with respectively 'the apparent colour of the surface water', 'the colour of the essential water put into a vase' and 'the essential colour of the water taken from a certain depth and put into a vase'. However, colours in his table are still defined as "greenish", "bluish" "ash-grey". Sailing in Mediterranean waters, he mentions that he could distinguish a red fish at a depth of eighteen meters. Such descriptive remarks can be found in other historic papers. At the time, research was merely 'descriptive' instead of 'quantitative' – the latter common practice nowadays.

TABLE 2

Des Poids et Couleurs des Eaux douces, de Puits, de Fontaine et de Riviere, prises vers le bord de la Mer, avec l'Areometre.

Ans	Endroits	Mois	Jours	Couleurs	Poids		
					Onces	Dragm.	Grains
1706	à Montpelier au puits de Mr. Matt.	Novembre	6	Claire	1	3	30
	Montpelier, Fontaine de St. Giles.	Novembre	6	Clair	1	3	28
	Siluu Royal au bord du petit Rosne	Novembre	22	Trouble qui se perd étant reposé dans un vase.	1	3	29 ¾
	aux Cabanes Dorgons au bord du petit Rosne à 500 pas de la Mer	Novembre	23	Trouble qui se perd étant reposé dans un vase	1	3	30 ¼
	Puits profond de 3 pieds de profondeur fait par moi aux Cabanes Dorgons à 500 pas de la mer, et à 12 pas du Rosne.	Novembre	25	Trouble qui se perd étant reposé dans un vase	1	3	29 ½
	aux Stes Maries au puits du Consul.	Novembre	26	Blanchâtre	1	3	33
	aux Stes Maries au puits de Lombard	Novembre	26	Blanchâtre	1	3	30
	aux Stes Maries au puits de Becheli	Novembre	26	Clair obscur	1	3	29 ¼
	au petit Rosne près Dorgon	Novembre	26	Trouble qu'on a filtré par le Papier gris	1	3	29 ¼
1707	à Cassis Eau de la Citerne de mon Laboratoire	Janvier	20	Claire	1	3	30

AREOMETRE

Qui a servi à toutes les observations pour le poids de diverses Eaux, qui est icy dessigné dans sa forme et grandeur naturelle, pesant une Once, trois Dragmes, et dix Grains. Au bas est une forme de petite Boule remplie de mercure. Les Anneaux de Plomb icy dessignez, et qui sont du poids marqué à chacun, ont servi pour l'Equilibre en ajoûtant la quantité nécessaire.

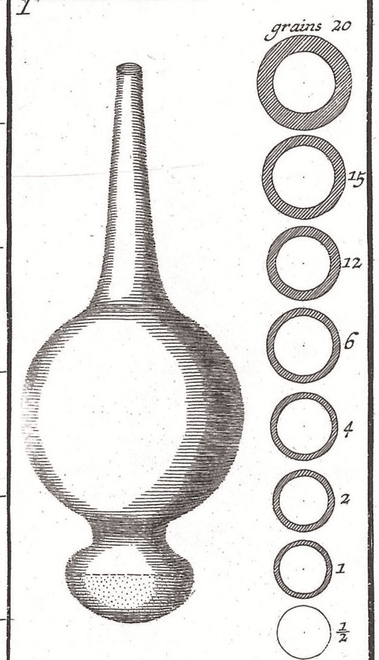

Figure 2.6 – The Table at the end of his thesis on *"The Natural History of the sea"*, where Marsilli describes the colour of the water (Column names: year, place, month, day, colours, weights). Source: Dutch translated version of 1786, NIOZ.

During the eighteenth century, a large number of explorers started their journeys all around the globe. Accounts of sea colour observations can be found in Captain James Cook's (1728-1779) journals during the first voyage round the World. On September the 10th (Wharton, 1893, p. 168) and October the 6th 1769 (Cook, 1769, p. 119) he wrote:

> Sunday, 10th of September. Fresh breezes and cloudy. At 9 a.m. we thought the Colour of the Sea was paler than Usual, which occasioned us to sound, but had no ground with 100 fathoms. Wind South-West, West-South-West; course North 52 degrees West; distance 97 miles; latitude 35 degrees 19 minutes South, longitude 150 degrees 46 minutes West. Friday, sixth of October. Little wind, and fine pleasant weather. Saw some Seals, seaweed, and Port Egmont Hens. P.M. Variation per Azimuth 12 degrees 50 minutes East. Per Amplitude 12 degrees 40 minutes. A.M. per Azimuth 14 degrees 2 minutes East; the difference is 1 degree 3 minutes, and the Ship has only gone 9 Leagues in the Time. The Colour of the water appears to be paler than common, and hath been so for some days past; this makes us sound frequently, but can find no ground with 180 fathoms of Line. Wind East-North-East; course South-West; distance 62 miles; latitude 39 degrees 11 minutes South, longitude 177 degrees 2 minutes West.

These descriptions imply that change of colour was explained in terms of bottom depth and therefore soundings were considered necessary. James Cook's journals contain more of these notes; observations of the colour of the sea helped him in navigating the unknown seas. However, Johann Reinhold Forster (1729-1798)[3], travelling with Cook on his second voyage (1772-1775), remarked that only a judicious eye, conducted by long experience, could allow proper interpretation of the relation between sea colour and depth (Forster, 1778, p. 53).

Goethe, while staying on Sicily during his trip to Italy, made another account of the ever-changing colour of the sea. It can be found in his book *Voyage to Italy*. On Tuesday April the 3rd 1787, after looking down to the sea surface, he notes (Goethe, 1786-1788, pp. 246-247):

> The northerly location of Palermo makes that the city and coast take an odd position regarding the large celestial bodies (sun and moon), from whom one will never see its reflection on the waves. Therefore also today, a day again full of sun, encountering a dark blue sea, sombre and turbulent, instead of at Naples, from noon on shimmering more cheerful, more ethereal and more blurry.

[3] *Johann Reinhold Forster**,** German naturalist and ethnologist accompanied his son Johann Georg Adam on several scientific expeditions, including James Cook's second voyage to the Pacific.*

On the trip back to Naples on May the 12th, when leaving the port of Messina, he writes (Goethe, 1786-1788, p. 339):

> The whole sky was covered in a white haze, through which the sun, without seeing its silhouette, illuminated the sea, which adopted the most beautiful heavenly colour, which one could ever imagine.

Monday the 14th, near the island of Capri, he continues his diary by writing (Goethe, 1786-1788, p. 341):

> Under an immaculate clear sky, the almost flat glossy sea, through the absence of wind, lay before us as a transparent pond.

Actually, due to the absence of wind, in combination with strong currents around Capri, Goethe was almost shipwrecked.

A NOTE ON 'BLUENESS'.

Neither standardised colour scales nor other instrumentation to record the colour of lakes, seas or oceans existed before the cyanometer[4] of 1791. Alexander Von Humboldt (1769-1859) who investigated the blueness of the equinoctial skies and surface waters (Humboldt & Bonpland, 1814, p. 254), used this colour-scale around 1799. According to him, it was the first time that such a scale was used at sea (Humboldt & Bonpland, 1814, p. 248).

Its inventor was Horace-Bénédict de Saussure (1740-1799) who used the scale to establish the 'bluishness' of the skies over the Swiss and French Alps (de Saussure, 1788-1789, pp. 409-424; de Saussure, 1791, pp. 199–208; de Saussure, 1842, pp. 202-203); he described this cyanometer in 1791. The scale consisted of a paperboard circle comprising fifty-three radial sectors with nuances of blue between white and ink-black numbered from zero to fifty-two. The paper-scale, shown in Figure 2.7, was first used on top of Mont Blanc, near Chamonix, in 1787. This scale is not to be confused with François Arago's (1786-1853) converted polarimeter instrument (Figure 2.8) with the same name, which came in use around 1845. This instrument is fully described by Arago himself (Arago 1858a, pp. 277281; Arago, 1858b, pp. 270-277) and by Bernard (Bernard, 1856, pp. 982-985).

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[4] *The cyanometer of Horace-Bénédict de Saussure, a carton colour scale with only variations in blue, used to study the blueness of the sky.*

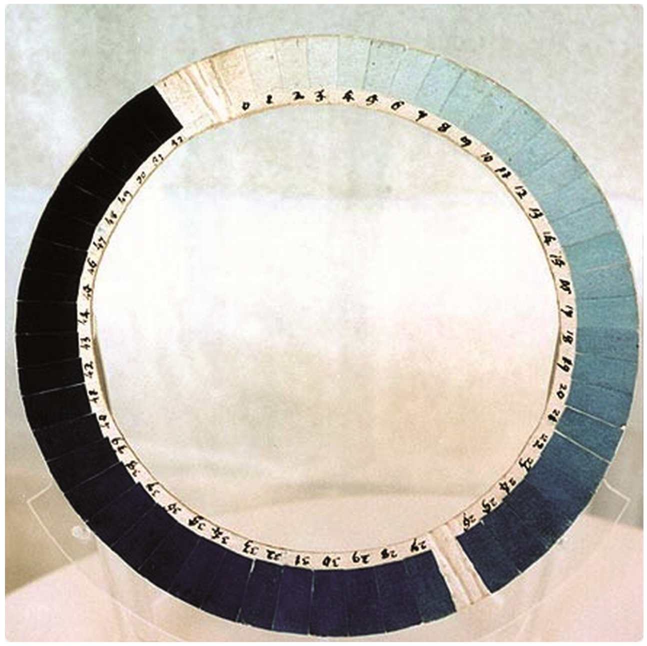

Figure 2.7 – The in 1791 by Horace-Bénédict de Saussure proposed cyanometer with 53 nuances (grades) of blue. The circular paper scale to establish the sky's colour was also used to establish the ocean's colour. Source: Musée d'Histoire des Sciences, Geneva.

During his travels towards the new continent, von Humboldt associated the deep blue of the sea with the skies above the Venezuelan steppe (Humboldt & Bonpland, 1814, p. 248) during a drought; he assumed that this deep-blue sky could somehow give the sea its colour. At another occasion, he employed the cyanometer by pointing it to the ocean and then looking through a pinhole. At that particular moment, he experienced 'the most beautiful ultramarine colour' as he wrote in his memoirs. However, since most of the investigated waters had a greenish tint, a match with the paper-scale colours of Saussure's cyanometer was not possible. Concerning the colour of water, von Humboldt commented in his travel reports (Humboldt & Bonpland, 1814, p. 255):

> All that is accounted to the colouring of natural water is problematic in the highest grade.[5]

At the beginning of the eighteenth century, Louis-Ferdinand Comte de Marsilli introduced modern oceanography. Mediterranean water properties were observed, sampled and tabulated in a systematic manner. For the first time, in a systematic way, colour and transparency observations were archived. Alexander von Humboldt pioneered with the first ocean colour scale

[5] *"Tout ce qui a rapport à la couleur de l'eau est extrêmement problématique".*

to determine the ocean's colour. According to him, its blue colour could be caused by reflection of the blue sky.

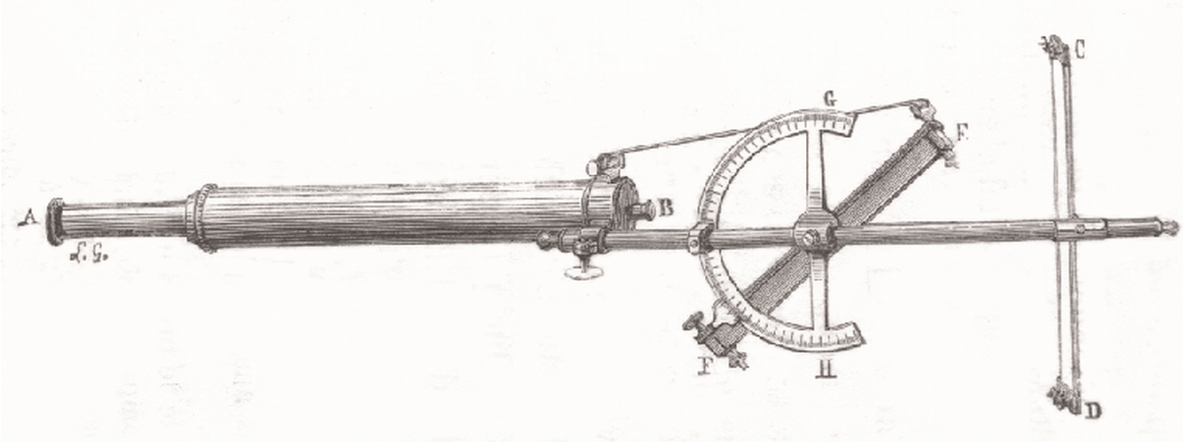

Fig. 10. — Cyanomètre de M. Arago.

Figure 2.8 – François Arago's cyanometer[6] (around 1845) to measure the blueness of the sky is an extended polariscope (AB) based on the development of colour in plates of rock-crystal when polarized light is transmitted through them. The instrument consists of a double refracting prism (side A), a plate of rock-crystal (B). The polariscope is looking through a pile of glass plates (EF) towards a piece of white paper (CD) used as a reference white light source. The specific blue tint of the light observed in A is derived from the inclination of the pile F on the circle HG. A comparison with the naked eye is made between the sky colour and the colour seen at A. When the colours match, the inclination of the pile EF is an absolute measure of the blueness of the sky.

THE 19TH CENTURY

In this century, water became one of the most intensively investigated substances on earth. In several publications written in the early nineteenth century it is assumed that the colouring of water could be due to impurities in the water. The question whether or not water itself had any colour was not answered in this approach. What that colour would be is in fact an interesting point, because the effect of impurities on water colour cannot be assessed without an answer to this question. At the same time, scientists became aware of the fact that pure water not only had a reflected colour (see above), but also one that had to do with transmission. In laboratories the

[6] *The cyanometer of Arago is an extended polarimeter.*

purest water found in nature (rainwater) combined with colour analysis of distilled water was investigated thoroughly to shed light on the cause of the colour of pure water.

During the beginning of this era and even before, studies on the cause of water colours continued to keep sailing scientists' interest alive, but a real solution to the problem remained elusive. The mathematician Louis Costaz (1767-1842) noticed on a trip to Egypt (Costaz, 1798, pp. 101-102) that was sponsored by Arago (Arago, 1857, p. 559) that the Mediterranean, Atlantic Ocean and Pacific Ocean were indigo blue:

> *Que le bleu indigo est la couleur vraie de la mer* [indigo blue is the true colour of the sea] *or au bleu le plus clair, dit le bleu céleste* [of a most clear blue named living blue].

The Polar Sea was 'greenish blue or ultramarine' (See Table 1, Scoresby Tables – Scoresby, 1820, pp. 182-183). William Scoresby junior (1790-1857), the son of the well-known whaling captain William Scoresby (1760-1829), was one of the pioneers with a scientific background to explain the colour of natural waters outside a laboratory. After a short stay at Edinburgh University in 1806, he sailed with his father to the higher latitudes and later wrote about the 'unbelievable' transparency of the water near Greenland (Scoresby, 1820, p. 175):

> The colour of the Greenland Sea varies from ultramarine blue to olive green, and from the most pure transparency to striking opacity.

Referring to deep waters (prevailing colour blue, or greenish blue), Scoresby junior concluded that all light rays except the blue were absorbed by water before they reached the bottom. In addition, he observed that there was a good deal of deception in the colour of the sea, owing to the effect of the sun and the colour of the clouds. By looking down into the sea surface through a submerged long tube the true shade of colour of the sea could be seen:

> When thus examined, the colour of the sea is not materially affected, by either sun or clouds.

This and the statements on absorption of the red to green colours by water were at that time remarkable conclusions that in a way still hold true. During his hydrographical surveys, Scoresby tabulated the seawater colours as shown in table 2.1 (cf. Marsilli).

Table 2.1 – Scoresby's Table 'On the observations of the sea' with the colour of the water (1820).

TABLE. *To face Page* 182. Vol. I.

		OBSERVATIONS on the SEA.				TIME.	
Latitude.	Longitude.	Specific grav. Temp. 60°.	Temp. at Surf.	Colour.	Tem. of the Air.	Da. Mon. Yr.	Situation and Remarks.
57.22	1°.16′ W	1.0269	41°.0	Greenish bl.	41°	25 Mar. 1814	At sea
57.42	0.45	1.0280	43.0	Ditto	42	12 —— 1810	Ditto
57.40	4. 8	1.0231	38.0	Ditto	32	14 —— 1810	In Murray Fr.
57.43	4. 9	1.0244	39.0	Ditto	39	18 —— 1810	In Cromarty
59.56	1.20	1.0272	42.0	Blue	32	21 —— 1810	At sea
60.09	1. 6	1.0278	44.0	Greenish bl.	46	4 Apr. 1814	In Brassa Sou.
——	——	1.0274	43.0	Ditto	55	22 Mar. 1811	Ditto
——	——	1.0262	41.0	Ditto	29	23 —— 1810	Ditto
61.46	0.23 E	1.0268	47.0	Ultram. blue	50	29 —— 1810	At sea
64.26	0.38	1.0269	43.5	Ditto	44	3 Apr. 1815	Ditto

Professor Christen Smith (1785-1816), a botanist who sailed with Captain James Kingston Tuckey (1776-1816) on his way to explore the River Zaire in at April 5, 1816, spoke about 'deep azure' and a 'dark sea-green' when he crossed the Tropic of Cancer (Tuckey, 1818, p. 235). In an extensive work *Précis de la Géographie Universelle*, first published between 1820 and 1827, geographer Conrad Malte-Brun (1816-1889) refers to sea colours as follows (Malte-Brun, 1847, p. 397):

> Other nuances in the colour of marine waters depend on local causes and sometimes on illusions. One says that the Mediterranean, in her superior part, sometimes appears purple. In the Gulf of Guinea, the sea is white, and round the Maldives, black. She is yellowish near China and Japan, greenish West of the Canaries and Azores. The vermillion sea, near California, has received its name due to the red colour as it often appears in.[7]

Other facts responsible for the colouring of the sea were more easy to explain, like the presence of organisms. As Malte-Brun, Smith mentions milky water (Tuckey, 1818, p. 48) sailing not far from Cape Palmas and entering the Gulf of Guinea (Southwest from Ivory Coast):

> After passing Cape Palmas and entering the Gulf of Guinea, the sea appeared of a

[7] *Les autres nuances dans la couleur des eaux marines dépendent des causes locales et quelquefois des illusions. On dit quela mer Méditerranée, dans sa partie supérieure, prend une teinte quelquefois pour-prée. DanslegolfedeGuinée, lamerest blanche, et autour des Maldives, noire. Elle est jaunâtre entre la Chine et le Japon, verdâtre à l'ouest des Canaries et des Açores. La mer Vermeille, près de la Californie, a reçu son nom de la couleur rouge qu'elle prend souvent*.

> whitish colour, growing more so until making Prince's island, and it luminosity also increasing, so that at night the ship seemed to be sailing in a sea of milk.

He found that this phenomenon was caused by lots of 'animals'; he thought these were Salps (free-floating filter feeders) and crustaceous *Scyllarus* (a genus of lobsters) present at the surface; according to him these influenced the water colour (we know now that tiny coccolithophorid microalgae, with their pure-white calcium-covered cells, were more likely the cause of the 'milk sea'). Like others before, he also reported on the carmine-red zones in the Atlantic Ocean (Tuckey, 1818, p. 263), at the height of Loango, Gabon:

> Some days ago the sea had a colour as of blood. Some of us supposed it to be owing to the whales, which at this time approach the coasts in order to bring forth their young. It is however, a phenomenon, which is generally known, has often been described, and is owing to myriads of infused animalculae. I examined some of them taken in this blood-coloured water.

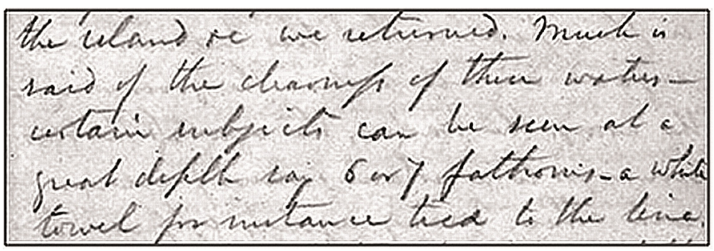
the island &c we returned. Much is said of the clearness of these waters – certain subjects can be seen at a great depth say 6 or 7 fathoms – a white towel for instance tied to the line

Figure 2.9 – Notes in Jackson Kemper's diary (1834) during his visit to Green Bay showed a white towel used to determine the transparency of water. Transcription: "Much is said of the clearness of these waters – certain subjects can be seen at a great depth say 6 or 7 fathoms – a white towel for instance tied to the line". Source: Wisconsin Historical Society.

We now know that mass occurrence of dinoflagellates, another class of microalgae, often causes the red colour of coastal waters and lakes; the speculation on 'animalculae' is in fact not far from the truth

For the determination of the transparency and colour of natural waters all kinds of equipment, such as plates, tins, kitchen-gear, cloths, white towels (see Figure 2.9) (Kemper, 1834, pp. 442-443) and even fruit, were submerged into the water.

During his first exploration trip (1815-1818) in the South Sea and to the Bering Strait, the Russian navigator Otto von Kotzebue (1787-1846) used a whitened surface to measure the water transparency (Kotzebue, 1821, 1: p. 81):

> The transparency of the sea water would be easiest measured by letting down a flat surface, fastened to the plumb line, painted white, with stripes, or letters of black, or other colour, on it. For want of this, a white earthen plate, or a board covered with white stuff, might be used. The depth at which the board became invisible or the marks upon it undistinguishable in different waters, would show their relative transparency.

Some of his measurements, including the apparent colour, were collected in a table (table 2.2) by the poet-naturalist Adelbert von Chamisso (1781-1838) who joined von Kotzebue on his exploration trip to the South Sea and Bering Strait between 1815 and 1818 to look for a North-Eastern Passage (Kotzebue, 1821, 3: p. 419).

Table 2.2 – Observations, among other things, of the transparency in fathoms of the seawater, made during Kotzebue's Voyage of *Discovery* in the year 1815 and 1816.

TEMPERATURE OF THE SEA WATER AT DIFFERENT DEPTHS.

In the Years 1815, 1816, 1817, and 1818.

Days.	Temperature of the Sea Water: on the Surface.	Temperature of the Sea Water: below the Surface.	Depth in Fathoms.	Temperature of the Air.	The Ship's Latitude.	The Ship's Longitude.	Transparency of the Water in Fathoms.	Observations.
1815.					° ′	° ′		
15. October	+68.5	+55.7	100	+71.1	39 27 N.	12 57 W.	10	In the Atlantic Ocean.
16. —	+69.1	55.0	138	72.5	39 4	13 8	10	
—	—	56.0	96	—	—	—	—	
25. —	74.3	56.3	196	74.3	30 12	15 14	11	
1816.								
8. January	54.9	38.8	196	57.6	44 47 S.	57 31	8	Cape Horn.
7. April morn.	78.5	68.5	125	79.2	18 17	124 56	13	In the South Sea.
—	—	57.5	175	—	—	—	—	
At noon.	79.6	68.0	125	80.0	—	—	—	
—	—	54.0	200	—	—	—	—	
13. April	80.0	79.0	10	79.8	15 26	133 42	13	
—	—	79.0	20	—	—	—	—	
—	—	78.8	50	—	—	—	—	
—	—	72.0	100	—	—	—	—	
—	—	56.0	200	—	—	—	—	
12. May	82.5	55.0	300	83.0	1 17 N.	177 5	14	At the Equator.
1. June	74.0	62.0	100	75.0	29 24	199 26	10	
—	—	52.5	300	—	—	—	—	

E E 2 APPENDIX. 419

In the North Pacific, a dinner plate could be seen to a depth of twenty-seven fathoms (forty-nine meters). Before that, such measurements were also performed with a piece of cloth, also on 19th November 1817 by one of Von Kotzebue's crewmembers (Kotzebue, 1821, 2: p. 227):

> I observed to-day the transparency of the water with a white plate, and found that it was visible at a depth of twenty-seven fathoms: the previous observations of this kind had been made with a piece of red cloth. I daily let down the Six-thermometer' about eighty fathoms, to observe the difference, when the water should have resumed its dark azure colour (The Six-thermometer also known as the maximum/minimum

thermometer invented by James Six (1731-1793) in 1780).

During a voyage around the world between 1822 and 1825 aboard the corvette *LaCoquille*, under the command of Louis Isidore Duperrey (1786-1865), a white-painted board with a diameter of two feet and an attached weight was lowered into the water to measure its transparency (Gray & Dochard, 1825, p. 203; Arago 1857, p. 203). The depths at which the disc disappeared were between nine (Ascension Island) and twenty-three meters (Offak, Island of Waigiou, Indonesia). Around 1832, Xavier de Maistre constructed a square iron plate of around thirty-five centimetres square, painted white, not to establish the visibility depth but to establish the colour of the sea (Maistre, 1832, p. 265).

U.S. Navy Lt. Charles Wilkes (1798-1877) joined a US-squadron on its trip around the world (The Wilkes Expedition between 1838 and 1842), performed ocean colour observations and water transparency measurements using a simple pot (probably a white fish-trap attached to a rope). During his trip from Porto Praya (Cape Verde Islands) to Rio de Janeiro, he observed 'pot visibilities' between two and a half and twenty fathoms (four and a half to thirty-six meters, Wilkes, 1851, pp. 22-31). Captain Auguste Bérard (1796-1852), during the Arago expedition in 1845 passing the South Pacific Wallis Island on July 16, measured a disappearance depth of forty meters using a porcelain dinner plate (Arago, 1857, pp. 487-488).

Captain Karl Koldewey (1837-1908), pioneer of the Arctic Ocean (Charton, 1874, p. 1 and 6), observed the water colour during his polar expeditions of 1868 and 18691870. He agreed with Cook and Forster that blue was the general colour for oceans and green seas were an exception to the rule. Captain Paul Friedrich Hegemann, on board the *Hansa*, accompanied Koldewey on the *Germania*. Sailing along Greenland he remarked (in agreement with Scoresby) that the true colour of the sea, avoiding sky glint, could only be seen through a tube submerged into the seawater (Charton, 1874, p. 6). Hegemann also noted that "the sea is orange, led-grey or gloomy-green" (Charton, 1874, p. 13).

All these observations were made, but at the time they remained totally unexplained. It was known that oceans had a general blue colour with an exception of green near coasts, and rivers and lakes had a green colour in general with blue as an exception to the rule (cited by Johann Philipp Gustav Von Jolly, 1809-1884 – Jolly, 1872, p. 125) and by Boguslawski (Boguslawski, 1884, p. 174). However, early in the 19th century European scientists became more and more anxious to find the cause of the sea colours. In 1812, the theologian Jean Pierre Guillaume Catteau-Calleville (1759-1819) published a book with the inspiring title *Tableau de la mer Baltique* [Painting of the Baltic] or *Gemälde der Ostsee* (Catteau-Calleville, 1815). The book is a physical, geographical and historical overview of what was known of the Baltic Sea. However, only a short phrase on the bright-blue colour of Baltic seawater was found in a chapter concerning 'colour, mirroring and phosphorescence of the water'. Without explaining its cause, Catteau-Calleville stated that the colouring could only be seen during the most beautiful season under bright and calm weather. He found it much more interesting to write about other phenomena such as so-called sun-smoke (sea fog) covering the sea surface (Catteau-Calleville, 1815, p. 123):

> The fog, appearing mostly in July, after diluting and letting the sunrays through revealed the most glossy shine and diversity in watercolours.

Just before he died in 1828 Sir Humphry Davy (1778-1829), one of the pioneers who tried to explain natural water colours, to him a mystery, wrote an interesting article on the colour of the water and the tint of the oceans (Davy, 1829, p. 115; Davy, 1842, p. 78). He was the first to say that a blue colour could be ascribed to pure water (rainwater and glacier melt water were of the purest kind at that time), but the processes causing this blue appearance were not clear at all. He ascribed the colour of the greenish ocean to the presence of iodine and bromine, not to algae or other particles, or dissolved substances. Davy tested his thoughts by performing an experiment in an icy lake near the Chamonix-Mont-Blanc valley at the France-Swiss border. He mixed a little iodine with melting water on top of the ice layer. Accordingly, he saw colour changes from dark blue towards the green of the sea to the green of grass to yellowish green:

> Possibly these halogens are also responsible for the decomposition of marine vegetation. Dissolved in small amounts colours the water yellow and together with the blue of pure water produces the green tint of some seas.

Although he never translated the outcome of this experiment to observations of green seas, rivers and lakes, he was quite happy himself with his assumption and reasoning, as he noted in his publication of 1829.

In a publication 9 years later François Arago mentions Davy's quantification of the colour of snow and glacier waters as living blue (Arago, 1838, p. 468):

> Sky blue, changing darkness, mixed with amounts of white light; this should be the right colour of the ocean.

According to Arago, colour classification could only be applied to pure seawater, while parts of the sea are contaminated with 'matter'. Examples of contaminated waters could be found near the green zones of the Polar region or in parts of the ocean where the yellowish colour, caused (according to him) by the presence of numerous Medusae (jellyfish), was mixed with blue deep water, resulting in a shade of green (Arago, 1838, p. 468). Scoresby writes in his Account of the Arctic regions (Scoresby, 1820, p. 180):

> There can be no doubt, I think, after what has been advanced, that the Medusae and

> other minute animals that have been described, give the peculiar colour to the sea, which is observed to prevail in these parts; and that from their profusion, they are, at the same time, the occasion of that great diminution of transparency which always accompanies the olive-green colour. For in the blue water, where few of the little Medusae exist, the sea is uncommonly transparent.

Scientists in those days, who were exploring all kinds of matter, often tried to explain the mystery of the colouring of natural water seen during their fieldwork with respect to this matter. One of them was Robert Wilhelm Bunsen (1811-1899, see Figure 2.10) around the mid-nineteenth century. After determining the composition of lava on Iceland, he published an article on the inner relation of pseudo-volcanic appearances of Iceland (Bunsen, 1847, pp. 44-59). In this article he mentions his visits to several (hot) springs under which the one at Reykir, Nordurlands Vestra.

Figure 2.10 –Portrait of a middle aged Robert Wilhelm Bunsen, one of the first scientists to investigate the colour of pure water in the laboratory. Source: Universität Heidelberg, Germany.

This site impressed him after having seen the beauty of its aquamarine crystal clear water, beyond any description (Bunsen, 1849, p. 95). Musing on this phenomenon, he writes:

> Nowhere this transparent greenish blue water can be found with such purity as on this particular spot. That chemically pure water was not colourless as in general was presumed I knew but that it had its own pure blue colour was less known to me.

Bunsen started to investigate the colour of pure water (distilled) in his laboratory by means of newly designed equipment. He described an experiment, in which he used blackened glass cylinders through which he looked at a piece of porcelain, either from the top of the cylinder down to the porcelain (sunlight falls through a window in the bottom) or through a slit in the bottom towards the porcelain (sunlight falls through the top opening of the tube). He was the first to discover that pure water was not without colour, as he found a bluish colour for both the reflected and the transmitted light.

This experiment was repeated by the author in 2003 using two black plastic tubes one meter longer than Bunsen's specifications, both filled with ultra-pure water. The tubes were stuck out of one of the laboratories windows, with the sun entering the tube through the lower slit illuminating the pieces of porcelain. A blue colour could hardly be determined. It is not clear if Bunsen truly observed the blue tint or he mistook the length of the tubes. The lack of a reference white (colour) to compare 'the blue of the water' which could also be the problem here (see the 1873 experiment by Kayser mentioned later).

In the years to come, more laboratory devices were constructed to investigate the 'purest water'. However, without any laboratory experiments, Karl Hermann Konrad Burmeister (1807-1892) became a strong supporter of the idea that the ocean's blue was caused by reflection of the blue sky. In 1853, this German zoology professor published a book on geological views on the history of the earth and its inhabitants (Burmeister, 1853, pp. 4-17). Observations made by him at sea during rain, under dark clouds or during sunshine and white clouds were in support of his opinion that the sky coloured the ocean from respectively greyish, greyish blue to dark blue. Burmeister continues:

> In case the water was blue of itself, the water should stay blue independent of the weather or sky condition.

He was convinced of the correctness of his sky-theory (Burmeister, 1853, p. 8) and found support in the earlier thoughts by von Humboldt (Humboldt & Bonpland, 1814, p. 249) already mentioned in this essay.

The brothers Adolf (1829-1856) and Herman (1826-1882) Schlagintweit identified a white stone at a depth of sixteen meters near the Island of Corfu, Greece. Using a similar stone in the Ganges water, the stone disappeared after twelve centimetres (Schlagintweit & Schlagintweit, 1857, p. 521). Subsequently, during his investigations from 1858 to 1860 in the Gulf of Quarnero (North Adriatic Sea), Josef Roman Lorenz von Liburnau (1825-1911) lowered a whitened tinplate of thirty centimetres in diameter (Liburnau, 1898, p. 80). He could still observe the disc to a depth of twenty to twenty-four meters. A few years after von Liburnau's expedition, the American Assayer to the State of Massachusetts Augustus A. Hayes (1806-1882) spending some time abroad, visited Lake Geneva. He came to the same conclusions as Burmeister that the cause of the Lake's azure colour was to be found in the peculiar hue of the Swiss sky, which was transmitted to the eye by the 'colourless water' (Hayes, 1870, pp. 188-189):

> I believe that extended observation will always connect the blue tint of white water with the deep azure hue of the clear sky above it. In other countries, there are bodies

of 'colourless water', which do not exhibit the colouration commonly seen in Lake Geneva. Such localities are not favoured with clear blue skies through atmospheric constitution, and bluish greenness of it is the nearest approach to an azure hue, which the sky permits, excepting perhaps at rare moments.

Figure 2.11 – Thomas Ender's landscape aquarelle of the Green Lake in the High Tatras, on the border between Slovakia and Poland (Landschafts aquarelle; Der Grünsee in der Hohen Tatra).The colour of the lake was characterised by Heinrich Wallmann as green-turbid. Source: Library of the Hungarian Academy of Sciences, Budapest.

Scientists were anxious to solve the colouring phenomenon not only of seawater but also of river and lake water. One of those scientists was Heinrich Wallmann (18271898). In the 1860s he described the colours of some hundred alpine lakes in Austria, Hungary, Switzerland, Italy and Germany. In the 1868 yearbook of the *Österreichischen Alpen-Vereines* (Wallmann, 1868, pp. 1-117), one of those lakes, the Green Lake (Der Grünsee) see Figure 2.11, pictured by Thomas Enders (1793-1875), was characterized by him as 'green turbid' (grüntrüb). In this work he mentions the fact that von Humboldt failed in solving the enigma of the colouring of the ocean (Wallmann, 1868, p. 51).

Parts of a comprehensive article on alpine lakes were written more from a philosopher's point of view than that of a scientist's. In the first pages, he imagines the utmost fascination of the traveller crossing the Alps, towards the appearance of alpine lakes and further on compares the different appearances of alpine lakes with the temper of a housewife (Wallmann, 1868, pp. 1-2):

Lots of travellers will remember a delightful feeling, after a day of severe hiking through small gloomy dales surrounded by sky-high rock-faces and along murmuring brooks, reaching an open spot discovering a dark-green or blue lake amphitheatre like enclosed by either pine tree woods or hundreds of fathom high rock formations. The Alpine lake, like the temper of a housewife, incline to be soft, tender and quiet; the serene restful lake and the other time she scares us and makes us feel uncomfortable through her eccentric and capricious touchiness; the lake during storm and thunder.[8]

Figure 2.12 –Thomas Ender; *"Ansicht der oberen und unteren Pasterze",* glacier in the Eastern Alps in Austria with the beautiful turquoise colour of the glacier ice as painted down in 1830 by the artist. Source: Oberösterreichisches Landesmuseum, Linz.

Heinrich Wallmann does not reveal the causes of the colouring of Alpine lakes but is without doubt aware of the fact that the birefringence of sunlight is causing the colouring of lakes, and certainly not a sort of (water) pigment (Wallmann, 1868, p. 53). In addition, he was aware of the

[8]. *Viele werden sich des Hochgenusses lebhaft erinnern, den sie empfunden, als sie nach mühevoller Wanderung durch düstere Thalengen zwischen himmelanstrebenden Felswänden und längs der Ufer eines rauschenden Giessbaches plötzlich eine Thalweite erreichten, die ein dunkelgrüner oder blauerSee, theils von Nadelholzwäldern, theilsvon steilen, mehrere hundert Klafter hohenFelswändern, amphitheaterartig umgrenzt.*

Der Hochsee; Dem Gemüthedes Wibes gleich, dasinderAnlage sanft, zart, ruhig, erfreut uns der stille ruhige See – aber erschreckt und beruhight uns auch manchmal durg seine excentrische und launenhafte erregbarkeit.

fact that transparent bodies like glass, water and ice in great masses are coloured greenish-blue. He suggested that these bodies are not colourless, as so many thought. An artist's impression of glacier ice with its marvellous turquoise colour is shown in Figure 2.12.

TRANSMITTING OR REFLECTING THE BLUE?

In 1832 the scientist, poet and balloonist Comte Xavier de Maistre (1763-1852), stated that water with enough depth reflects light in the same way as the sky, giving it a blue colour. More specifically, he presumed that the scattering by air molecules causes the sky's blue colour. However, his statement that at the time it was not understood why only the shorter rays (indigo and violet) were affected (Maistre, 1832, pp. 259 and 263) directly followed this presumption. Furthermore, Xavier de Maistre was convinced that small particles, present in the water column, could change the water colour from blue to green. A similar phenomenon can also be observed in case one looks at the water from great heights. During a visit to the island of Capri he looked down into the sea and became intrigued by the brilliance of green luminous 'clouds of water' surrounded by a sombre blue. What he noticed was that the shallow rocky bottom tinged the water intensively green, while the surrounding deep water showed up indigo blue. On the spot, he prepared a square plate of white-ion of fourteen pouces (inches), painted with white lead. To establish the colour of the water at different depths, he lowered the plate near to the coast of Capri. Accordingly, it turned up greenish at a depth of twenty-five feet and this colour became more intense with a tinge of yellow at a depth of forty feet. At eighty feet, he only saw a greenish glimmer, which soon disappeared, after he lost sight of the plate. After this experiment, he remarked that this colouring was easy to explain (Maistre, 1832, p. 264):

> We can see at this point that the light of the sun, transmitted by the seawater and reflected by a white surface, produces a green colour. One can easily understand its cause, by admitting the existence of the same opalescent property in deep water that is found in air. The light, after having penetrated a mass of water of hundred feet to reach the plate and return to the surface, must appear yellow like that transmitted by an opalescent liquor; this colour reflected by the plate, mingling with the blue of the interior, produces the green colour. If the bottom of the sea was white, the water near the margin would present the same green tint which the white plate produced at different depths; but the bottom is usually of a dark grey which reflects the light imperfectly, and can give rise only to dark and indeterminate shades of green; it is therefore to the reflection of the bottom that the green colour of the sea near the shores is to be ascribed.

The assumption that a mixture of yellow and blue colours turns up green was true but the thought that light reaching a white disc through a water column of a hundred feet had a yellow colour was of course not right. Notice that Xavier de Maistre quotes Léonardo da Vinci who mentions the bluish, instead of blood red, colour of the veins seen through the opalescent human skin (Maistre, 1832, p. 274). The opinion of Arago, on the cause of natural water colours, was slightly different. In his 1838 publication, he states (Arago, 1838, p. 470):

> The water, after it has bluing its illuminated sunlight, scatters also one part into all directions, and this scattered light gives every fluid its specific colour. The rest, irregular transmitted rays are being greened on their passage through the water, the greater the mass of the water, the stronger.

Figure 2.13 – Bracing The Waves, a painting by Aivazovsky Ivan Konstantinovich (1817-1900), 1890. Source: Wikimedia, in private collection.

Here we find a rather amazing agreement in the description of different phenomena. At this point in time the idea was accepted that (sun-) light was transmitted and reflected by water. Some of Arago's predecessors also believed in these two different phenomena. Known was the fact that only the blue from the sunlight was reflected into the eye by the water column, but it was not clear at all that the transmitted rays had a predominant green colour. Arago explains this fact by means of waves and predominant colours as shown brilliantly by an artist's impression shown in Figure 2.13. On a rough sea surface, looking into a wave, the transmitted green colour dominates over the reflected blue colour (Arago, 1857, p. 109).

According to Arago, we can compare a wave with a prism. With the observer in the East and the sun in the West the by the wave transmitted sunlight shows up green. On a rough sea surface the transmitted green dominates over the reflected blue (see the artist's impression).

MOLECULE OR GERM

In 1847 Alexandre Edmond Becquerel (1820-1891, Figure 2.14) explains the origin of the sea colours in a dedicated chapter of his *Elements of terrestrial physics and meteorology [Élements de physique terrestre et de meteorologie]*. Having the same opinion as Arago *i.e.* water has a blue reflected colour, caused by the 'water molecules' (at the time invisible particles were called molecules) and a green to yellow transmitted colour (Becquerel, 1847, pp. 257-260).

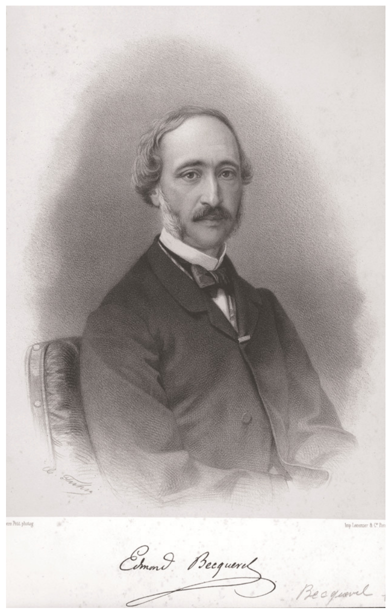

Figure 2.14 – Alexandre Edmond Becquerel. "Water has a blue reflected colour and a green to yellow transmitted colour". Source: Dibner Library of the History of Science and Technology.

At present it is hard to say what nineteenth century scientists meant with 'molecules': almost invisible microscopic particles or were they 'germs' that could not be seen by the naked eye in a liquid? Alternatively, was it the molecule (Brown, 1827, p. 467; Brown, 1828, p. 297) of which Robert Brown (1773-1858) spoke in his article on microscopic observations of the pollen of plants and on the general existence of active molecules in inorganic and organic bodies being present in particles (now known as 'Brownian movement)? Augustin-Jean Fresnel (1788-1827) called photons light-molecules (Fresnel, 1831, p. 374). In an 1873 dictionary, a molecule is described as the smallest quantity of a compound body that can take part in any chemical reaction (Watts, 1873, p. 1027). Tyndall states that germinal or life-producing matter out of which bacteria originate exhibits no structural characteristics that can be appreciated by microscope (Tyndall, 1877. p. 354).

In a publication of 1860, Theodor Wittstein (1816-1894) supposes that the ocean's blue reflected colour was intensified by the presence of minerals and that a blue colour of pure water (like ocean water) could only be affected by dissolved organic matter (Wittstein, 1860, pp. 603-624).

WATER TRANSPARENCY: THE SECCHI DISC ERA

Even the Vatican contributed to the increasing knowledge of the sea by seeking an explanation of its appearance, *i.e*, transparency and colouring of the sea. In 1865 Captain Alessandro Cialdi (1807-1882), on the corvette *L'Immacolata Concezione* under the papal flag, took the astronomer (Father) Angelo Secchi to sea. From the papal corvette and from one of its sloops they used differently coloured discs with a diameter of 0.43 to 2.73 meters (Secchi, 1864, pp. 206-207). The largest disc was made of a circular iron frame covered with white-lead painted linen canvas. For one of the small discs a white ceramic dinner plate was attached to a circular iron frame. The other iron frames were all stringed with coloured linen and weights were attached to the discs to assure the horizontal position of the discs during deployment. The first experiments were performed in April, about six to twelve nautical miles off-coast of Civitavecchia, a small town Northwest of Rome. Bottom depths varied between ninety and three hundred meters. During their observations, the sea had been calm for a long time, perfectly clear and with a beautiful colour. The results of some of Cialdi's and Secchi's experiments are shown in table 2.3 (one of the linen colours was referred to as silt colour that I interpret as khaki).

Table 2.3 – Some of Cialdi's and Secchi's visibility results in Mediterranean waters using different disc colours and diameters.

Disc diameter	***3.75 m***	***0.4 m***	***0. 4m***
Colour/material	Lead-white linen	white ceramic	yellow and khaki linen
Sun height	$60^0 17'$	$59^0 48'$, $38^0 42'$	?
Visibility depth (m)	42.5	35, 42 (only once)	17 – 24

The best results were obtained by lowering the discs on the shady side of the vessel. Repeated observations using the large disc all stayed within an accuracy of one meter at depths of around forty-five meters. Their findings contain remarks on the disc observation technique proposed by Arago who used a polarisation filter in front of the eye to exclude surface reflections and the disadvantages of the use of smaller discs which are more sensitive to image distortion and therefore harder to detect at greater depths.

Figure 2.15 – Chromolithograph of the Rescue of the balloon *Tricolore* in 1874 by Charles Leduc (1831-1911). Two years after the balloonists Jules and Caroline Duruof almost got drowned in the North Sea near Grimsby, England, they and Moret did there astonishing observation near Cherbourg, France, seeing the eighty meters deep bottom of the sea from their balloon. Source: Library of Congress Prints and Photographs Division, Washington.

They also made remarks on the brightness of different disc materials. Secchi stated (Secchi, 1864, p. 225):

> Normally I use two eyes to look at the submersed disc, with the polarising filter I only use one eye to look through it and therefore it is harder to keep the disc in sight. The small white ceramic disc under the most favourable circumstances could even be seen at a depth of forty-two meters. Submerged, the white of the ceramic dinner plate reflected much brighter than the white of the white-lead painted linen.

Referring to the larger disc, Cialdi and Secchi concluded that under a perfectly clear sky the visibility depth increased by up to four meters compared to observations under a cloudy sky. Another experiment they performed was by means of a spectroscope to determine the colour of the submerged white disc. It was established that red and yellow disappeared first, after lowering the disc, then green, whereas the colours blue, indigo and violet stayed vivid (Secchi, 1865, p. 236). Scoresby already mentioned this result at the beginning of the nineteenth century.

Two years after their unfortunate crash, illustrated in Figure 2.15, balloonists Jules Duruof (1841-1898) and A. Moret made interesting observation of extremely clear water over the English Channel near Cherbourg (France) on August 21, 1876. From an altitude of seventeen-hundred meters, they could see every detail on the sixty to eighty meters deep bottom of the sea (Moret, 1876, pp. 576). This observation and the one of John Wood belong to the oldest records of extreme water transparency.

During the summer of 1880, Julius Wolf and Josef Luksch on their trip with the yacht *Hertha* used a large white painted disc during their investigations of the Adriatic and Ionian Sea. A maximum depth of fifty-four meters was found on the 6th of August near the island Zante (Wolf & Luksch, 1887, p. 22). Some years later, between 1890 and 1898, Luksch, onboard the steamer *Pola* crossing the eastern Mediterranean and Red Sea (Luksch, 1901, pp. 400-401), used a small forty-five centimetres disc (already called Secchi disc, see Figure 2.16). West of Beirut at 33°47'N and 34°8'E the disc could be seen at sixty meters depth, in the northern Red Sea until fifty meters depth and in the south only until thirty-nine meters depth.

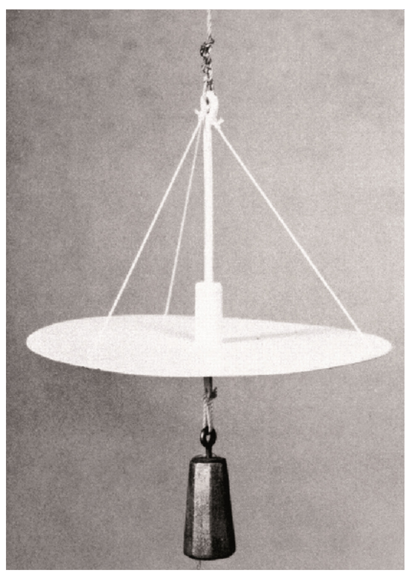

Figure 2.16 – Luksch polished white painted 'Secchi' disc of forty-five centimetres in diameter used onboard the Pola (around 1890). Source: Photograph by P. Roggero, Musée Océanographique de Monaco.

Around 1882, John Aitken (1839-1919) experimented with fruit submersed into the Mediterranean. An orange as it sunk into the water appeared to become unripe. A lemon became quite green (Aitken, 1882, p. 474). According to Georg von Boguslawski (Boguslawski, 1884, p. 184), more and more observations were made with the help of white painted discs. He remarked that these kinds of measurements could be hampered by variations in the diameter used by the different researchers. Sun height and the visual abilities of the observer were also described as ‘having influence on results’. However, Krümmel was aware of the fact that Secchi disc measurements were more or less independent on the height of the sun (Krümmel, 1907, p. 256). However, the sea state due to surface winds could largely influence the measurements. During storms, waves and air bubbles rapidly decreased the transparency of the water. During observations in the North Sea and Baltic Sea onboard the Prussian frigate *Niobe* (1889) Captain Aschenborn used a two meters diameter white disc and found a light penetration depth of 13.7 meters in the North Sea and around 10 meters near Stavanger, Norway (Aschenborn, 1890, pp. 134-136). During the German Plankton Expedition of 1889 organised by the Humboldt Society a similar disc was used. Water transparency was measured and the colour of the water was compared to the Forel-scale (see Figure 2.30). Examples of these colour-and transparency measurement are shown in table 2.4. Otto Krümmel wrote the narrative of the expedition and a dedicated chapter on geophysical observations (Krümmel, 1895, p. 110).

Table 2.4 – Original table (by Krümmel, in German) containing colour and transparency data collected during the 1889 plankton expedition. Column names from left to right: Colour, after the Forel-Scale, Number of occasions with visibility depths of, Total number of cases, Average visibility depth.

Farbe	nach Forels Skala	Zahl der Fälle mit Sichttiefen von					Gesammtzahl aller Fälle	Mittel sämmtlicher Sichttiefen
		40 m und mehr	30 m und mehr	25 m und mehr	20 m und mehr	unter 15 m		
blau	0—2	7	25	43	53	3	66	26.7
entfärbt blau . .	2—5	0	1	4	6	1	9	23.2
grünblau	5—9	0	0	1	2	5	8	16.2
grün	9—20	0	0	0	1	3	4	15.8

In the same period, François Alphonse Forel investigated Lake Geneva and concluded that the maximum water visibility according to the Secchi method (with a twenty centimetres white disc) came to twenty-one meters (Forel, 1895, p. 442). Von Liburnau, like Kotzebue, used a white disc to establish the transparency of the water seven years prior to Secchi. In his article on physical limnology, published 1898, he complained on the fact that the method was already named after Angelo Secchi. He preferred to call it ‘disc system’ (‘Scheibensystem’, Liburnau, 1898, p. 70). Nevertheless, the depth at which a white painted disc disappears from the eye is now called the Secchi-depth. Considering the naming of the disc Hans Otto Eckart Freiherr von und zu Aufsess (1866-1944) supported Von Liburnau (Aufsess, 1905, p. 47) but as we can conclude from earlier observations in the Bering Sea and the Pacific, the device could also have been called the Kotzebue-disc.

DICHROISM, DINNER PLATES AND TUBES

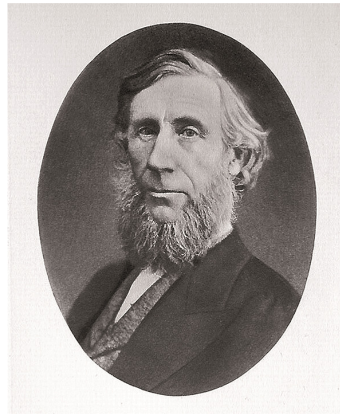

Figure 2.17 – John Tyndall (around 1889). "The surmise of thirteen years ago has become the verity of today". Source: Portraits from the Dibner Library of the History of Science and Technology.

In his 1870 article in *Nature*, John Tyndall (1820-1893, Figure 2.17) gives a vivid example of a so-called dichroic action (light splitting up into two different colours). A correspondent mentioned such an effect looking through Salviati's shop window (at that time a decorative Murano glassware shop in St. James's Street, London) at some dishes and vases (Tyndall, 1870a, p. 64). Literally, he quoted:

> Glass exhibits the phenomena of scattering in every degree of intensity. Exceedingly fine examples of dichroic action on the part of this substance are to be seen in Salviati's window in St. James's Street. By reflected light the dishes and vases there exposed exhibit a beautiful blue by transmitted light, a ruddy brownish yellow. The change of colour is very striking when, having seen the blue, a white cloud is regarded through the glass. Where the opalescence is strongest, the transmitted light, as might be expected, is most deeply tinged. From these examples, where the foreign ingredient is intentionally introduced, we may pass by insensible gradations to M. Lallemand's glass. The difference between them is but one of degree. Many of the bottles of our laboratory show substantially the same effect as the glass of Salviati.

During one of his Royal Society lectures, he shared his findings on bottle experiments (the bottles contained a variety of coloured seawater) with the audience. The experiment showed that yellow-greenish water scattered most and water, obtained from a dark indigo sea, least of all (Tyndall, 1870, p. 64):

> Nowadays it is well known that when the white light plunges into the sea the red rays

> are first quenched, then successively the orange yellow and green rays and so on. If there were no particles at all in the sea to backscatter unabsorbed rays the sea would look inky-black.

Finally he showed the audience an experiment where he used the purest water he was able to make by fusion of selected specimen of ice. The melted water was filtered over cotton and placed in a funnel illuminated by an electric lamp. Most particles had been filtered out, not all since the track of the beam could vaguely be seen; the colour within the beam was described as the most delicate blue, a blue purer than that of the sky (Tyndall, 1870, p. 64). At the time, Tyndall was of course unaware of the fact that molecular scattering also plays a role here and therefore the water still would have a dark blue (indigo) appearance. The indigo coloured sea according to Tyndall was the closest to pure water. Furthermore, he told the audience about the dinner plate experiment he performed during his voyage with the H.M.S. *Urgent* to Algeria to observe the eclipse. From one side of the ship Tyndall's assistant Mr. Thorogood lowered a white porcelain plate with a lead weight securely fastened to it. Fifty or sixty yards of strong hemp line were attached to the plate. From the stern, Tyndall looked at the submersed plate and saw at considerable depth the green hue of the plate in a surrounding indigo. This experiment was done to prove his underlying theory on the attenuation of light by seawater described in his *Fragments of Science* (Tyndall, 1871, pp. 203-204):

> The indigo, already referred to, is I believe, to be ascribed in part to the suspended matter, which is never absent, even in the purest natural water; and in part to the slight reflection of the light from the limiting surfaces of strata of different densities. A modicum of light is thus thrown back to the eye, before the depth necessary to the absolute extinction has been attained. An effect precisely similar occurs under the moraines of glaciers. The ice here is exceptionally compact, and, owing to the absence of internal scattering common in bubbled ice, the light plunges into the mass, were it is extinguished, the perfectly clear ice presenting an appearance of pitchy blackness.

THE MIRROR BOX OF BEETZ (1862)

Wilhelm Beetz (1822-1886, Figure 2.18), one of the founders of the German Physical Society, investigated the colour of sunlight both reflected and transmitted by water using a wooden box with mirrors inside (Beetz, 1862, pp. 137-147). With this device, he came to the (correct) conclusion that the transmitted light as well as the reflected light both had the same blue colour (Beetz, 1862, p. 145). To investigate the transmitted colour of water, Beetz constructed a box, shown in Figure 2.19, made of 25 cm long 'Guttapercha' plates a and a'. The other ends band b' are closed by means of very white (transparent) thin high quality glass. Two surface mirrors c and c' are placed inside in which two small slits are scratched out, d and d'. By means of a 'heliostat', sunlight is brought into slit d, which then reflects between the mirrors. In this way, once the box is filled with water, the incoming light-beam will be reflected through the solution more than once.

Figure 2.18 – Wilhelm Beetz. "Recently views are given, stated on real research, concerning the colour of water of seas, lakes and rivers". Source: Wilhelm Beetz Gesellschaft m.b.H, Wien.

The number of reflections can be minimized or maximized by simply changing the angle of the incoming light at slit *d*, by means of turning the whole box. The outgoing beams through slit *d*′ can be projected on a screen. Also the observer can directly look through slit *d*′, looking through the inside of the box towards the first slit *d* and will then see numerous diminishing light beams coming towards him. Beetz first tested the influence of the mirror-glass itself on the colouring of sunlight. By turning the silver-surface mirrors *c* and *c*′ upside down in air, the light beam had to go twice through the glass during each reflection. Even after eight reflections, the light still was whitish. However, comparing each reflection, looking through slit *d*′, one could see a successive emerging of a vague yellowing, which was ascribed to the relative thick glass-layer through which the light was reflected. Further tests where made with the coating of the surface mirrors pointing to the inside of the box. In addition, the influence of the silver coating was discussed to be of minimal influence on the results if the coating was of a supreme quality and shine. The outcome, *i.e.* the colours on the screen in front of *d*′ in case the box was half-filled with distilled water, the lower part of the slit appeared blue, the other half was still whitish. Looking through *d*′ into the upper-part of the beams, one could again see a weak yellowish tint. However, looking through the lower part each of the beams coming towards the slit becomes bluer with a vague green blur. Subsequently, the box was filled with water originating from different German lakes. These results were similar to those of Wittstein. Even topsoil was mixed with water, filtered and diluted with distilled water and measured accordingly. Being strongly, diluted this resulted in a yellow-green colour, being less diluted resulted in a brownish colour.

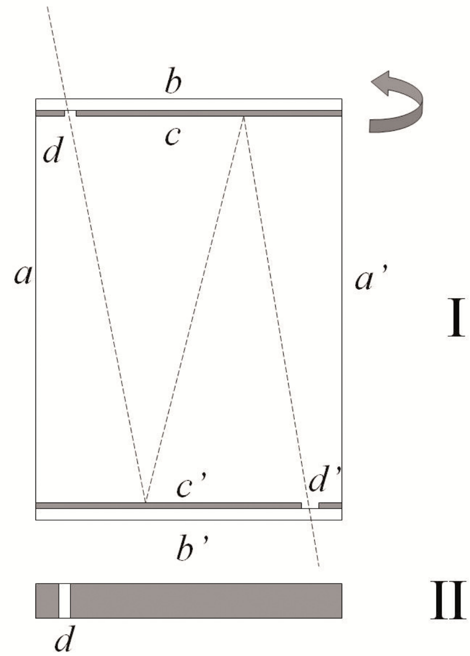

Figure 2.19 – Top view I and side view II of the water-box of Beetz to test the colour of the transmitted and reflected sunlight in distilled water and natural water. In the above figure *c* and *c*′ are the mirrors and *d*is the entrance slit to be illuminated by the sun and *d*′ is the slit to be able to look inside the box.

Johan Kayser (1826-1895) performed in 1873 a laboratory experiment similar to the box-experiment of Beetz, with satisfactory results concerning the true colour of the water, either transmitted or reflected. In his *Physik des Meeres* he describes seawater as a transparent medium that could be characterized by a reflected and a transmitted blue colour (Kayser, 1873, p. 161). The device he constructed, shown in Figure 2.20, existed of a four and a half meters long tube, placed horizontally, half-filled with distilled water and illuminated by a lamp (Kayser, 1873, pp. 154-165).

In this way the direct transmitted lamp colour (reference) could be compared with the beam colour transmitted through water. Wernand repeated this experiment in 2003 using milliQ (very pure) water and a fine blue colour could be experienced as can be seen on a photograph taken of the tubes exit window and is shown in Figure 2.21.[9]

[9] *Author's note: A simple and adequate set-up to show that blue is the apparent colour of pure water.*

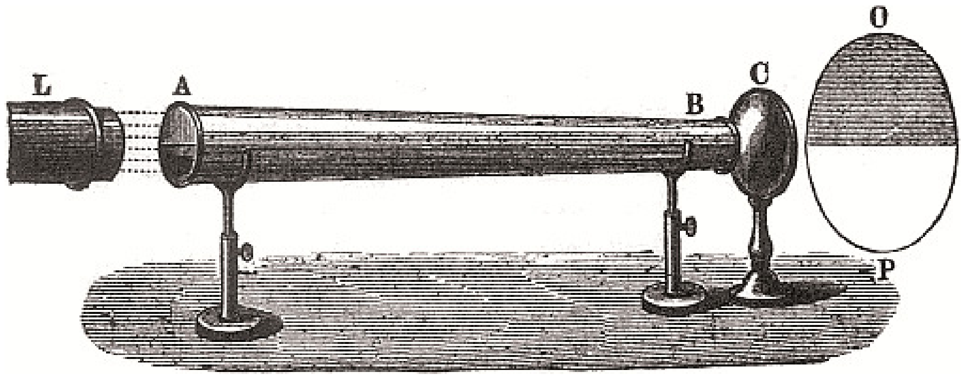

Figure 2.20 – Reproduced print of Kayser's four and a half meters long metal tube, A-B, half-filled with distilled water. Colourless glass windows closed the tube at both sides. White light of an electric lamp L is transmitted through the tube. The lens C mirrors the image on a screen (OP). The white of the lamp can be seen in the bottom half (P) and the blue as resulting colour of the by water filtered rays can be seen at the top half of the screen (O).

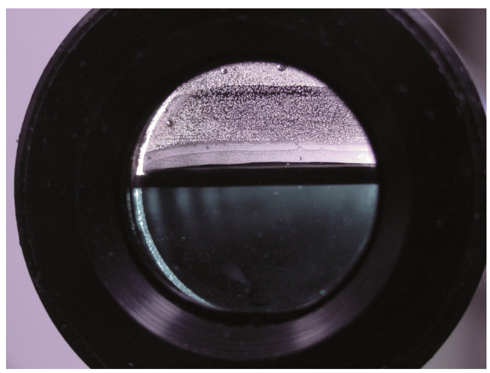

Figure 2.21 – In 2003, the Kayser tube experiment was repeated by means of a 4 meters long polyurethane tube half filled with mill-Q water. The resulting blue of the purest water could easily be compared with the 'white light' travelling through air. Source: Photograph by B. Aggenbach, NIOZ.

Walthère Victor Spring (1848-1911) started his colour determination experiments using blackened glass tubes of five meters long and four centimetres wide, having read the work of Bunsen, Beetz and Tyndall on the causes of the true colour of water. The tubes were placed against the window to receive sunlight. Freshly distilled water, put into the tubes, gave a pure sky-blue. However, after a few days the water turned bluish-green again. Spring was aware that germs were not being killed during the distillation process. He continued by adding bi-chloride of mercury to one of his tube setups, which, after six days, resulted in a perfect blue colour again and stayed this way even after three weeks. As the added chemical killed all the germs, (the organic) present in the distilled water Spring was convinced that the blue colour was not caused by minute particles (inorganic material disappears after proper distillation). Therefore, there was something else in the water causing the blue colour (Spring, 1883, pp. 71-72). The absorption of water was also spectrally investigated. An example of such a device is shown in Figure 2.22.

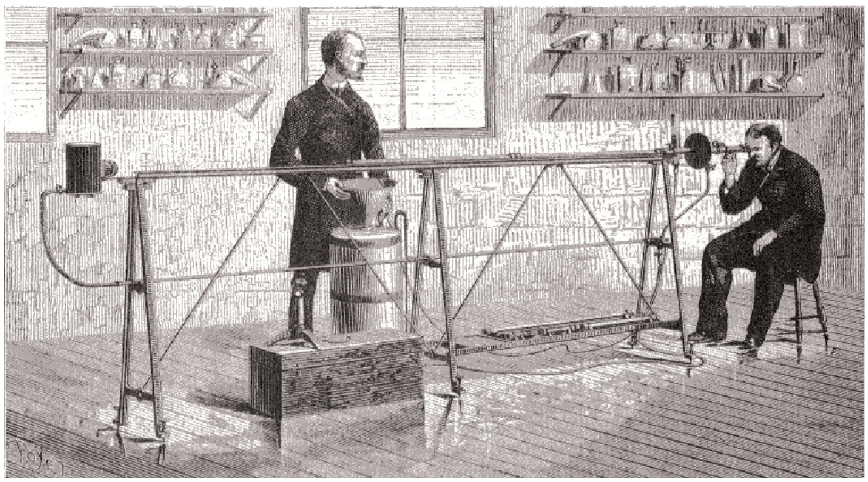

Figure 2.22 – An absorption spectroscope designed by Maurice de Thierry. A device similar to the one Spring was using to investigate the true colour of water. Spring used the sunlight instead of an electric lamp to illuminate the water column. Source: *La Nature;* Revue des Sciences of 1886.

On the basis of experiments with distilled water, Bunsen, Beetz and Kayser found a blue colour for both the reflected and transmitted light, contrary to results obtained by Becquerel and Tyndall. Most scientists, including Newton, Arago, Wittstein and Xavier de Maistre, were of the same opinion: blue was the reflected colour of water. It is remarkable that around 1832 Xavier de Maistre (Maistre, 1832, p. 259) mentioned the reflectance and dispersion by air molecules without knowing why it only affected the indigo (blue). This was long before John William Strutt, later known as Lord Rayleigh (3^{rd} Baron Rayleigh, 1842-1919), developed his theory on the blue scattering of air molecules. The disagreements between nineteenth century scientists on the apparent properties of water can probably be ascribed to the impurity or quality of the investigated water at that time.

La Grotta Azzurra

One of the finest examples of pure blue natural waters can be found inside the *Grotta Azzurra* ('Blue Grotto', Figure 2.23) on the island of Capri in front of Naples, Italy. In 1826, the Berlin poet and painter August Kopisch (re-) discovered the blue cave and announced it to the world. In 1885 the original story was written down by Ferdinand Gregorovius (1821-1891) in his travel book *Die Insel Capri* (Gregorovius, 1885, pp. 72-78):

> It was on August the 27th 1826 when Kopisch, Fries, Pagano and bargeman Ferraro first entered the Grotto.

Figure 2.23 – La *Grotta Azzurra*, painted by Heinrich Jakob Fried (1802-1870) in 1835. The inside of the 'Grotto' appears blue like *lapis lazuli*. Source: Collection Kunsthalle, Bremen.

A few years after its discovery whilst performing transparency measurements in the Gulf of Naples Comte Xavier de Maistre visited the 'Grotto' and wrote about its splendour (Maistre, 1832, p. 259).

At the end of the nineteenth century, this cavern became one of the most desirable places to visit by travellers, who read about its splendour in travel guides (Miller, 1879, pp. 336-337) and by scientists to perform their spectrographic measurements. During one of those visits, Kayser saw the magnificent Lapis Lazuli colour inside the cavern and noticed the parallels with the outcome of his laboratory experiments. He emphasized that the apparent blue of the ocean was due to the absorption of only the red to green colours with the resulting blue light scattered upwards by suspended matter. Raman later proved his assumption concerning the purest ocean's colour to be almost right, albeit that the scattering was due to molecules and not to suspended matter.

Kayser as well as Gregorovius had a glance of the original notes made by Kopisch, which over the years were safely kept by the, at that time already aged, proprietor Pagano.

Some years later, Herman Wilkelon Vogel (1834-1898) experimented with his spectrograph in the 'Grotto' and came to the same conclusion as Kayser: red was the first colour to disappear, then followed yellow and green until blue, indigo and violet remained (Vogel, 1875, pp. 325-326). This is why the inside of the 'Grotto' appears blue like *lapis lazuli*. Sunlight enters the cavern not via the small air-opening but through the huge underwater opening. All colours are 'filtered out', except indigo blue. In the last part of his publication on spectral observations of the cavern, Vogel apologies for skipping a planned spectral study of the nearby Green Grotto water due to a sudden illness:

> My plan to study the light of the green cavern unfortunately could not take place due to a sudden upcoming illness; in any case it would be worth the effort to do so and if by these notes I would like to give an initiative to use the spectroscope more than already has been done, for the reason that there are still numerous parts with an enigmatic water colouring (Berlin, July 1875).[10]

PHOTOGRAPHIC PLATES

Around 1840 Louis Jacques Mande Daguerre (1787-1851) and his friend Joseph Nicephore Niépce (1765-1833), in France and William Henry Fox Talbot (1800-1877) in England discovered the art of photography (Arago, 1839, pp. 1-6; Talbot, 1843. pp. 312-314). Apart from capturing a composition on a photosensitive plate, it could be used also to measure the intensity of (sun) light.

The discovery in 1869 of a blind crab caught at the bottom of Lake Geneva became the start of the use of photosensitive materials to measure the penetration depth of sunlight. First experiments with this material were performed in Lake Geneva during a dark night in April 1873 (Forel, 1875, pp. 24-35). François Alphonse Forel lowered glass bottles filled with a silver-chloride

[10] *Meine Absicht, auch das Licht der "grünen" Grotte zu untersuchen, konnte ich leider egen plötlicher Erkrankung nicht ausfüren; jedenfalls dürfte sich aber solches der Müheverlohnen und möchte ich durch diese Notiz Veranlassung geben, dass Spectroskop bei Untersuchung der noch vielen Stücken räthselhaften Wasserfarbung mehr als bisher zu benutzen (Berlin im Juli 1875).*

solution to a depth of sixty meters. After a few nights, the bottles were recollected during the night and found to be unchanged (no blackening). Not satisfied with the results, he started to use albumin-paper soaked in an 8% silver-nitrate solution. The dried paper was cut into square pieces of seven centimetres. Accordingly, the paper was sealed between two glass plates. Half the plate was covered with an opaque wax. Lead was attached to the plates to facilitate easy lowering into the water. For the first experiments in Lake Geneva, the plates were let down into the water to depths of forty to a hundred meters and were exposed to possible light during one or two days. The summer experiments showed that complete darkness existed beyond fifty meters and during winter experiments plates were still blackened until a maximum of ninety meters.

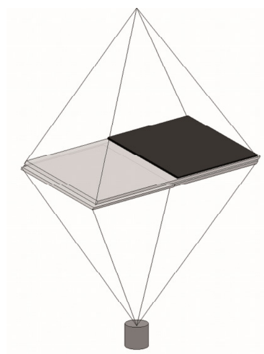

Figure 2.24 – The photographic plates as lowered, at night, by Asper in Lake Zurich in 1881 to establish the light levels per depth. At the top side, the photographic plate is half blackened for the separate determination of down- and upwelling light. A weight kept the plates horizontally.

A few years later, on August 3rd 1881, the Swiss researcher Gottlieb Asper (1854-1889) lowered photographic plates in Lake Zürich (Zürichsee, Switzerland). He used more sophisticated photographic plates, similar to those used by photographers (Asper, 1881, pp. 318-319). These plates were much more light-sensitive than the albumin paper used before. In Lake Zürich, sighted crabs were still caught at a bottom depth of a hundred-thirty-five meters. They tested if this Lake was more transparent than Lake Geneva. Nine centimetre square plates were mounted in a wooden frame and kept horizontally by thin wires with an attached weight. Asphalt-lacquer was used to blacken the top and bottom half of the plate (see Figure 2.24). At night, the plates were lowered in the middle of Lake Zurich between Wollishofen and Zollikon and brought to the surface again the next night. The plate lowered to a depth of eighty to ninety meters was completely darkened upon exposure and the opposite site was smoky-grey. This meant that at that depth light was still reflected, perhaps back from the bottom as Forel later concluded. A similar experiment was performed 22nd of October 1881 in the two-hundred meters deep Swiss Wallensee fed by the turbid river Linth. Even under overcast conditions, the photographic plates darkened at a depth of a hundred and forty meters. Based on the previous results Asper guessed that complete darkness would be present only at depths beyond two hundred meters, in lakes clearer than the ones he studied.

In an article appearing in 1885 he again doubted this conclusion (Asper, 1885, p. 177). By comparing, the silhouettes of trees and mountains during his nightly experiments as seen by the naked eye with results of photographic plates, which were not influenced by the dusk made him believe that daylight would perhaps penetrate much deeper. Deeper than could be measured using this sort of photochemical emulsions which where only sensitive to 'chemically active' light.

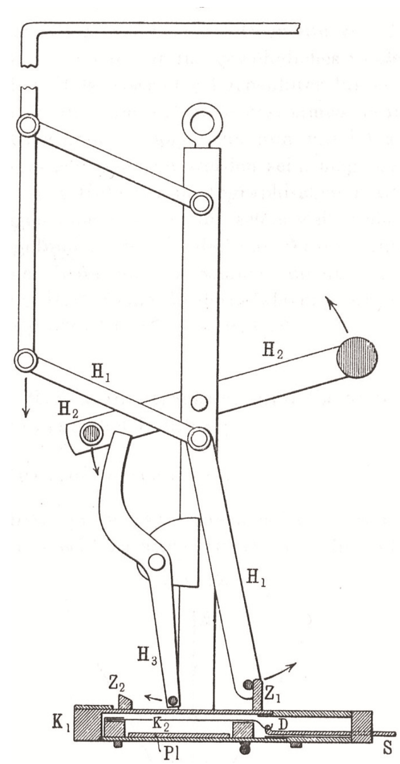

Figure 2.25 – The photographic apparatus proposed by Willi Ule in 1901 to investigate the penetration depth of sun light. The cassette K_1 contains the sensitive plate. S is an extra cover to keep the sunlight out and is removed shortly before the apparatus is lowered into the sea. By means of falling weights, the shutter Z-Z can be opened (H) and closed (H). Aufsess modified the apparatus in 1905. A glass window with a possibility to include a colour filter kept the seawater out.

Willi Ule studied the amount of light at different depths more accurately at the beginning of 1900 (Ule, 1901, pp. 176-178). He designed an apparatus containing a photo graphic plate (Figure

2.25) in a holder. It was now possible to lower such a device during daylight. The plate is kept in a closed cassette (K_1, figure 2.25), which could be opened and closed by means of falling weights along the cable by which the apparatus was lowered into the water. According to Aufsess (Aufsess, 1905, p. 48) half of the photographic plates exposed to saline water were blackened on their way to the laboratory for development. In 1905 therefore, Aufsess proposed a change of Ule's photographic apparatus by means of a new cassette closed by a glass-plate. It was now possible to investigate the penetration depth of different coloured light by placing an optical filter between the glass window and the photographic plate (Aufsess, 1905, p. 38).

THE REVELATION: SEEING THE LIGHT AT LAST

As we have argued, researchers came close to explaining the cause of the blue colour of lakes and seas around 1870, each in their own way, after experimenting with different types of sea and lake water. Tyndall and Jacques-Louis Soret (1827-1890) based the scattering of light on the presence of small particles, *i.e.*, particles small enough to scatter only the blue light (Soret, 1870, p. 358; Soret, 1870, pp. 180-181; Soret, 1870, pp. 129-175). It was known that absorption in water affects the longer (red) wavelengths much more than the shorter (blue) wavelengths. After he observed the transmitted light of a lake sample Tyndall remarked (Tyndall, 1870, p. 489):

> In the Lake of Geneva, we have not only the blue of scattering by small particles, but also the blue arising from true molecular absorption.

At the time it was believed that water free of particles would not reveal its colour and would appear black to the observer (the darkness of true transparency), which was proven wrong later. John Tyndall was already interested in the numerous attempts made to account for the colour of Lake Geneva well before 1857, when he visited the Lake himself. Shortly after this visit, he wrote some notes concerning the cause of this colouring. Tyndall asked himself as Xavier de Maistre did forty years earlier (Maistre, 1832, p. 264) if perhaps 'finely divided matter' could have any influence on the colour of some Swiss lakes and more specifically the colour of Lake Geneva. According to him, this lake was nothing more but an expansion of the river Rhone that runs down from the Rhone glacier transporting fine or minute matter (Tyndall, 1870, p. 489):

> Numerous other small streams join the Rhone right and left during its downward course, and these feeders being almost wholly derived from glaciers, carry with them the fine matter ground by ice from the rocks over which it has passed. Particles of all sizes must be thus ground off, and I cannot help thinking that the finest of them must remain suspended in the lake throughout its entire length.

Concerning deposit times of small particles Tyndall was aware of the work of Faraday who investigated the experimental relations of gold to light. Part of Faraday's study was on the aggregation of small particles (precipitate) of gold in liquid and on (a long) deposit time of this metal when caught in a small bottle (Faraday, 1857, p. 161). Tyndall notes:

> When put in a five-inch high bottle of water it would take a month to sink the particles to the bottom. This means that it might take ages to deposit all particles of Lake Geneva.

Reason enough for Tyndall to find out if such particles suspended in water would contribute to its magnificent blue. In his article he writes in *Nature* dated October 20, 1870 (Tyndall, 1870, p. 489):

> It seems certainly worthy of examination whether such particles, suspended in water, do not contribute to that magnificent blue which has excited the admiration of all who have seen it under favourable circumstances. Through the observation of Soret, and through those here recorded, the surmise of thirteen years ago has become the verity of today.

His friend Soret brought him water samples taken from the Mediterranean and Lake Geneva. Tyndall thoughts before experimenting with these samples:

> In optically homogeneous water (*i.e.* in water of the purest kind), a beam of light remains unseen as in the case of a light beam travelling through optically 'pure air'.

One by one, the bottles were placed in a convergent beam of light. The cone of light traversing the bottles showed a distinctly sky-blue (the colour of the Lake Geneva sample especially being rich and pure). Thus, something had to be present in the liquid, which intercepted and scattered the shorter wavelength of the beam. His own observations and the ones of Soret made him state that through the interaction of light and small particles an efficient mechanism was generated to produce the blueness as observed in general. However, this was not the only operative cause. In Lake Geneva, the blue was not only caused by small scattering particles but concurrently by colour-selective molecular absorption of all (red to green) but the blue rays. At this point, Tyndall remarks that if there was no molecular absorption the water would show up yellow, orange or red, like the light of sunrise or sunset. Therefore, a combination of scattering and absorption gives the Mediterranean and Lake Geneva its blue colour (Figure 2.26). Tyndall refers to experiments performed by Alexandre Lallemand (1816-1886) in 1867 on the optical phenomena exhibited by certain liquids and solids when illuminated (Lallemand, 1869, pp. 189-195).

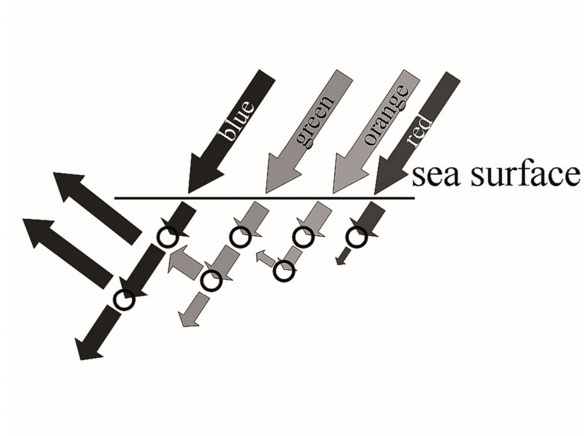

Figure 2.26 – How the water will absorb the red and green and how the blue is scattered by small particles, according to Tyndall and Soret.

Around 1870 Lallemand supposed that the scattering of light in liquids was not affected by foreign particles, but was due to the molecules of the different liquids he experimented with (Lallemand, 1869, p. 190). This was a novel, but thorough, conclusion, but at the time a thought 'out of the blue' and criticized by fellow scientists like Soret and Tyndall. Soret believed that the scattering of light was an affair of particles (Soret, 1870, p. 129) and not of molecules. In this view, Tyndall supported him (Tyndall, 1870, p. 490). According to the latter, Lallemand assumed a purely hypothetical cause based only on experiments with clear glass and distilled water using ordinary daylight, while a true cause was at hand (Tyndall, 1870, p. 489). Tyndall found Lallemand's test a very deceptive one. Instead of daylight he used a highly concentrated beam of electric light and could actually see the light-path of the beam. As Tyndall continues in his *Nature* article:

> This occurrence is based upon the presence of small scatterers or foreign particles present in the liquid. This event will not be revealed under normal daylight conditions.

Then, Tyndall used lake-ice (exceedingly instructive) to prove that Lallemand was wrong. Again, by using a concentrated light beam ice shows signs of breaking up internally. The ice used also contained a sparkle of cracks. In some parts the track of the beam appeared bluish, but rarely uniformly blue. The beam was sent in different directions through the ice, resulting in remarkable variations in scattering intensity. After the ice experiments Tyndall literally said:

> In some cases, the light completely disappears into the dark, the darkness of true transparency. Should the scattering be molecular it ought to occur everywhere, but it does not so occur, therefore it is not molecular.

Lallemand was right, although now we know that Tyndall and Soret were not far off the truth considering only inorganic particles.

Different laboratories in the British capital did their best to provide Tyndall with the purest distilled water (London's drinking water at that time was exceedingly thick and muddy). The samples seen in ordinary daylight looked 'clear as crystal' (in common parlance). When the samples were brought into the beam of an electric lamp, the notion of purity simply became ludicrous. Tyndall also mentioned Thomas Henry Huxley (1825-1895), for he had claimed that particle free solutions could be obtained through normal distillation. Tyndall fulminated in *Nature:*

> Such a statement can only be based upon defective observation.

Moreover, it was really difficult at that time to produce optically clean water. Félix Archimède Pouchet (1800-1872), a French experimenter, claimed to have the recipe producing pure water. Tyndall warned him about the abundance of air particles that could be consumed by distilled water. He checked the water using his lamp and again saw scattering in the beam's path. He then advised adventurous newcomers, who might have been disposed to rush into inquiries taxing the skill of the greatest experimenters, of some of the snares and pitfalls that could be encountered in making pure water according to Pouchet's protocol. Yet, if optically pure water really could have been made at that time, Lallemand's ideas could have been proven right much easier and earlier.

Heinrich Wild (1833-1902) in 1856 and Paul Glan (1846-1898) in 1870 with Franz Boas (1858-1942) were among the first pioneers to determine the attenuation properties of water in the laboratory (Wild, 1856, pp. 235-274; Glan, 1870, pp. 141: 58-83). In his thesis, Boas (Boas, 1881, pp. 26-33) describes the retrieval of the attenuation coefficient α (Boas called it the absorption coefficient) of distilled water (see Figure 2.27).

Boas Absorption Setup

> The set-up was placed in a darkroom with a total length of eight meters and consists of a one-meter long brass tube R_1R blackened inside by nitric acid with glass windows. *W* consists of the same glass windows and enclosed a 1 mm thick water layer. A monochromatic light source *L* illuminates both the moveable white paper screens *S* and the fixed screen S_1. S_1 is placed 10 cm sideways of *S* and 125 cm away from *L*. *S* can be moved along *D* and D_1 by pulling an endless cord at the observers position *A*. The cord is situated 10 cm above the tube. Two rectangular equilateral prisms *P* and P_1 collect the light from *S* and S_1 and accordingly reflect this light towards the observer's eye at *A*. Half the rectangular side of P_1 opposite to *P* is

covered with tinfoil to prevent influencing the light coming from the tube and reflected by *P* towards *A*. A black screen S_2 is placed in front of the eye with a hole the size of the observed images reflecting from P_1 and *P*. When *a* is the distance *SL* and *a'* is the distance S_1L, the intensities of light backscattered from the screens are equal to respectively I/a^2 *a nd* I/a_1^2. The absorption coefficient *α* for a length 1 and a tube length of *tl* can be calculated according to:

$$(1-\alpha) = \left(\frac{a}{a_1}\right)^{\frac{2}{tl}} \tag{2.1}$$

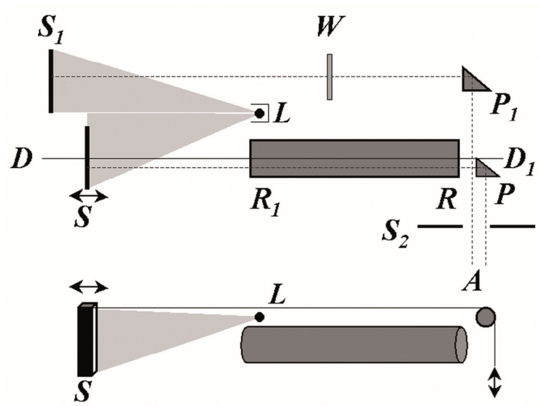

Figure 2.27 – Top-view and side-view of Boas set-up to determine the quasi-absorption coefficient of distilled water. Source: Redrawn by the author.

After his experiments with rain and melted glacier water, Sir Humphry Davy was the first to say that a blue colour could be ascribed to pure water and was supported finally ib his thoughts by Boas although half a century later. Both also agreed upon the idea that a green and yellow tint was due to the presence of organic matter (Boas, 1881, p. 14).

During his experiments with distilled water, Boas was intrigued by the colour difference of its green-bluish transmitted light and the bright blue reflected colour of the Mediterranean Sea samples. According to him, it was not easy to explain what matter caused this colour shift. A possible explanation could be ascribed to the presence of tiny suspended particles in the Mediterranean water. An article *On the scattering of light by small particles* (Strutt, 1871, pp. 447- 454) by John William Strutt made him believe so and was based upon John William Strutt's law, as described in the same journal (Strutt, 1871, p. 111):

> When light is scattered by particles which are very small compared with any of the wavelengths, the ratio of the amplitudes of the vibrations of the scattered and incident light varies inversely as the square of the wavelength, and the intensity of the lights themselves as the inverse fourth power.

AITKEN'S THEORY

In 1882, John Aitken wrote the first papers proposing that both the absorption and reflection were responsible for the blueness of natural waters (Aitken, 1882, pp. 472483), a year before Boas finished his thesis on related matter (Boas, 1881). Both tried to answer the question by what part the selective reflection or the selective absorption contributed to this blueness of pure water.

THE SELECTIVE REFLECTION THEORY:

The colour is due to the light reflected by extremely small particles of matter suspended in the water. These particles being so small they can only reflect short waves of light, or those, which belong to the blue end of the spectrum (Figure 2.28).

THE SELECTIVE ABSORPTION THEORY:

The colour is due to a selective absorption for the rays of the red end of the spectrum. In fact, the water is a blue transparent medium (Figure 2.29).

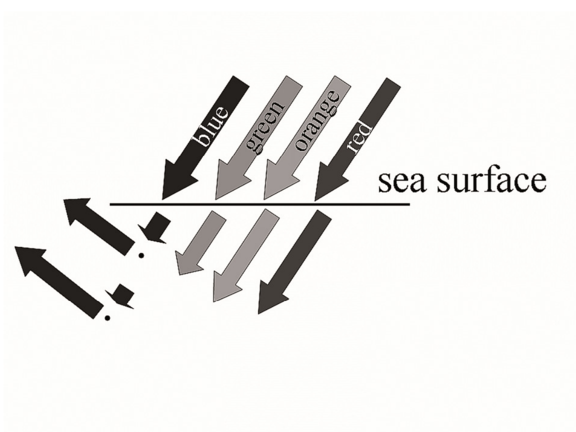

Figure 2.28 – The selective reflection theory: In water, only the blue is reflected by particles so small they can only reflect the short wavelengths.

Aitken adopted three different methods to test the correctness of the two rival theories. Firstly, he took a six meters long metal tube closed at the bottom with a glass plate. Sinking it vertically in the water, he looked at different coloured objects fixed near the bottom of the tube, including a white one, all illuminated by solar radiation. The white object showed a most beautiful deep and delicate blue. Literally, he concluded (Aitken, 1882, p. 473):

> If the selective reflection theory was true, submerged objects would be illuminated with a colour complimentary to that reflected by small particles and would therefore appear orange or yellow, the exact colour depending on the amount of green in the reflected blue.

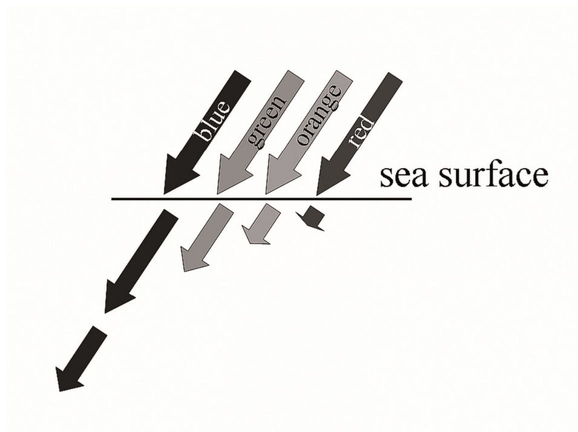

Figure 2.29 – The selective absorption theory: Water is a blue transparent medium. Selective absorption by water only concerns the red end of the spectrum.

Secondly, Aitken looked at a white surface through a considerable length of water contained in a blackened tube. The transmitted light was found to be blue. He concluded that this showed that water had a selective absorption for rays of the red end of the spectrum. Thirdly, he sunk white, red, yellow and purple objects into the water and found that these colours changed in the same way as when seen through a blue transparent medium, such as a piece of (coloured) glass. The white changed to blue, the red darkened very rapidly as it descended. At two meters depth, the very brilliant red turned into a dark-brick red. Yellow changed to green and the purple changed to dark blue or violet. These changes, being all due to the elimination of the red, are caused by selective absorption of the water according to the experimenter. Aitken, believing in the impossibility of the preparation of 'absolutely pure' water, prepared distilled water in two different ways. All necessary materials in the first distillation apparatus were made out of glass and in the second were made out of brass. In the third case, he only used a condensing tube made out of platinum. In his paper he wrote:

> If all distillation techniques would produce the same blue colour this would mean that this colour is due to the water itself and not to the impurities, eroding from the different materials used, present in the samples.

In other words, the results were as expected; the colour of water could be described to the water itself, namely blue.

At the end of the nineteenth century, John William Strutt concluded that the scattering of light by air molecules caused the blue colour of the sky, even on very clear days (J. Strutt, 1899, p. 382; R. Strutt, 1918, p. 453). In addition, there was a general awareness that the sky's colour could deepen the observed sea colour, *i.e.*, it could deepen but not causing 'the blue'.

COLOUR COMPARATORS

Navigators have observed with great attention the varying tints displayed by the ocean and the circumstances that apparently influence those tints. The general tenor of the evidence collected is to the effect that the colour of the ocean approaches a deeper blue colour than anything else. Concerning observations on the colour of the sea a general question remained to be answered: what is the true colour of the sea (F. Arago, 1842, p. 78)?

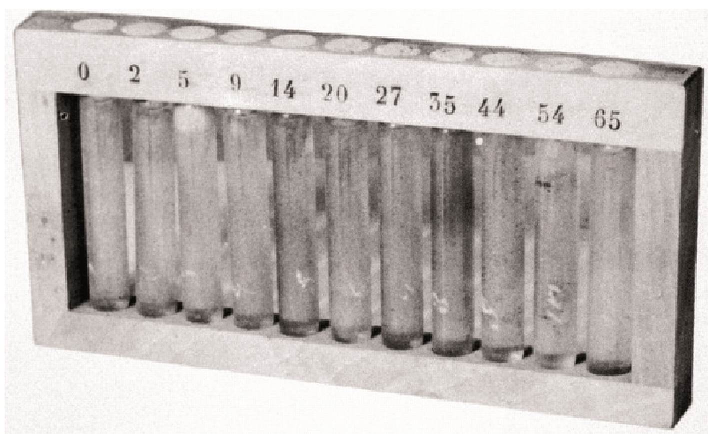

Figure 2.30 – Forel-scale covering the blue to green region. The eleven tubes are filled with a mixture of copper-sulphate and potassium chromate. The numbers above the tubes present the percentage yellow. Tubes no. twelve and no. thirteen are not shown in this setup. Willi Ule completed the scale in 1887 by covering the green to browns. Source: Photograph by P. Roggero, Musée Océanographique de Monaco

To answer this question, scientists proposed techniques to establish the colour of natural water by means of comparison against some colour(ed) standard. The first note mentioning such a standard, if we do not take into account De Saussure's cyanometer (1791), already mentioned before and Arago's cyanometer (1845), dates back to a session of Société Vaudoise des Sciences Naturelles, Lausanne 21st of December 1887. At that session François Alphonse Forel (Forel, 1890, p. 25) proposes a thirteen-colours scale (see Figure 2.30) for a quick identification of the colour of sea, lake or river water. The scale, a mix of solutions of copper-sulphate and potassium-chromate, covers the blue to green region.

In 1892, Willi Ule extended the scale towards the brownish colours (Ule, 1892, pp. 70-71) adding cobalt-sulphate. Since then the scale became known as the Forel-Ule scale (21 tube colours) or Xantho-meter and evolved to the most common and well-known colour scale used to determine the colour of seas, lakes and rivers. In the past hundreds-thousands of such measurements (scale-comparisons) were performed all over the world (around 250,000 archived by the U.S. National Oceanographic Data Centre) and even at this moment, the scale is still in use.
An example of a sea colour map (Schott, 1912, pp. 125-127 and Table VIII) obtained from Forel scale observations was published by Schott in 1912 in his *Geographie des Atlantischen Ozeans* (Geography of the Atlantic Ocean) and is shown in Figure 2.31.

Table 2.5 – Mineral colours for comparison to sea colours proposed by Lorenz von Liburnau (1898).

Clear Blue	***Diffuse-Blue***	***Blue-green***	***Apple-green***	***Yellow-green***
Azurite	Indigo	Dioptase	Heliotrope	Serpentine
Chalcanthite	Ultramarine		Actinolite	
Sapphire				Epidote
Halite	Lapis Lazuli		Emerald	
			Malachite	Olivine
Beryl	Turquoise		Chrysoprase	Nephrite

Strangely enough a few years after Ule extended the scale, Lorenz von Liburnau criticized the new-born colour scale due to its limited range of the blues to greens (Liburnau, 1898, p. 87). He therefore proposed a colour scale as shown in table 2.5 according to the colours of minerals (Liburnau, 1898, p. 89). However, no field observations are known in literature of the use of his mineral-scale to establish the colour of the sea.

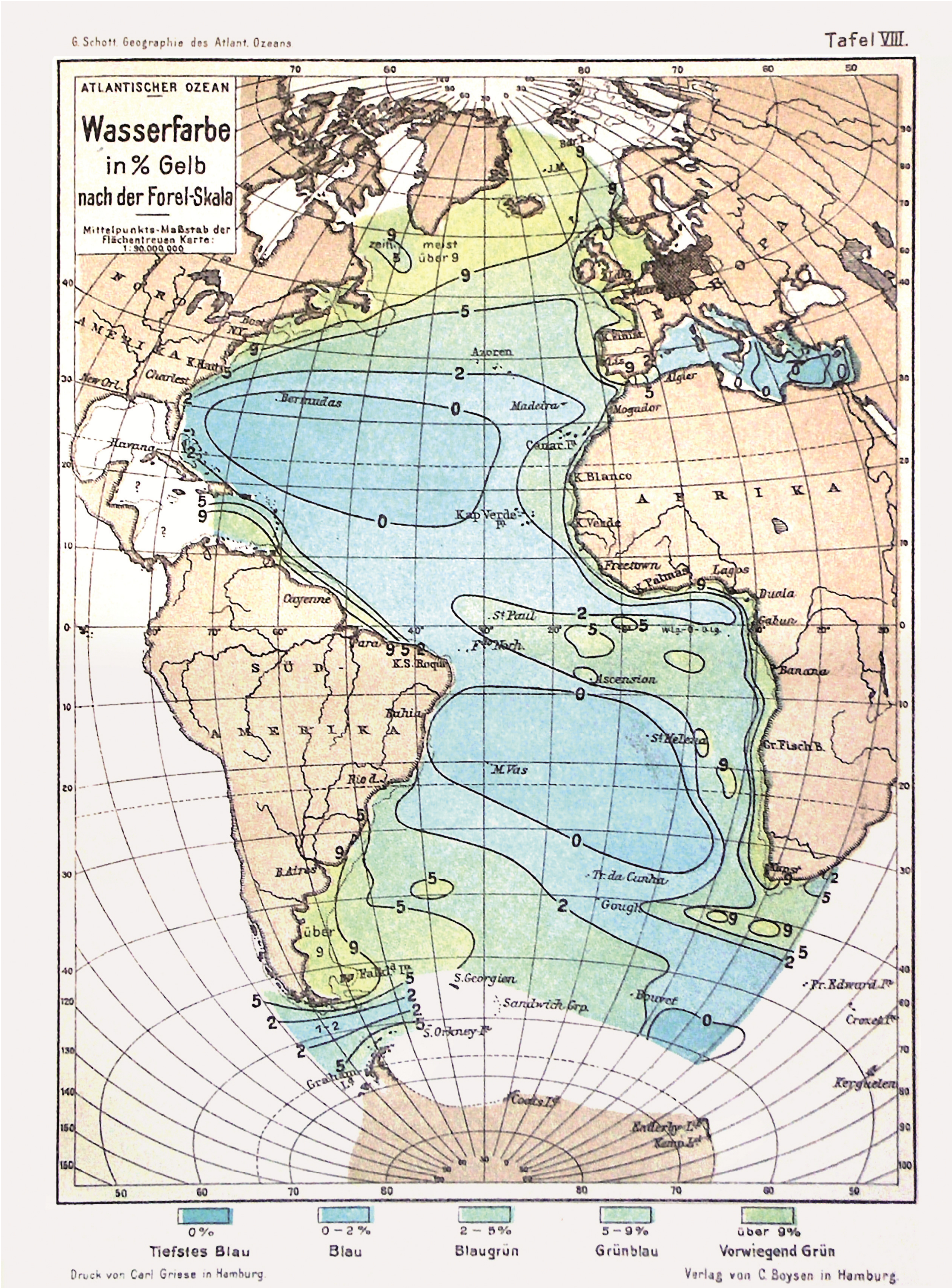

Figure 2.31 – Schott's 1912 sea colour map established with Forel scale measurements. The percentage given in the index is the percentage of yellow (solution) used to establish a tube colour. 0% = *FU*-scale 1, 9% = *FU*-scale 4.

In his publication of 1898, Von Liburnau mentions the International colour scale (Radde, 1898) to determine the colour of natural waters proposed by Otto Radde (1869-1941). Again, no field comparisons with this scale were found in literature. The scale was originally developed as a reference to painters, architects and decorators around 1877 (Thomsen & Thomsen, 1877, pp. 82-85). An original paper-scale consisting of forty-two coloured stripes, twenty centimetres long and eight centimetres wide, is still kept at the University of Munich.

At the end of the nineteenth century water supply companies developed instruments to identify the colour and clearness of drinking water. To present their skills in purifying water they exhibited their achievement to the public as shown in Figure 2.32.

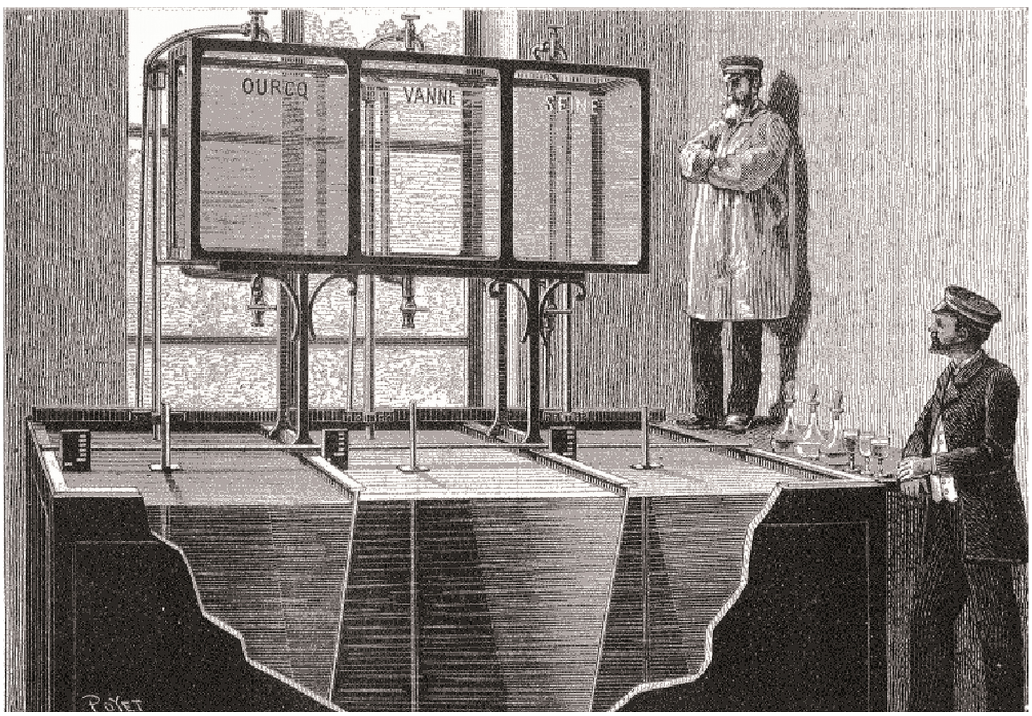

Figure 2.32 – At an exposition in Paris around 1886 the water company showed the optical results of purifying water of the Ourcq, Vanne and Seine river water. The aquariums were placed in front of a window, lit by the sun, to show the transparency. Source: La Nature, 1886.

The physicist and chemist William Crookes (1832-1919), the chemist William Odling (1829-1921) and forensic pathologist Charles Meymott Tidy (1843-1892) compared the colour of drinking water for the London Water supply by means of two horizontally placed tubes in front of a uniformly lighted window (Crooks *et al.*, 1881, p. 174). One tube contained the water sample under investigation; the other tube contained distilled water with at the end a glass wedge with different coloured liquids (potassium bi-chromate and copper sulphate). One changes the position of the wedge until equal colouring is achieved.

Frederick S. Hollis of the Metropolitan Water Works in Boston proposed another colorimeter in 1898. Two tubes, shown in Figure 2.33, were placed vertically. One contained a water sample and the other a standard solution of which the level could be varied (Hollis, 1898, pp. 94-118). By looking through an eyepiece, with a magnifying lens, towards two totally reflecting prisms on top of the tubes, a colour comparison could be made of the height of the standard solution in millimetres. Platinum standard solutions were made of a mixture of potassium platonic chloride and cobalt chloride with hydrochloric acid.

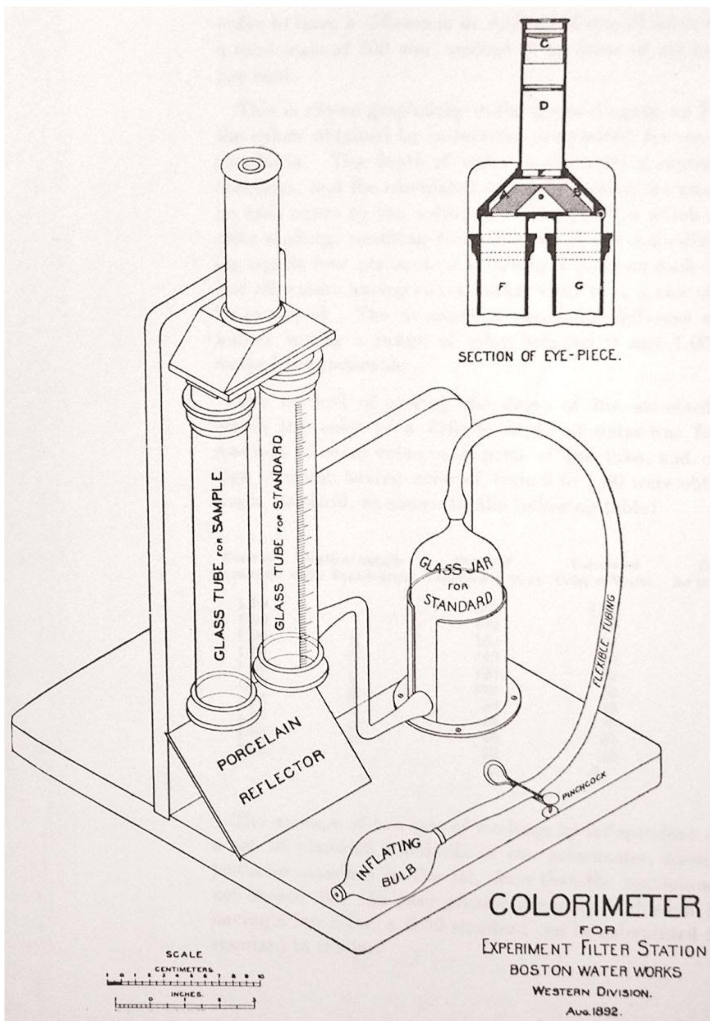

Figure 2.33 – A draft of the colorimeter as described by Hollis and devised in 1892 by Mr. W.E. Foss for use at the Experimental Filter Station of the Boston Water Works.

THE 20TH CENTURY

According to an article published at the beginning of the twentieth century (Strutt, 1910, p. 541) Rayleigh stated that the proper colour of water cannot be seen unless the sunlight traverses a sufficient depth before, on its way back, it reaches the observer, which occurs when looking into the ocean; a true statement. But Rayleigh continues by saying that in case the ocean's water is very clear there is nothing in it that could send light back to an observer and therefore, under those conditions its proper colour cannot be seen and the dark-blue colour of the deep see is simply 'the blue of the sky' by reflection (Strutt, 1910, p. 540). The latter statement is a wrong conclusion. It was criticized by Raman (see Figure 2.34) in his publication '*On the molecular scattering of light in water and the colour of the sea*' (Raman, 1922, p. 65).

Figure 2.34 – Chandrasekhara Venkata Raman around 1925. Source: Photograph by A. Bortzells Tryckeri, AIP Emilio Segre Visual Archives, W. F. Meggers Gallery of Nobel Laureates.

In the *Handbook of Oceanography* (Boguslawski, 1884), originally written by Boguslawski and reedited in 1907 by Otto Krümmel, who joined the Plankton Expedition of 1888, we find a chapter on the colour of water. In this chapter, Krümmel combines the results of several researchers in explaining the blue colour of water and comes to a remarkable conclusion (Krümmel, 1907, p. 275). Krümmel notes:

> Concerning the water particles, as Lord Rayleigh has stated more than once, in spite of the small size of the water-molecule, however of the same size as the wavelength of the more fragile side of the spectrum. The long red light-waves can also bring these molecules in vibration; on the contrary the blue shorter waves will be backscattered by

them, in such a way that the reflectance is inversely proportional to the fourth power of the wavelength.[11]

This conclusion however should be called empirical as the Einstein-Smoluchowski theory of fluctuations for water (fluctuations of density in terms of compressibility of a substance and the intensity of light scatter due to such a deviation of density) and Raman's theory to explain the origin of blue colour of pure water still had to be written.

CLOSURE: THE THEORY OF FLUCTUATIONS

Strangely enough it were scientists involved, instead of oceanographers or limnologists, in molecular-kinetic research who introduced the final ideas on the phenomenon responsible for the blue colour of pure or oligotrophic water. At the beginning of the twentieth century, Marian Ritter von Smolan Smoluchowski (1872-1917), Albert Einstein (1879-1955) and Willem Hendrik Keesom (1876-1956) were looking for an explanation of the opalescent behaviour of gasses, vapours and liquids close to their critical state (a specific condition of pressure and temperature under which the state of matter of gas, vapour or liquid cease to exist). Smoluchowski showed that the opalescent behaviour in a substance was based upon thermodynamic effects of statistical deviations of density (Smoluchowski, 1908, pp. 205-226). A little later Einstein came up with a connection between the intensity of light scattering caused by these density deviations (Einstein, 1910, pp. 1275-1298). This, later called theory of fluctuations, showed that the fraction α of the incident energy scattered in a substance per unit volume could be calculated according to

$$\alpha = \frac{\pi^2}{18} \cdot \frac{RT}{N} \cdot \frac{\beta}{\lambda^4} \cdot \left(\mu^2 - 1\right)^2 \left(\mu^2 + 2\right)^2 \qquad (2.2)$$

Here R is the gas constant, T is the absolute temperature, N is Avogadro's number per gram-molecule, β is the isothermal compressibility of the substance, μ is the refractive index and λ the wavelength of the incident light. This relationship, experimentally tested by Keesom using ethylene near its critical state, generated satisfactory results (Keesom, 1911, pp. 592-598).

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[11] *Was die Wasserteilchen selbst anlangt, so ist, wie Lord Rayleigh mehrfach dargelegt hat, die Grösse der Moleküle zwar sehr gering, aber doch von ähnlicher Grössenordnung, wie die Wellenlängen der stark brechbaren Seite des Spektrums. Die langen roten Lichtwellen bringen also diese Moleküle selbst in Schwingung, dagegen werden die blauen kurzen Wellen von ihnen zurückgeworfen, und zwar verhalten sich die Reflexionen umgekehrt proportional der vierten Potenz der Wellenlängen.*

John William Strutt's eldest son Robert John Strutt (4th Baron Rayleigh, 1875-1947) tested the validity of his father's theory on the scattering of gas molecules with good results (Strutt, 1919, pp. 151-176). Furthermore, if we compare the Einstein-Smoluchowski relation with Rayleigh's equation to calculate the extinction coefficient α (Strutt, 1919, p. 169) as given below we can see that these theories agreed substantially with each other:

$$\alpha = \frac{32\pi^3}{3} . \frac{(\mu - 1)^2}{n\lambda^4} \tag{2.3}$$

In 1922, Raman wrote an article on the molecular scattering of light in water and the colour of the sea. With the knowledge that the 3rd Baron Rayleigh developed the theory of molecular light scattering by gasses, which is a simple relationship between the refractivity of the medium and the energy laterally scattered by it, Raman was not convinced that the same assumption could be made in case of a liquid. He literally writes (Raman, 1922, p. 66):

> A gramme-molecule of steam occupies at 100 °C over 1600 times the volume which an equal mass of water would occupy, and it is clear, *prima facie*, that volume for volume, water would not scatter light 1600 times as strongly as pure steam, but only in a lesser degree. The question is, by how much less?

Then he tested the Einstein-Smoluchowski theory of fluctuations. Firstly, by reducing it almost to the Rayleigh's formula, he calculated that water, at thirty degrees Celsius, scattered light one hundred and fifty nine times more than dust-free air (Raman, 1922, p. 67). Accordingly, Raman illuminated different types of water to validate this theoretical relationship. From these experiments, it was proven that the calculated values agreed with the experimentally derived values. Therefore, he concluded that the intensity of molecular scattering in water could be calculated from this so-called theory of fluctuations. Furthermore, the extinction coefficient of light in water was calculated according to theory and agreed with experimentally obtained results in parts of the spectrum where absorption played a small role. Finally, Raman remarks:

> A sufficient deep layer of pure water exhibits by molecular scattering a deep blue colour more saturated than sky-light and of comparable intensity. The colour is primarily due to diffraction, the absorption only making it of a fuller hue. The theories hitherto advanced that the dark blue of the deep sea is reflected sky-light or that it is due to suspended matter are discussed and shown to be erroneous.

Raman's views were tested a year later by Kalpathi Ramakrishna Ramanathan (18931985). After experiments on scattering of lights in vapours and liquids, he concluded, similar to Raman, that the intensity of scattering in any case could be represented by the Einstein-Smoluchowski formula (Ramanathan, 1923, p. 160).

A remarkable publication on the colour of the sea by the Russian scientist Was Shoulejkin cannot be omitted at this point. After he had sent the account of part I of his investigation (Shoulejkin, 1923, pp. 85-100) to *The Physical Review* he became aware of the publication of Raman and Ramanathan. In the second part of Shoulejkin's *On the colour of the sea*, he disagreed with both investigators on their conclusion that the blue colour of the sea was primarily caused by molecular dispersion (Shoulejkin, 1924, pp. 825-826):

> Therefore, I do not make the mistake that Raman has made. A final remark from me is that, during my work, no special attention was given to make my expression more precise; as this is aimless, for the reason that in nature complete molecular scattering never will occur.

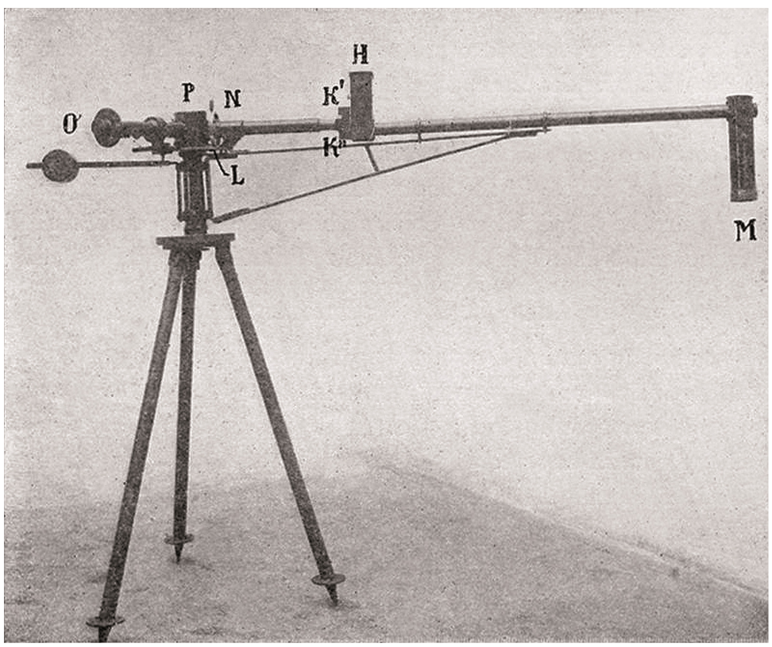

Figure 2.35 – Shoulejkin 'Sea Spectrophotometer'. To our knowledge, the first remote sensing device measuring the colour of seawater. The objective m stretched overboard to measure the upwelling radiance. The objective H measured the incoming sun and sky light. Light was passed towards slit K'' of a double collimator by prisms and lenses.

Shoulejkin meant that molecular scattering played a minor role in the seas he studied and that most of the scattering was caused by suspended matter. In a way he is right when looking purely at the amount of scattering caused by molecules or by minute particles, but the colour of pure ocean water is accounted for by the scattering of the water molecules and not, as suggested in Shoulejkin's paper, by the colour of the sky reflecting off the sea surface (Shoulejkin, 1924, p. 751). However, Shoulejkin did a lot of good experimental work on deriving diffusion and absorption coefficients of different types of water. He was probably the first to obtain remotely sensed reflectance spectra of the sea using his 'Sea Spectrophotometer' shown in Figure 2.35.

Shoulejkin's remark can be accepted now, as in most of the seawater, besides water molecules, there is also suspended matter. Exceptions are extremely oligotrophic waters far from the influence of land, encountered in the Antarctic by Gieskes (1987) and observed in the Arctic by Woods (see Wernand, 2010) these are waters that can be compared with the purest water in which only molecules are responsible for the blue colouring of the water. In conclusion, the sunlight penetrating into a column of water is altered spectrally through molecular absorption, which takes out the longer wavelengths. At the same time, the reflected light is altered by the water itself through the mechanism of molecular (back) scattering of the blue rays. The search for the solution to the mystery of the blue colour of clear natural waters ended with Raman's Nobel lecture on December 11th 1930, in which he put forward his ideas and theory (Raman, 1930).

DISCUSSION AND CONCLUSION

This essay has been written to offer a history of growing scientific insight into ocean and freshwater optics over the last 3 centuries. At the same time, it is a tribute to those early scientific explorers who addressed a phenomenon that to them was a mystery**.** For most of these men (to our knowledge, no women have ever written reports on their thoughts on water transparency or colour; why this is so is a subject outside the scope of the present article), an explanation of the blue shades of the open ocean was not a first priority, but no more than marginal science, approached only when there was time left. Therefore, the true search did not start before the first decade of the eighteenth century, with the observations of the Italian gentleman Louis Ferdinand Comte de Marsilli. However, the observation of differences in colour of seas, oceans and of lakes was used much earlier, namely by fishermen and sailors who knew about the association of regional shifts in sea and lake water colouration with fish school behaviour and occurrence, and in Arctic regions colour shifts were considered a signal of the nearness of icebergs. Explorers of the new and old continent also used this knowledge in the 16th and 17th century, including Hudson and Cook, for safer navigation of their ships across the ocean, and through coastal waters. This practical application, *i.e.* using a natural phenomenon with success, did not give an impetus to true ocean optics science or the development of theories as an urgent matter. Only at the end of the 19th century the explorer Alexander Von Humboldt started to use an artificial colour scale to categorize equatorial waters by means of the cyanometer of Horace-Bénédict de Saussure for scientific purposes. He made therewith the first step towards a theory of ocean optics.

Not much later, the Forel-Ule scale was introduced and this device has stood the test of time (Wernand, 2010). The long time series that now exists can be explored today, in a period of global change ascribed often to the warming effect of increasing concentrations of atmospheric carbon dioxide (CO_2), an important greenhouse gas. Hindcasting of CO_2 release learns that changes in water quality have taken place in response to ocean warming. The heat capacity of the ocean has increased over the last half century. Plankton ecosystems have reacted with changes in distribution and biodiversity (Beaugrand, 2008): a northward shift of warm-temperate species, a disappearance of cold-water species from temperate regions in the North Atlantic Ocean. It would be of great interest to analyse the record of the Forel-Ule scale over the time period of observations, which now spans 2 centuries nearly. Indeed, this record should be expected to change along with the shifts in ocean properties just mentioned.

The same holds true for Secchi disc observations that have been done on a routine basis by sailors and scientists alike over many decades by now. It can be questioned (Wernand, 2010) whether or not the Secchi disc has been named appropriately, although Captain Alessandro Cialdi and Father Angelo Secchi have introduced this white disc in the clearest way, as scientists who tried to fathom the background of the phenomenon they studied in a systematic manner. Years before these Italians performed their seawater transparency measurements in the Tyrrhenian Sea by means of a white disc, the Russian navigator Otto Von Kotzebue, the French commander Louis Isidore Duperrey, the Savoyard Xavier de Maistre and the Austrian naturalist Josef Roman Lorenz von Liburnau used quite similar devices for their observations of water clarity and transparency.

The search for an explanation of the mechanisms responsible for water colour and transparency really ended in 1922 with Raman’s publication *On the molecular scattering of light in water and the colour of the sea*. He argued convincingly that the colour blue, attributed both to the purest water and to the most oligotrophic oceans, is caused, besides molecular absorption, by molecular diffraction and scattering. In view of the complexity and interdisciplinary aspects of underwater optics, it may not come as a surprise that a scientifically underpinned explanation did not come from early oceanographers or limnologists but from scientists working in the field of molecular-kinetic research (Smoluchowski, Keesom, Einstein). In the period from the 16th to the 20th century not enough was known of the source of particulate and dissolved matter in water, both fresh and marine, and of the nature of such matter, mostly organic but on occasion inorganic: from sand and sediment, to calcium-covered micro-algae of the class Coccolithophorids that cause what was known for centuries as ‘milk sea’. In fact, the early mariners were not interested in what caused water colour, as long as they could make use of the phenomenon: to spot fish schools, to detect the approach of an iceberg. No theory was seen as interesting, because the explanation of nature was too time consuming in a world that was explored for economic purposes, nothing else.

From the last part of the 20^{th} century onward, ocean colour is recorded from space by satellites. The twentieth century has brought a variety of other advanced optical instruments too. Parameters measured by these instruments such as absorption, attenuation (Ohi *et al*., 2008), scattering (Lee & Lewis, 2003) and water-leaving radiance (Heuermann *et al*., 1999) are now understood, defined and refined continuously. The road 'to get the picture' has, however, been paved in the nineteenth century by William Scoresby junior, Humphry Davy, François Arago, John Tyndall, Johan Kayser, John William Strutt, Marian Smoluchowski, Albert Einstein and last but not least Chandrasekhara Raman.

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ARCHIVES

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CHAPTER 3 - ON THE HISTORY OF THE SECCHI DISC

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ABSTRACT

The first records on regular, tabulated, measurements of transparency of natural waters are those performed by the German naturalist Adelbert von Chamisso during the Russian "*Rurik*" Expedition 1815–1818 under the command of Otto von Kotzebue. A standardized method to determine the water clarity (transparency) was adopted at the end of the nineteenth century. This method (lowering a white painted disc into the water until it disappeared out of sight) was described by Pietro Angelo Secchi in Il Nuovo Cimento and was published in 1865. The Austrian scientist Josef Roman Lorenz von Liburnau, experimenting with submersible objects, like white discs, in the Gulf of Quarnero (Croatia) in the eighteen-fifties, well before Secchi started his investigations, questioned the naming of the white disc. However, the experiments performed by Secchi and Cialdi in 1864 on such an intensive scale were never performed before. At the beginning of the twentieth century, water transparency observations by means of a 30 cm white disc, was named the Secchi-disc method.

Keywords: Secchi disc, water transparency, history of marine optics

INTRODUCTION

From the time of Louis Ferdinand de Marsilli (1658–1730) until roughly the beginning of the nineteenth century, sea water was analysed both on its colour and its transparency by visual perception. For a judgement on its transparency sea water was put into a vase and described as misty, turbid or clear accordingly. Throughout history, ship's log, of many ocean explorations, regularly refer to the colour and transparency of seawater.

One of the oldest records describing the transparency of the ocean water (directly connected with its colour) was the one made near Novaya Zemlya by Captain John Wood Jr. (1620– 1704), member of the Royal Society and leader of an expedition in search of the Northeast Passage, before he was shipwrecked which dates back to 1676. Years later, a narrative of the expedition was published and written down in collaboration with the English naval commander Sir John Narborough (1637–1688). One of the observations [1], looking overboard into the sea and noticing the ocean floor, has been quoted frequently over the past centuries:

> *We sounded and had 80 Fathoms of Water green Oar, at which time we saw the Ground plain, being very smooth water. The Sea Water, about the Ice and the Land, is very salt, and much saltier than any I ever tasted, and a great deal heavier and I may say the clearest in the World, for I could see the ground very plain in 80 Fathoms water and I could see the shells at the bottom very plain.*

From his frigate, "*Speedwell*" Wood could see shells at the bottom of the sea at a depth of eighty fathoms or 140 m. Probably what he saw were Mya truncata shells (first described by taxonomist Carl Linnaeus (1707–1778) in 1758) [2] on a dark coloured bottom. It is disappointing that until now Wood's observation never has been confirmed by other oceanographers. Apart from the original paper of Narborough the observation of John Wood can be found in Histoire Générale Des Voyages by Jacques Philibert Rousselot de Surgy (1737–1791) [3] and in Histoire des Naufrages of 1789 [4].

If the surface of the sea is ruffled, or in state of agitation, it is hard to see the objects below by any instrument which is not immersed in the water. To overcome this problem, David Brewster [5] in 1813, invented a small floating telescope for viewing objects underwater (see Figure 3.1) that was recognized by the Academy of Sciences at Copenhagen for its great practical utility.

Captains and scientists, exploring the sea, noticed the sea's great ability of transmitting sun rays until great depths. To measure and quantify the transparency of the sea, several methods were described during the nineteenth century and the accounts of methods used by captains or scientists are sketched in a chronological manner in the following chapter.

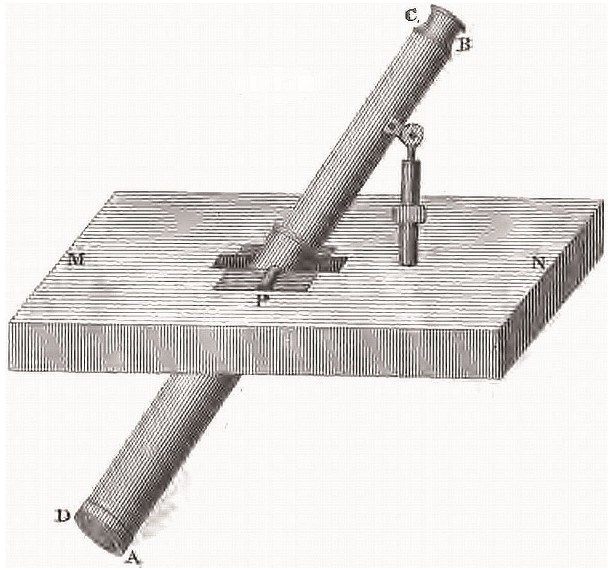

Figure 3.1 - Brewster's hydraulic tube telescope for viewing objects underwater (1813); when the apparatus is plunged into the sea, the floating parallelepiped m-n will keep the tube a-b-c-d in a vertical plane, and by moving it around the pivot p, it may be directed to any object under water or at the bottom (reproduced by the author from the original work).

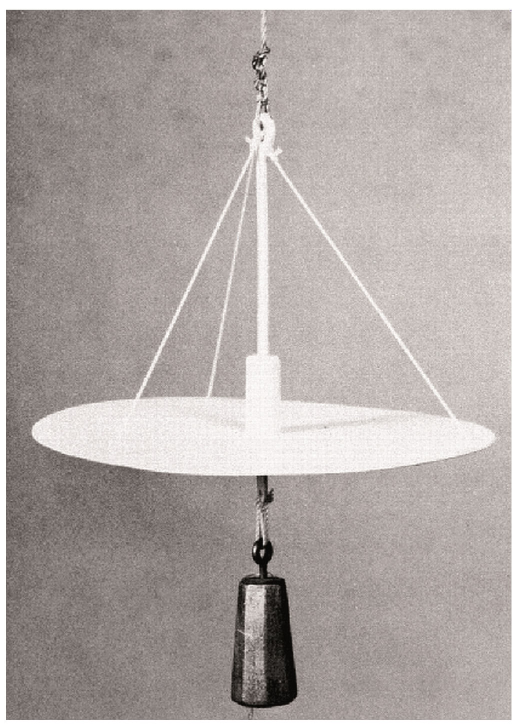

Figure 3.2 - Luksch polished white painted Secchi disc of 45 cm in diameter used onboard the "Pola" around 1890.

An illustrated example of the Secchi disc is presented in Figure 3.2. Luksch, on-board the steamer "*Pola*" crossing the eastern Mediterranean and Red Sea between 1890 and 1898 used this small 45 cm disk [6]. West of Beirut at $33^{0}47'$ N and $34^{0}8'$ E the disc could be seen at 60 m, in the northern Red Sea until 50 m and in the south only until 39 m.

HISTORICAL BACKGROUND

Table 3.1 - Observations of the sea surface and air temperature (in degrees Fahrenheit) and of the transparency of the water (in fathoms) measured with a white disc. The observations were collected during the first part of Kotzebue's voyage of discovery during the Atlantic and Pacific crossing.

TEMPERATURE OF THE SEA WATER AT DIFFERENT DEPTHS.

In the Years 1815, 1816, 1817, and 1818.

Days.	Temperature of the Sea Water: on the Surface.	Temperature of the Sea Water: below the Surface.	Depth in Fathoms.	Temperature of the Air.	The Ship's Latitude.	The Ship's Longitude.	Transparency of the Water in Fathoms.	Observations.
1815.					°	°		
15. October	+ 68.5	+ 55.7	100	+ 71.1	39 27 N	12 57 W.	10	In the Atlantic Ocean.
16. —	+ 69.1	55.0	138	72.5	39 4	13 8	10	
—	—	56.0	96	—	—	—	—	
25. —	74.3	56.3	196	74.3	30 12	15 14	11	
1816.								
8. January	54.9	38.8	196	57.6	44 47 S.	57 31	8	Cape Horn.
7. April morn.	78.5	68.5	125	79.2	18 17	124 56	13	In the South Sea.
—	—	57.5	175	—	—	—	—	
At noon.	79.6	68.0	125	80.0	—	—	—	
—	—	54.0	200	—	—	—	—	
13. April	80.0	79.0	10	79.8	15 26	133 42	13	
—	—	79.0	20	—	—	—	—	
—	—	78.8	50	—	—	—	—	
—	—	72.0	100	—	—	—	—	
—	—	56.0	200	—	—	—	—	
12. May	82.5	55.0	300	83.0	1 17 N.	177 5	14	At the Equator.
1. June	74.0	62.0	100	75.0	29 24	199 26	10	
—	—	52.5	300	—	—	—	—	

E E 2

APPENDIX. 419

It was already under command of the Russian navigator Otto von Kotzebue (1787–1846) on his first exploration trip (1815– 1818) in the Bering Sea and looking for a north-eastern passage that transparency measurements were mentioned. On board the *Rurik*, it was the accompanying German writer and naturalist Adelbert von Chamisso (1781–1838) who used a whitened surface attached to the sounding lead to measure the water transparency [7]:

> The transparency of the sea water would be easiest measured by letting down a flat surface, fastened to the plumb line, painted white, with stripes, or letters of black, or other colour, on it. For want of this, a white earthen plate, or a board covered with

white stuff, might be used. The depth at which the board became invisible or the marks upon it undistinguishable in different waters, would show their relative transparency.

Some of the observations of Adelbert von Chamisso are depicted in Table 3.1 [8]. In the North Pacific, he experienced that a dinner plate could be seen until a depth of 27 fathoms (49 m) [9]:

I observed to-day the transparency of the water with a white plate, and found that it was visible at a depth of twenty-seven fathoms: the previous observations of this kind had been made with a piece of red cloth.

dissemblables. A Offak, dans l'île Waigiou, par un temps calme et *couvert*, le 13 septembre, le disque disparut quand il fut descendu de 18 mètres (55 pieds). Le lendemain 14, le ciel étant *serein*, on ne cessa de voir le même disque qu'à la profondeur de 23 mètres (70 pieds).

Figure 3.3 - Louis Isidore Duperrey (1786-1865). Text as noted, by the commander himself, in a chapter on marine observations published in Annales de chimie et physique (1825).

During a French voyage around the world (1822–1825) under the command of Louis Isidore Duperrey (1786–1865) on the corvette *La Coquille*, a white painted plank, with a diameter of 2 feet and an attached weight, was lowered into the water to measure its transparency [10], [11]. The depths at which the disc disappeared were between 9 m, close to Ascension Island, South Atlantic Ocean and 23 m near Offak, Island of Waigiou, Indonesia (see the French note in Figure 3.3).

Around 1832, Xavier de Maistre constructed a square iron plate of around 35 cm^2, painted white, not to establish the visibility depth but to establish the colour of the sea [12], [13]:

I prepared a square sheet of tinned iron, fourteen inches long, painted it white on one side, suspended it horizontally to a cord, and sunk it in a deep place, where the water under the boat, was blue without any mixture of green, watching the effect under the shade of an umbrella which was held over my head. At the depth of twenty five feet, it acquired a very sensible green tinge, and this color became more and more intense to the depth of forty feet when it was of a beautiful green, inclining to yellow; at sixty feet the color was the same, but of a darker shade, and the square Figure of the plate was no longer distinguishable; until at eighty feet, there was apparent only an uncertain glimmering of green which soon disappeared.

For the determination of the transparency, all kinds of equipment such as plates, tins, kitchen-gear, painted thermometers or copper balls (“diaphanometer”, see [14]) were submerged into the water and lowered until they disappeared. Kemper around 1834 [15] used a white towel to measure the clearness of the water (see Figure 3.4).

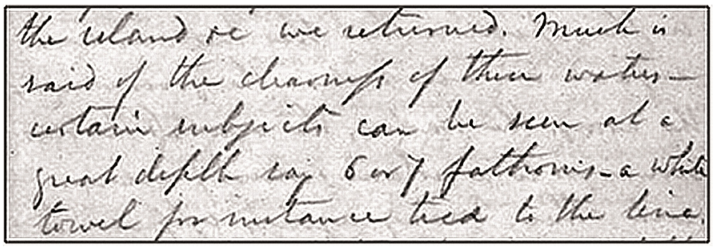
the island &c we returned. Much is said of the clearness of these waters — certain subjects can be seen at a great depth say 6 or 7 fathoms – a white towel for instance tied to the line

Figure 3.4 - Notes in Jackson Kemper’s diary (1834) during his visit to Green Bay showed a white towel used to determine the transparency of water. Transcription: Much is said of the clearness of these waters -certain subjects can be seen at a great depth say six or seven fathoms -a white towel for instance tied to the line (Reproduced from the archives of the Wisconsin Historical Society, USA).

The variety of objects used to measure transparency is also illustrated by the remarks of some captains. U.S. Navy Lt. Charles Wilkes (1798–1877) joining an US-squadron on its trip around the world (The Wilkes Expedition between 1838 and 1842) performed water transparency measurements like Navy Captain James Glynn (1800–1871) some years later [16], both using a simple white painted iron pot. During Wilkes trip from Funchal (Madeira) via Porto Praya (Cape Verde Islands) to Rio de Janeiro he observed “pot visibilities” (see Table 3.2) between 2 1/2 fathoms and 20 fathoms (4 1/2 m to 36 m) [17]:

> First we tried an iron pot, painted white, next we tried a sphere of hoops, covered with white cotton cloth. Then we tried a mere hope, covered with a canvas. At last we took a common white dinner plate. It was good enough.

Captain Auguste Bérard also used a porcelain dinner plate, mounted in a fish net, during the French Arago Expedition in 1845. Passing the South Pacific Wallis Island on July 16 he measured a “dinner plate” disappearance depth of 40 m [18].

Under command of Samuel Phillips Lee (1812–1897) the transparency of the sea was measured from the U.S. Surveying Brig *Dolphin* by means of lowering white painted foot square blocks [19].

Table 3.2 - Part of a meteorological table filled with data collected during the U.S. Exploring Expedition during the years 1838, 1839, 1840, 1841, 1842 under the command of Charles Wilkes (see under remarks on "pot visibility").

28 METEOROLOGICAL OBSERVATIONS.

U. S. SHIP VINCENNES.

FROM PORTO PRAYA TO RIO DE JANEIRO.

1838.	Lat. North.	Long. West.	Thermometers. Air.	Water.	Mast-head.	Barom.	Hygrom	Wind. Direc.	Force.	Clouds.	Weather.	Remarks.
Oct. 13.												
1 A. M.			79°	83°				S.W.byS.	1	Nimbi.	c. u.	
2 "			80	83								
3 "			78	83	78°	30·100					r.	Rain ·5 in.
4 "			77	82				Calm.	0		c.	
5 "			79	83				Var.	1	Clear.	b. m.	
6 "			79	83								
7 "			82	83				Calm.	0			Steering S. W.
8 "			82	83								
9 "			83	83		30·120	84° 68°					
10 "			83	83						Nimbi.	c.	
11 "			84	84				N^d.	1			Current S. E. by E., ½
12 "	9° 21′	24° 11′	83	84								knot per hour; pot
1 P. M.			83	85							c. p.	visible at 20 fathoms.
2 "			81	85								
3 "			83	85	86°	30·020	84° 70°			Clear.	b. c.	
4 "			82	85								
5 "			84	85				N. N. E.				Current S. E. by S., ⅜
6 "			81	85						Nimbi.	c.	knot per hour; pot
7 "			80	84								visible at 15 fathoms.
8 "			80	83					2		c. u.	

As mentioned before, all kinds of attributes were used to establish the clarity of natural water. From a complete different field of science came Michael Faraday (1791–1867) who, in 1855, crossed the Thames River on a steamboat. He had subsequently done good service by calling public attention to what he then observed. Literally he stated [20], [21]:

> The appearance and the smell of the water forced themselves at once on my attention. The whole of the river was an opaque pale brown fluid. In order to test the degree of opacity, I tore up some white cards into pieces, moistened them so as to make them sink easily below the surface.

During his 1858 to 1860 investigations in the Gulf of Quarnero (Croatia), Josef Roman Lorenz, later known as Josef Roman Lorenz Ritter von Liburnau, measured the transparency of the sea by lowering a "batho-"thermometer[12] [22] with a white painted lid (see Figure 3.5) [23]. During later investigations, for instance in the Halst¨attersee (Lake in Austria), he used a white painted tin disc of 30 cm diameter [24]. The naming of the Secchi-disc was especially questioned by Josef Roman Lorenz von Liburnau at the end of the era who himself called the method "the disc system". Literally Lorenz writes in a chapter on limnology [24]:

> As substantially different methods are not commonly conceivable one always falls back to one and the same method to establish the boundaries of the visibility under water, I used it in 1858–1860, seven years before Secchi, during my investigations in the Quarnero, without considering it as a memorable invention. However, the procedure became commonly known as the 'Secchi System'; I call it 'Disc-System'.[13]

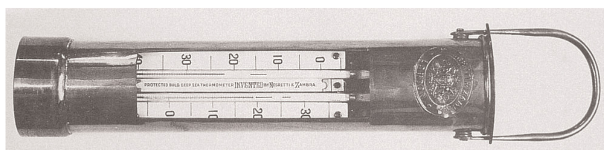

Figure 3.5 - The so-called batho-thermometer with a white painted lid (right). The instrument was used in vertical position in the Adriatic to establish the sea's visibility, next to the temperature.

In all mentioned publications thus far, including the one of Lorenz, it was never investigated nor explained why discs were used of an approximate 30 cm to 35 cm (1 foot). Perhaps the porcelain dinner plates used on several occasions were close to this diameter.

---

[12] *Das Instrument ist bei den Untersuchungen des Verfassers im Quarnerischen Golfe zur Anwendung gekommen, wo es sich um Tiefen von nicht mehr als 60 Faden handelte, also m¨oglichste Einfachheit und leichteste Handhabung verlangt wurden. Translation: During the author's research in the Gulf of Quarnero, the instrument has been used, at depth not over sixty Fathoms, for its simplicity and the ease of handling.*

[13] *Da eine wesentlich andere Methode nicht wohl denkbar ist und auf die selbejeder verfallen muss, der sich über die Grenzen der Sichtbarkeit unter Wasser informieren will, habe ich dieselbe als selbverständlich schon 1858–1860, sieben Jahre vor Secchi bei meinen Untersuchungen im Quarnero angewendet, ohne darin eine nennenswerte Erfindung zu erblicken. Es ist nun üblich geworden, dieses Verfahren System Secchi zu nennen; ich nenne es das Scheiben System.*

THE WHITE DISC AS STANDARD

Two years after Lorenz's 1863 publication on physical properties of the Quarner Gulf, including his transparency observations, an article on the same topic appeared in a weekly magazine of the French Academy of Science. Alessandro Cialdi and Angelo Secchi (see Figure 3.6) performed transparency measurements in the Tyrrhenean Sea in front of Civitavecchia near Rome. In a barely three pages long article, observations onboard the papal corvette "Immacolata Concezione" and methods to establish the water transparency were described [25] with a brief description of the size, material and colour of the employed discs.

As lots of scientists and captains dealt with the transparency phenomenon of the sea far before Secchi and looking at the published material before and around the time of Cialdi and Secchi, we can still not make it plausible why the method at the end of the nineteenth century became known as the Secchi disc method.

Figure 3.6 - Padre Pietro Angelo Secchi (1818-1878)

However, looking at forgotten chapters published in the Italian scientific Journal Il Nuovo Cimento in 1865 [26] and in Cialdi's book Sul Ondoso del Mare [27] of 1866, it definitely clarified the naming of the method. In the two identical thirty-two paged chapters all aspects of transparency disc measurements are described. The colour of the disc, its diameter and the height of the sun are described in relation to its disappearance depth. Furthermore the positions, such as the bow of the ship, from which measurements were performed, were taken into account. In Table 3.3 an example of the height of the sun and the disappearance depths per disc diameter (grande = large, piccolo = small) are shown. At this point it goes too far to mention all of Secchi's results. But by reading Secchi's original work it became clear why the method finally becomes known as the Secchi-disc method. (Requests for a copy of Secchi's publication in the scientific Journal Il Nuovo Cimento can be made to marcel.wernand@nioz.nl).

ALTEZZA DI SOLE		PROFONDITA' DI VISIBILITA'	
		disco grande	disco piccolo
25°.43'	....	24m.5	....
....	30°. 4'	....	22m.7
45. 24	....	33. 9	....
....	41. 53	....	27. 3
59. 52	....	36. 7	....
....	59. 39	....	32. 2

Table 3.3 - In an experiment on 21 April 1865, Secchi tabulated the results of the disappearance depths of a small and a large disc used under different sun heights.

POSTSCRIPT

In 1984 five observers, sailing in the eastern Mediterranean, viewed a marine standard, 40 cm, white Secchi disc through a 20 cm hole in the "hero platform" (the bucket in which scientists stand while deploying instruments over the side of a research vessel) and determined a depth of 53 m [28]. However, two years later this record was broken by Gieskes and three other observers [29] in the Antarctic and the Secchi depth was determined at a depth of 79.5 m. Until the time of writing a world record with French oceanographers following with a Secchi depth of 74 m observed near Easter Island [30]. A world record Secchi depth has been claimed but we have to bear in mind the observation mentioned at the beginning of this contribution, which is still a robust water visibility record that stands for over 3 centuries: a bottom seen at 146 m depth by Captain John Wood near Nova Zembla in June 1676. Theoretically, in the purest natural waters, according to calculations of René Dirks [31] the maximum Secchi-disc visibility is between 150 m and 170 m.

The late twentieth century has brought us a variety of advanced optical instruments to determine the transparency of sea water electronically. However, the author recommends a reintroduction of the Secchi disc to expand the historical Secchi depth database to facilitate climate change research. One option is to mount a Secchi disc on an instrumental-or CTD frame. Historic Secchi depth data can be retrieved from oceanographic and meteorological databases archived by the United States National Oceanographic Data Centre (NOAANODC). The NODC global oceanographic dataset contains over 400000 Secchi depth observations and belongs to the oldest instrumental datasets quantifying the world seas for over more than a century.

A detailed analysis of the physical and physiological aspects of the Secchi disc can be found in Preisendorfer [32], Graham [33] and Tyler [34] and W. Hou *et al*. [35]. The basic part of this contribution originates from a paper presented at Ocean Optics 2008 by Wernand which was extended in various ways including the addition of historic illustrations.

ACKNOWLEDGEMENTS

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CHAPTER 4 - SPECTRAL ANALYSIS OF THE FOREL-ULE OCEAN COLOUR COMPARATOR SCALE

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ABSTRACT

François Alphonse Forel (1890) and Willi Ule (1892) composed a colour comparator scale, with tints varying from indigo-blue to cola brown, to quantify the colour of natural waters, like seas, lakes and rivers. For each measurement, the observer compares the colour of the water above a submersed white disc (Secchi disc) with a hand-held scale of pre-defined colours. The scale can be well reproduced from a simple recipe for twenty-one coloured chemical solutions and because the ease of its use, the Forel-Ule (*FU*) scale has been applied globally and intensively by oceanographers and limnologists from the year 1890. Indeed, the archived *FU* data belong to the oldest oceanographic data sets and do contain information on the changes in geo-bio-physical properties of natural waters during the last century. In this article, we describe the optical properties of the *FU* scale and its ability to cover the colours of natural waters, as observed by the human eye. The recipe of the scale and its reproduction is described. The spectral transmission of the tubes and their respective chromaticity coordinates are presented. The *FU* scale, in all its simplicity, is found to be an adequate ocean colour comparator scale. The scale is well characterized, stable and observations are reproducible. Thus, the large historic data sets of *FU* measurements are coherent and well calibrated. Moreover, the scale can be coupled to contemporary multi-spectral observations with hand-held and satellite-based spectrometers. A reintroduction of the *FU* scale is recommended to expand the historical database and to facilitate a tie-in with present satellite ocean colour observations by transforming MERIS normalized multi-band reflectance image into a *FU* indexed image.

Keywords: Forel-Ule scale, reflectance, transmission, ocean colour, chromaticity

INTRODUCTION

Colour classification of natural waters started at the end of the 19th century with the introduction of the Forel-Ule scale (*FU*-scale). In 1890 François Alphonse Forel proposed his colour standard, a type of a combination of a cyanometer and xanthometer [1], to classify the blue to green waters [2]. A paper version of this scale is shown in Figure 4.1. Initially, the tube colours were given as a percentage of the Yellow agent (Potassium-chromate) added to the basic Blue (Copper sulphate) solution (mark the indicated percentage below the coloured bars of Figure 4.1). In 1892 Willi Ule [3] complemented the scale by adding the blue-green to brown colours. The combined scale (Forel's 1 to 11 and Ule's 12 to 21) became known as the Forel-Ule scale.

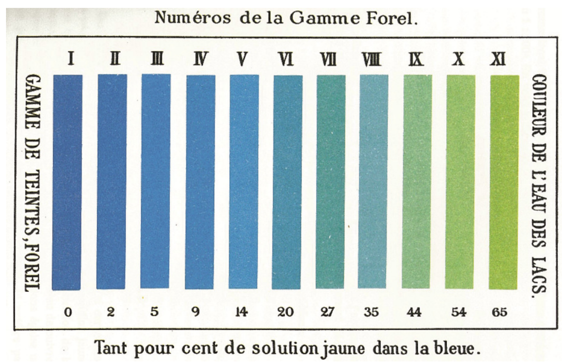

Figure 4.1 - The tints of the scale as printed in Forel's Volume II of his, three volumes covering, limnology monograph 'Le Léman' published in 1895 [6].

Table 4.1 - The dominating transmission wavelength for the *FU* scale numbers 0% Yello w (*FU*1) to 20% Yellow (*FU*6) as measured by Krümmel in 1893 [7]. At the time Forel's part of the scale was expressed in percentages of Yellow solution added to the basic Blue solution. Translation: 1) After comparing it with a small spectroscope it matched at first approximation with: Translation bottom: The scale grade 2 coincides more or less with the Fraunhofer line F, grade 20 with E.

1) Nach meinen Vergleichen an einem allerdings nur kleinen Spektroskop würden in erster Annäherung entsprechen:

Forels Skala =	0	2	5	9	14	20,
Wellenlänge λ =	479	486	495	504	514	527 μμ.

Die Skalenstufe 2 Forels fällt ungefähr mit der Frauenhofer'schen Linie *F*, Stufe 20 mit *E* zusammen.

The mathematician Von Drygalski and the German geographer Krümmel (located in Kiel) were amongst the first, besides Forel and Ule, to use the comparator scale at open sea during the Greenland Expedition of the Geographical Society between 1891-1893 (Die Grönland-Expedition der Gesellschaft für Erdkunde [4]) and the plankton expedition of 1889 (Ergebnisse der in dem

Atlantischen Ocean von Mitte Juli bis Anfang November 1889 ausgeführten Plankton-Expedition der Humboldt-Stiftung) [5]. Since then**,** the scale since has become the most commonly used and most simple comparator scale to determine the colour of seas, lakes and rivers.

Krümmel spectrally investigated the scale, which was offered to him by Forel, with "*a small spectroscope*" [7]. From Table 4.1 it can be seen that the recorded transmission wavelengths are typically 10 nm apart for the first 6 *FU* solutions, here expressed as the percentage of Yellow solution added to the basic Blue solution.

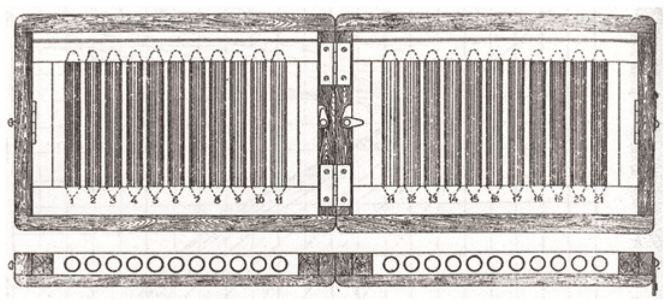

Figure 4.2 - The Forel-Ule scale in a protective wooden case, parts can be closed to protect it from sunlight, as proposed by Schokalsky [9] around 1930.

The old and the modern version of the *FU* scale are shown in Figure 4.2 and Figure 4.3. It comes in two parts, includes an extra tube containing distilled water and is kept in the dark, in a refrigerator, to avoid discolouration. In the field, the operation of the comparator scale is almost identical to the procedure suggested by Forel (see Figure 4.4).

Figure 4.3 - The modern *FU*-scale with an additional tube filled with distilled water (next to the brown *FU*=21).

The scale is held above the sea surface and the operator is looking to the water through one of the observation windows next to each tube. The best match between the colour of the water column and one of the tube-colours is established and is documented as an integer number representing the *FU* scale equivalent. To reduce the effect of reflection of direct sunlight at the tubes the operator stands in the shadow or under a black umbrella, as Forel himself advises. In order to enhance the signal strength of the water leaving the observation are taken from a submersed Secchi Disc [11] (at half the Secchi-depth [12]) near the shady side of the vessel. A detailed analysis of the physical and physiological aspects of the Secchi Disc can be found in Preisendorfer [13].

Figure 4.4 - A Forel-Ule observation is taken, at the shady side of the vessel, above a submersed Secchi disc, with the disc lowered to a depth of approximately half the Secchi disc depth. The reading of the scale should be done in the shadow.

In this paper we revisit the spectral properties of the full *FU* scale. First the reproduction of the scale and the spectral transmission between 380 and 780 nm (visible part) is described. Subsequently, the transmission curves are transformed to chromaticity coordinates and compared to field samples (section 3). The paper concludes with some arguments for continuation of these measurements and inter-calibration with modern ocean colour measurements.

METHODS

FOREL-ULE RECIPE AND SCALE DIMENSIONS

The recipe for reproducing the coloured liquids is described in Forel's monograph [14]. A mixture of three standard solutions is used to obtain the colour-palette of the scale. The standard solutions are made with distilled water, ammonia, copper-sulphate, potassium-chromate and cobalt-sulphate. The concentrations for the three standard solutions are given in Table 4.2 and the mixing ratios of the 21 *FU*-scale solutions are presented in Table 4.3 and Table 4.4. For the Forel part of the scale, *FU*1 to *FU*11, mixtures of the solutions Blue and Yellow (see Table 4.2) are used. The first *FU*-scale colour (*FU*1) consists for 100% of the chemical base solution Blue. For the Ule part of the scale, *FU*12 to *FU*21, the Green solution, a combination of the mixture 35% Blue and 65% Yellow (which gives a green colour) and the Brown solution are mixed to obtain the colour nuances between green and brown (see Table 4.2)

Table 4.2 - Chemical base solutions of the *FU*-scale.

Blue solution:	Amount
Copper-sulphate:	1 gram
Ammonia:	5 ml
Distilled water:	194 ml
Yellow solution:	
Potassium chromate:	1 gram
Distilled water:	199 ml
Brown solution:	
Cobalt-sulphate:	1 gram
Ammonia:	5 ml
Distilled water:	194 ml

Table 4.3 - The mixing proportions (volume %) of copper-sulphate and potassium chromate to derive the *FU*-scale colours blue to green, respectively *FU*1 to *FU*11.

Solution	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
% Blue	100	98	95	91	86	80	73	65	56	46	35
% Yellow	0	2	5	9	14	20	27	35	44	54	65

Table 4.4 - The mixing proportions of (volume %) copper-sulphate (35%) and potassium chromate (65%) plus cobalt sulphate to derive the *FU*-scale colours green to brown, respectively *FU*11 to *FU*21.

Solution	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
% Green = XI	100	98	95	91	86	80	73	65	56	46	35
% Brown	0	2	5	9	14	20	27	35	44	54	65

The solutions are filled into glass tubes with a diameter of 10 mm, sealed and fixed in a holder. This holder, shown in Figure 4.5, has a dimension of 30 x 12 cm, a white background (D, whiteopal Perspex or white painted wood) with, half way the tubes, a broad observation window to look through and has a handle on both sides (C). The glass tubes (A) are mounted between two strips B with holes.

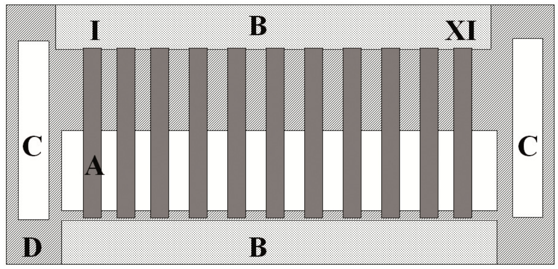

Figure 4.5 - The layout of half the *FU*-scale. A white Perspex housing (D), with the glass tubes locked between two bars (B). Half the surface behind the tube is closed by white Perspex. The scale can be held by means of the handles at both sides (C). The white rectangle, behind A, indicates the open area to look through to the submersed Secchi disc.

SPECTRAL TRANSMISSION OF THE SCALE

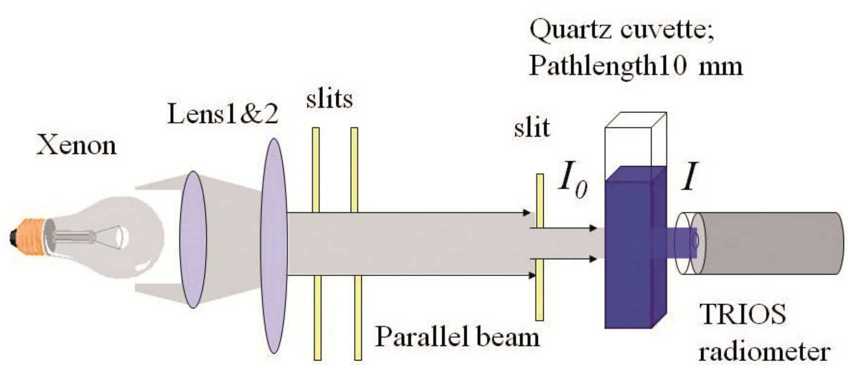

Figure 4.6 - The spectral transmissions of the Forel-Ule tube colours were determined using a Xenon lamp and a TriOS spectral radiometer.

A TriOS-Ramses spectral radiometer with a FOV of 7 degrees and a wavelength resolution of 4 nm was used for the determination of the spectral transmission [15]. With the setup of Figure 4.6 the radiant flux of wavelength λ, $I(\lambda)$, leaving a cuvette, containing one of the basic solutions or *FU*-mixtures, has been determined. $I(\lambda)$ was measured three times for each *FU*-mixture to establish the accuracy of the measurement. During the experiment the stability of the radiant flux leaving the light source $I_0(\lambda)$ was measured before, half way and after the mixture measurements. Per *FU*-mixture the transmission $T(\lambda)$ was calculated from the ratio of $I(\lambda)$ and $I_0(\lambda)$ according to

$$T_{FU}(\lambda) = \left(\frac{I(\lambda)}{I_0(\lambda)}\right) \tag{4.1}$$

For easy comparison, the transmission $T_{FU}(\lambda)$ was normalised to the maximum of T_{FU} between 380 and 780 nm (visible spectrum), where

$$T_{FU,MAX} = MAX\ (T_{FU}, \lambda \in [380, 780]) \tag{4.2}$$

and the normalised transmission T_{FUN} is defined as

$$T_{FUN}(\lambda) = \frac{T_{FU}(\lambda)}{T_{FU,MAX}} \tag{4.3}$$

Colorimetry

Colorimetry can be described as the science of measuring colour or as 'a system for colour measurements'. It was introduced in 1931 by the Commission Internationale de l'Eclairage (CIE) or also known in its early days as International Commission on Illumination (ICI). An explanation of colorimetry can be found in Curtis Mobley's book 'Light and water' [15]. He explains colorimetry as the branch of science, concerned with specifying numerically the colour of a sample of radiant power over the electromagnetic spectrum; *i.e.* a technique by which an unknown colour is evaluated in terms of standard colours. Apel explains the colour of the sea as the specification of the chromaticity (objective specification of the quality of a colour irrespective of its luminance) of the upward radiance and continues by saying; *"it is this intrinsic character that establishes the hue (colour) and the chroma, or strength of the colour of the sea"* [16].

Our eye can distinguish colours between dark blue (380 nm) to dark red (780 nm). A colour can be described as a mixture of three other colours or "tristimuli". The CIE 1931 tristimulus values, called *X, Y*, and Z, are parameters derived from the RGB colours [17]. Equal values of *X, Y*, and Z produce white. Tristimulus values can be calculated from the spectral reflectance, transmission or radiance scattered by an object, in this case seawater or the *FU*-tube colour, by the following equations;

$$X = \int S(\lambda)\bar{x}(\lambda)d\lambda \quad Y = \int S(\lambda)\bar{y}(\lambda)d\lambda \qquad Z = \int S(\lambda)\bar{z}(\lambda)d\lambda \tag{4.4}$$

Where *S(λ)* stands for the spectral properties of any coloured light source, for instance spectral reflection or spectral transmission, and $\bar{x}$, $\bar{y}$ and $\bar{z}$ are the 1931 Colour Matching Functions (CMF's). The chromaticity coordinates *x, y* and z can be calculated by an operation that normalizes out intensity from the ratio of each of the tristimulus values and the sum of the values according to:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z} \tag{4.5}$$

As *x*+*y*+*z* = 1, and therefore z = 1-x-y, the third coordinate offers no additional information and only two coordinates (by convention *x* and *y*) are used to represent the colour in a so-called chromaticity diagram as shown in Figure 4.7. The outer curved boundary is called the spectral or monochromatic locus with the wavelength in nanometres. The so-called white point W has the chromaticity coordinates x = y = z =1/3. If a line is drawn from the white point through a particular (*x, y*) chromaticity coordinate F, then the ratio of the distance between this point to the white point, distance (a), and the distance from the locus to the white point, distance (a+b), gives us the colour saturation or colour "purity" a/(a+b).

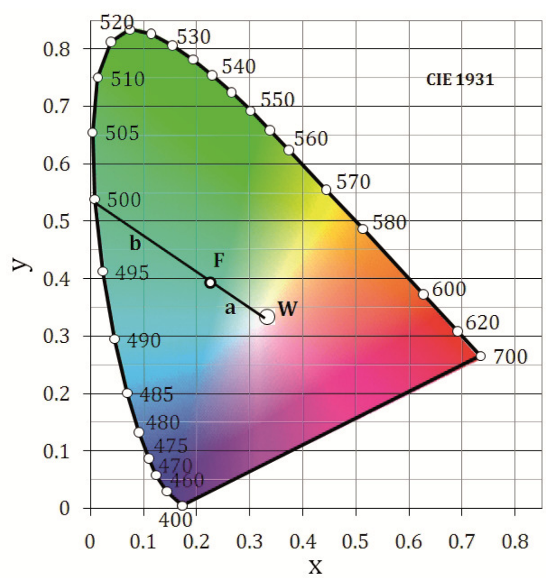

Figure 4.7 - The CIE1931 chromaticity diagram for monochromatic colours. The outer curved boundary is the spectral or monochromatic locus, with wavelengths in nm. The colour saturation is defined as (a/(a+b). F is a specific colour defined by its chromaticity coordinates (*x, y*).

As an example, imagine chalky water and clear water both with the same chlorophyll content. The colour of the water is determined by the amount of chlorophyll present in the water. In case of the chalky water, where the impact of the white calcite on its colour is zero, the (*x, y*) chromaticity coordinate will be closer to the white point then in case of clear water. Therefore the saturation of the colour will be less in case of chalky water but the actual colour of the water stays the same.

Due to a possible underestimation of the sensitivity for wavelengths below 460 nm Judd [18] derived a new set of CMF's in 1951 which were corrected again by Vos in 1978 [19] and are known as the Judd and Vos-modified CIE 2-degrees colour matching functions. However, an evaluation of the CIE CMFs by Shaw and Fairchild in 2002 [20], resulted in a firm confirmation of the original standard: *"Since 1931 the standard has withstood an onslaught of technical pressures and remained a useful international standard"*.

FIELD MEASUREMENTS

During several ship cruises on numerous occasions the remote sensing reflectance $R_{RS}(\lambda)$ [21] was determined by means of a set of TriOS spectrometers [22] with identical spectral response as the laboratory instrument. $R_{RS}(\lambda)$ is calculate from the ratio of the water leaving radiance $L_w(\lambda)$ and the surface incident irradiance or solar radiation $Es(\lambda)$ according to:

$$R_{RS}(\lambda) = \frac{L_W(\lambda)}{E_S(\lambda)} \tag{4.6}$$

Subsequently the R_{RS} was included as source term in Eq. 4.4 and the chromaticity coordinates of some different coloured natural water were calculated according to Eq. 4.5 and presented.

RESULTS

The spectral transmission of the Forel-Ule scale has been established from the freshly prepared mixtures as described in section 2. With the setup shown in Figure 4.6 the spectral transmission $T_{FUN}(\lambda)$ for each of the four base solutions (Figure 4.8) and for each of the 21 *FU* solutions was determined (Figure 4.9). After adding 2% basic Yellow potassium chromate solution to the basic Blue copper-sulphate (*FU*1) solution to create *FU*2, we clearly see a shift in the maximum of the $T_{FUN}(\lambda)$, from 420nm to 465nm. Figure 4.9 shows a smooth spectral shift of the peak wavelength, from the blue to the green (*FU*1 to *FU*11) in combination with an increase of the transmission above 600 nm. The spectral discrimination between the *FU*-scale colours is clearly visible.

The result of adding the Brown solution to the Green solution for *FU*12 to *FU*21, shows a clear decrease in the T_{FUN} at 510 nm. Note that maximum transmission is outside the visual range, resulting in a T_{FUN} of 1 at 780 nm. The spectrum shifts from green towards the red (brown). In summary the colour shift from *FU*1 to *FU*21 can be described as follows; the blue maximum diminishes and gets more pronounced in the green and subsequently the green diminishes and the spectrum of the Brown solutions slowly appears, resulting in a smooth transition from a Blue to a cola Brown solution.

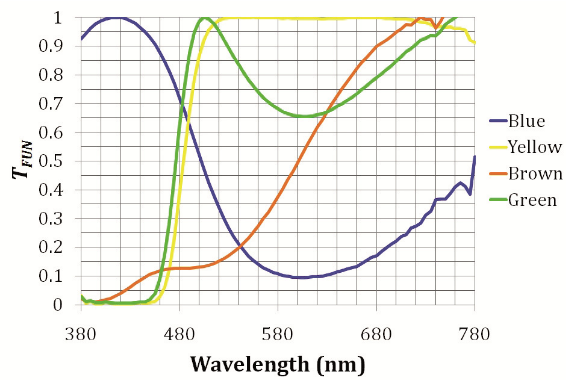

Figure 4.8 - The spectral transmission of the base solutions Blue, Yellow, Green and Brown of the *FU*-scale as established with a TriOS spectral radio-meter according to the setup of Figure 4.6. The spectra were normalised to the maximum transmission between 380 and 780 nm.

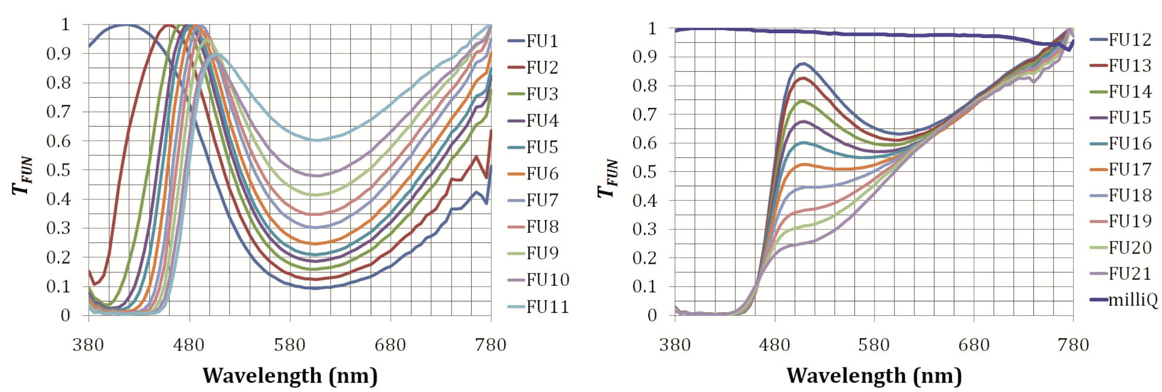

Figure 4.9 - The normalised transmission (T*FU*N) of the 21 *FU*-tubes plus an extra tube containing purified water (milliQ).

The chromaticity coordinates, derived from the spectral transmission measurements of both the basic solutions and the mixtures are given in Table 4.5. From three independent measurements we estimate the error in the *x, y* coordinate to be of order 0.001. Figure 4.10 shows the chromaticity coordinates of the Forel-Ule tube colours in a chromaticity diagram.

These colours cover a large range of water types that are found in nature: Oligotrophic waters appear indigo-blue and cover the Forel-Ule scale numbers 1 to 4, mainly due to the scattering and absorption of pure water. The colour of natural waters changes when more substances are present in the water, like algae, suspended (inorganic and organic) material and dissolved organic material. The colour range of mesotrophic water is approximately bluish green to greenish blue (Forel-Ule 5 to 9), of eutrophic water greenish blue to yellowish green (Forel-Ule 10 to 14) and hypereutrophic waters from yellowish green to greenish brown (Forel-Ule 15 to 18). The last scale numbers (Forel-Ule 19 to 21) brownish green to brown cover the colour of humic acid dominated waters.

Table 4.5 - The chromaticity coordinates, based on transmission measurements, of the *FU*-scale and the basic solutions. The white point refers to the coordinates equal to 1/3.

$T_{FUN}(\lambda)$	x	y	$T_{FUN}(\lambda)$	x	y
*FU*1	**0.189**	**0.161**	*FU*14	**0.404**	**0.482**
*FU*2	**0.196**	**0.194**	*FU*15	**0.410**	**0.478**
*FU*3	**0.213**	**0.255**	*FU*16	**0.418**	**0.472**
*FU*4	**0.229**	**0.301**	*FU*17	**0.427**	**0.466**
*FU*5	**0.242**	**0.331**	*FU*18	**0.440**	**0.458**
*FU*6	**0.263**	**0.373**	*FU*19	**0.453**	**0.448**
*FU*7	**0.290**	**0.415**	*FU*20	**0.462**	**0.440**
*FU*8	**0.311**	**0.439**	*FU*21	**0.473**	**0.429**
*FU*9	**0.337**	**0.463**	White	**0.333**	**0.333**
*FU*10	**0.363**	**0.480**	Blue	**0.189**	**0.161**
*FU*11	**0.388**	**0.490**	Yellow	**0.436**	**0.496**
*FU*12	**0.394**	**0.488**	Brown	**0.498**	**0.383**
*FU*13	**0.397**	**0.486**	Green	**0.386**	**0.489**

As an example, we compared the chromaticity coordinates of the Forel-Ule scale with chromaticity coordinates of five natural waters. With a set of TriOS spectrometers we performed at various cruises radiometric measurements for the determination of the remote sensing reflectance $R_{RS}(\lambda)$. Subsequently the R_{RS} was calculated according to Eq. 4.6 and was included as source term in Eq. 4.4. The chromaticity coordinates of five selected water types were calculated according to Eq. 4.5, presented in Table 4.6 and included in Figure 4.10.

Table 4.6 - An example of the chromaticity coordinates based upon spectral reflection measurements, of different types of natural waters.

$R_{RS}(\lambda)$	x	y
Atlantic	**0.170**	**0.150**
North Sea - open	**0.210**	**0.230**
North Sea -coastal	**0.305**	**0.400**
Wadden Sea	**0.380**	**0.430**
Puddle	**0.499**	**0.450**

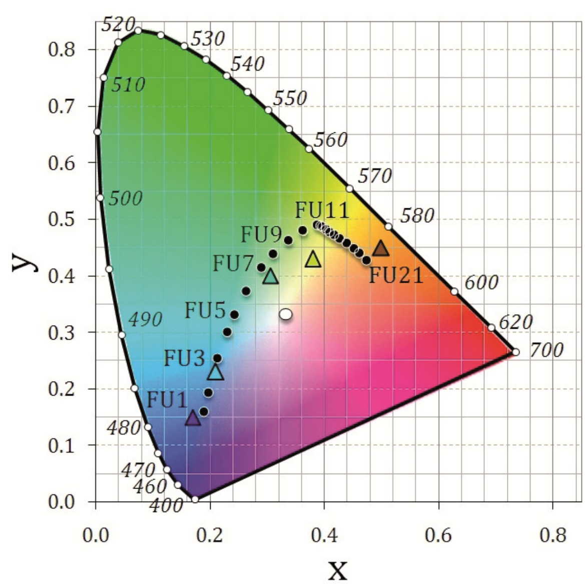

Figure 4.10 - The CIE1931 chromaticity coordinates, based upon transmission measurements, of the *FU*-scale colours 1 to 21 (black circles) including the white point (x=y=1/3, white circle). Coloured triangles represent the chromaticity coordinates of, from blue to brown, Atlantic, open North Sea, coastal North Sea, Wadden Sea and a puddle in the woods of the island Texel.

The coloured triangles represent the chromaticity coordinates of (from blue to brown) Atlantic Ocean, open North Sea, coastal North Sea, Wadden Sea and a puddle in the woods of the island Texel. By drawing a line from the white point through one of the triangles, representing the chromaticity coordinates of the different water types, we can derive the corresponding Forel-Ule number. The colour of the Atlantic Ocean can be compared with *FU*1, the colour of the open North Sea is close to *FU*3, the coastal North Sea *FU*7 and the Wadden Sea around *FU*15. The colour of a puddle in the woods of Texel can be classified as *FU* 21.

Measurements with the Forel-Ule scale have been part of a yearly returning oceanography course organised at the Royal Netherlands Institute for Sea Research. The reproducibility of the scale was tested by reading the scale at least by 5 different persons over the Wadden Sea. For this shallow tidal basin that receives water from the North Sea and various rivers, Forel-Ule colour varies between 13 and 17. The variation in the observation, in one of the five cases, was at most half a scale number. A similar experiment, during an expedition on the Atlantic Ocean (*FU* varying from 1 to 4), again testing the reproducibility of the scale amongst crew members, generated the same result.

CONCLUSIONS AND RECOMMENDATIONS

The introduction, in the late nineteen seventies, of satellite based radiometers like the Coastal Zone Colour Scanner (CZCS) in 1978 and the introduction of low cost spectral radiometers in the eighties have shifted the focus of ocean colour measurements away from the *FU*-scale. However, this scale, introduced in the late nineteenth century as a colour comparator to classify the colour of natural water, is the basis of one of the oldest oceanographic datasets that roughly covers the period 1890-2000. Hundreds of thousands of observations by the *FU*-scale have been collected globally, digitized and stored in the U.S. National Oceanographic Data Centre's World Ocean Database [23].

In this article we provide a reappraisal of the Forel-Ule scale by analysing the spectral transmission curves and corresponding chromaticity coordinates. Based on this analysis, it can be concluded that the *FU*-scale and its operational use make it a good colour comparator for assessment of the colour of natural waters. The scale has enough spectral discrimination and coverage to classify most of the planet's natural waters. The reconstruction of the scale is simple and is well characterized. In our (limited) tests we have found no marked dependence of the classification on the observer. Of course it remains to be seen if the limited number of scales (21) provides sufficient precision to capture all phenomena in natural waters. Nevertheless, the simplicity, elegancy and robustness to express the colour of water in one number create a simple possibility to compare the past and present status of oceans and inland waters.

We recommend a reintroduction of the Forel-Ule scale to expand the historical database and to facilitate a tie-in with present satellite ocean colour observations. One option is to mount a

Secchi disc on an instrumental- or CTD frame. Thus for each station both a Forel-Ule reading and a Secchi depth can be measured and archived together with the already collected historic data.

A link between historic *FU* observations and satellite observation can be achieved by tranforming MERIS (enough spectral bands) normalized multi-band reflectance image into a Forel-Ule indexed image.

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CHAPTER 5 - OCEAN COLOUR CHANGES IN THE NORTH PACIFIC SINCE 1930.

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ABSTRACT

In this paper we present an analysis of historical ocean colour data from the North Pacific Ocean. This colour is described by the Forel-Ule colour index, a sea colour comparator scale that is composed of 21 tube colours that is routinely measured since the year 1890. The main objective of this research is to characterise colour changes of the North Pacific Ocean at a timescale of decades. Next to the seasonal colour changes, due to the yearly cycle of biological activity, this time series between 1930 and 1999 might contain information on global changes in climate conditions. From seasonal independent analyses of the long-term variations it was found that the greenest values, with mean Forel-Ule scale ($\overline{FU}$) of 4.1 were reached during the period of 1950-1954, with a second high ($\overline{FU}$ = 3) in the period 1980-1984. The bluest ocean was encountered during the years 1990-1994. The data indicate that after 1955 a remarkable long bluing took place till 1980.

Keywords: Ocean colour, North Pacific, Forel-Ule scale, Global Change

INTRODUCTION

In 1992 the physical oceanographer Bruce Parker investigated the retrieval of historical oceanographic data and emphasized the importance of the so-called oceanographic ”data archaeology” [1]. He stated that ”a critical requirement for climate and global change research is the availability of global oceanographic data covering long time periods” [1]. The colour of the ocean surface waters is one of parameters that is described for more than 3 centuries [2] and one that is measured quantitatively since the year 1890 [3]. Only records on water temperature [4, 5, 6, 7], -salinity [8] and -visibility [9, 10] are collected over a longer time period.

Changes in water colour are caused by a change in the composition of the optically active water-quality parameters, like suspended particulate matter, pigments (mainly chlorophyll-a) in algae and dissolved organic matter. Therefore ocean colour measurements do contribute to understanding the ecology and biochemistry of the ocean [11]. Because large water masses play a critical role in the Earth’s climate, the colour of seawater is listed by WMO as an Essential Climate Variable [12]. For instance Dongyang *et al*. [13] found that abnormal weather, in this case snowstorms and low temperatures, influenced the ocean colour environment. Venrick *et al*. [14] found a significant increase in total chlorophyll-a, during the summer, over a 20 year time span in the central North Pacific Ocean and concluded in Nature (1987) that long-period fluctuations in atmospheric characteristics (decrease in sea surface temperature, increase in wind forcing in winter) changed the carrying capacity of the central Pacific Pelagic ecosystem.

Since the 1980s ocean colour data is collected on a massive scale, be means of sophisticated optical sensors, from ships, aircraft and satellites. However, the collection period of the newly gained data is limited and covers only the latest decennia, see e.g. Antoine *et al.* [15]. In this paper, by means of the result of oceanographic data archaeology, this period is extended backwards by approximately 50 years. The retrieved historical data were collected with the first ocean colour remote sensing device; the Forel-Ule scale [3].

Limited literature is available on the classification of seas by the analysis of Forel-Ule observations. A few geographical maps, based on interpolation of a limited set of Forel-Ule data, exist from before nineteen-hundred [16, 17, 18, 19]. Furthermore, the U.S. Navy Hydrographic Office published three atlases on marine geography, including Forel-Ule contours of the Sea of Japan, Korea and Indochina [20, 21, 22]. In her 1970 master thesis Margaret Ann Frederick presented the first extended atlas on Forel-Ule scale numbers for some of the world seas [23]. To create this atlas on the colours of the sea, Frederick had around 24,000 Forel-Ule observations, collected globally, to her disposal. Frederick analysed her data per Marsden square, but did not look for trends.

In this paper we present a trend analysis of 17,171 Forel-Ule observations made in the North Pacific Ocean between the years 1930 and 1999. These observations, extracted from the U.S. National Oceanographic Data Centre (NODC), belong to the oldest instrumental datasets that quantifies the Pacific Ocean. The analysis was focussed on data from the open North Pacific at a distance at least 500 km off the coast, in order to avoid direct effects of anthropogenic pressure in the coastal zones like enhanced loading of nutrients (euthrophication) or higher sediment loading by changes in land use.

First the Forel-Ule scale is briefly introduced and a summary is given of the data-selection procedure. Subsequently the statistical analysis is presented, providing insight in the ocean colour changes in the last century.

THE FOREL-ULE SCALE

The Forel-Ule (*FU*) scale, recently described by Wernand and van der Woerd [3], consists of 21 discrete colours (sealed glass tubes each containing a specific chemical solution) in the range indigo blue to coca-cola brown. This scale was introduced in the late nineties of the 19th century and covers adequately the colours of natural waters, ranging from the purest (oligothrophic) waters, via waters with higher biological activity (mesothrophic) to waters with high sediment load, high algae concentration or high dissolved organic matter loading. In Figure 5.1, a colour bar is shown representing the Forel-Ule colours.

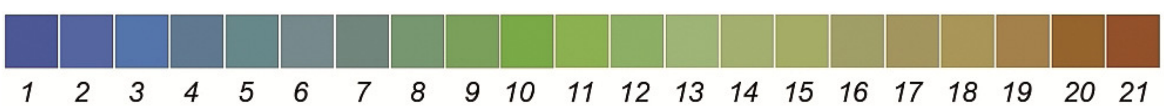

Figure 5.1 - The colour bar represents the colours of the Forel-Ule scale with belonging scale number.

In the field the tube colour of the scale is matched with the actual colour of the sea. The observer holds the scale above the sea surface with the sun at the back and compares the tube-colours to the colour of the water column over a submersed Secchi-disc located at half the Secchi-depth [24, 25]. In a previous study [3] it was shown that the *FU*-scale is a robust and rather objective method for classification of natural waters.

DATA SELECTION

FU- observations were retrieved from oceanographic and meteorological databases archived by the United States National Oceanographic Data Centre (NOAA-NODC). The NODC global oceanographic dataset, retrieved in 2007, contained 221,137 *FU*-observations. First the comma separated values were converted into Excel format and data with NODC codes higher than 21 were removed. The codes 31 to 37 are colours outside the Forel-Ule comparator range (see Table 5.1). Two new columns were added to flag the season and 5-year time interval. The seasons were selected according to a meteorological division, *i.e.* winter covers the months 12, 1 and 2, spring covers months 3, 4 and 5, summer covers months 6, 7 and 8 and autumn covers months 9, 10 and 11. The winter period starts with month 12 of the previous year. Because the size of the data collection was not uniform over the years, multiple years were binned to increase the statistical significance. In this analysis data are binned in 5-years intervals, starting with the years 1930 – 1934.

Table 5.1 - The NODC *FU*-codes explained.

NODC code	Observed colour
1 to 21	FOREL-ULE
31	GREEN
32	BLUE
33	GREY
34	RED
35	CHALKY
36	BROWN
37	LUMINESCENT

Data collected with a sea area flag of NP or PHS (Philippine Sea), based on the latitude and longitude conventions of the U.S. Geological Survey (USGS), were merged and are referred to as the North Pacific dataset. To avoid the influence of terrestrial run-offs on open ocean water a so-called mask was created to extract data, at a distance of 500 km off the coast, for statistical analysis. The mask was created using the GIS (Geographic Information System) software package from ESRI, ArcMap 9.3.

METHODS

The analysis is based on a univariate representation of quantitative data samples (in this case the Forel-Ule numbers) in a "box and whisker" diagram [26]. This is a simple and quite complete representation of the statistical properties of the dataset that is graphically displayed. The plot displays the position of the 1st quartile (Q1), median (Q2), arithmetic mean and 3rd quartile (Q3). In addition, limits are displayed in black (lower and upper limits are the ends of the "whiskers") beyond which values are considered anomalous. Consider a sample made up of n *FU* observations, denoted by ($FU_1, FU_2, ..., FU_n$). The arithmetic mean of this dataset $\overline{FU}$ is defined as [27]:

$$\overline{FU} = \frac{1}{n} . \sum_{i=1}^{n} FU_i \quad (5.1)$$

Outliers are defined as values that are more than 1.5 times outside the interquartile range. In Figure 5.2 an example of a box plot is shown. The arithmetic mean ($\overline{FU}$) is displayed by a red plus sign (+), and a black lines corresponds to the quartiles (Q_{1} $,_{2}$ $,_{3}$). The blue rhombuses (◊) correspond to the minimum and maximum values. Outliers, more than 1.5 times the interquartile range, *i.e.* values that are in the [$Q_1 - 1.5 * (Q_3 - Q_1)$; $Q_1 - 1.5 * (Q_3 - Q_1)$] or the [$Q_3 + 1.5 * (Q_3 - Q_1)$; $Q_3 + 3 * (Q_3 - Q_1)$] intervals, are represented by a hollow circle (o). Extreme outliers, more than 3 times the interquartile range are displayed by an asterisk (*).

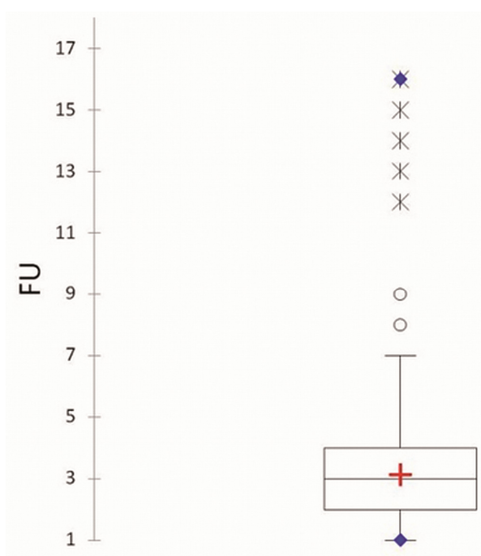

Figure 5.2 - An example of a box- or univariate plot.

Accordingly, from the North Pacific *FU*-data a graph is presented with the mean, upper and lower bound per season and per five-year interval to detect possible trends. Let $S(n\text{-}1)$ be the standard deviation from the set of n *FU* observations. From the standard error of the mean

$$SE_{\overline{FU}} = \sqrt{\frac{S(n-1)^2}{n}} \quad (5.2)$$

the lower bound on mean, corresponding to the lower bound of the 95% confidence interval of the mean, is defined by

$$L_{\overline{FU}} = \overline{FU} - SE_{\overline{FU}} * z \quad (5.3)$$

where z = 1.96 for a confidence interval of 95 %) [28]. The upper bound $U_{\overline{FU}}$on the mean, is calculated accordingly (sign changes to +).

RESULTS

A total number of 17171 *FU*- observations were selected over the period winter 1930 to autumn 1999. In Table 5.2 the number of observations for each season with belonging percentage of the total is given. This table demonstrates that the observations are well spread over the seasons.

Table 5.2 - The total number of *FU*-observations collected at a distance > 500km off coast during 1930 to 1999 in the North Pacific and the number of observations with a percentage of the total per season.

Total	Winte	W-%	Spring	SP-%	Summer	S-%	Autumn	A- %
1717	3481	20.3	3923	22.8	5371	31.3	4396	25.6

Figure 5.3 shows the *FU*-data distribution over the North Pacific. The shape of the applied data extraction mask, >500 km off coast, can be clearly seen East of Japan. The North Pacific is very well covered; with the exception of the Eastern part (135° to 145° E) and the North-Eastern part (above 30° N and East of 170° E). In Table 1 the $\overline{FU}$ for the North Pacific for each season is given, together with the lower (L) and upper (U) bound on mean with a 95% confidence.

From Table 5.3 we conclude that the North Pacific can be called a "blue ocean", with a mean Forel-Ule colour scale of 2. During the winter and autumn the ocean turns slightly bluer towards a $\overline{FU}$=1.8 (bluing of the ocean) and in summer the ocean's $\overline{FU}$ shifts upwards to 2.3 (greening of the ocean) by enhanced biological activity (presence of algae). A prominent influence on the results of the calculation of the overall $\overline{FU}$ is due to the numerous observations collected during 1985-1994.

Table 5.3 - The $\overline{FU}$ for the North Pacific with, the lower (L) and upper (U) bound on the mean (95% confidence) for all seasons and for each of the four seasons (w=winter, sp=spring, s=summer and a=autumn).

$\overline{FU}$	**2.0**	$Winter$	**1.8**	$Spring$	**2.0**	$Summer$	**2.3**	$Autumn$	**1.8**
$L_{\overline{FU}}$	2.0	$L_{\overline{FU-w}}$	1.8	$L_{\overline{FU-sp}}$	2.0	$L_{\overline{FU-s}}$	2.2	$L_{\overline{FU-a}}$	1.8
$U_{\overline{FU}}$	2.0	$U_{\overline{FU-w}}$	1.9	$U_{\overline{FU-sp}}$	2.0	$U_{\overline{FU-s}}$	2.3	$U_{\overline{FU-a}}$	1.8

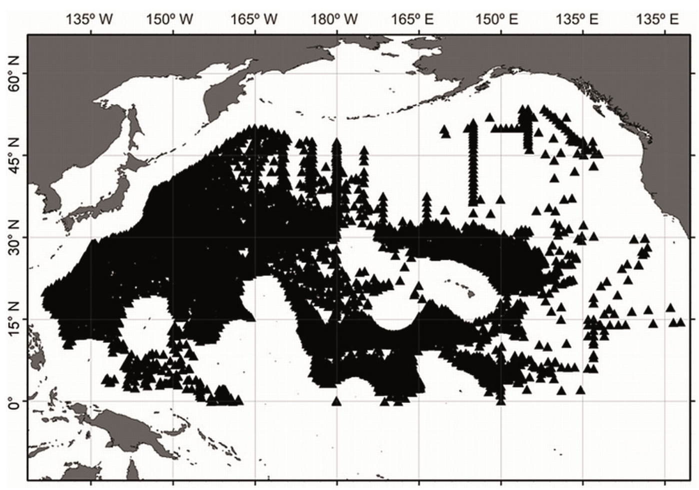

Figure 5.3 - All North Pacific *FU*-observations collected between 1930 and 1999 at a distance of over 500 km off coast.

A box plot of the *FU*-data grouped in 5-years bins is shown Figure 5.4 with respectively in red the variation of $\overline{FU}$ over time, the Q_1 and Q_3 values, outliers and in blue the minimum and maximum *FU*-values. The Figure shows two anomalies; an increase of the $\overline{FU}$ colour from 2 to 4 during 1930-34 to 1950-54 and a less pronounced increase of the $\overline{FU}$ from 2 to 3 between 1975 and 1985. In both cases the ocean is greening. During 1950-54 to 1975-79 and 1980-84 to1990-94 the ocean slowly turns blue again.

The greening of the ocean starts again after 1994. We have to bear in mind that data are not seasonally split at this point. During 1945-49 only two colour observations were made in total, therefore the period is omitted from the data analysis.

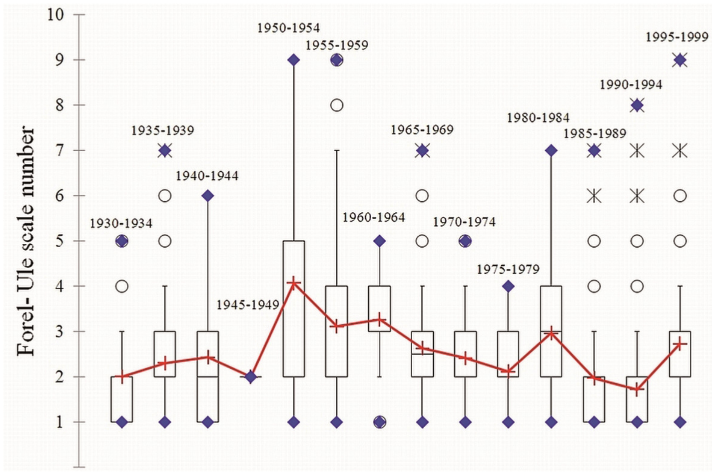

Figure 5.4 - A box plot of all *FU*-data collected in the North Pacific binned in 5-year intervals. The red line indicates the variation of the mean *FU*-number over time. The greening of oceanic water reaches a maximum between 1950 and 1954. After this period the water is bluing again to a $\overline{FU}$=2.1 in the 1975-1979 period. Hereafter follows an increase to a $\overline{FU}$=3 and during the 1990-94 decade the $\overline{FU}$ reaches its overall minimum value $\overline{FU}$=1.7. The ocean is at its bluest.

In order to investigate if this temporal behaviour is related to changes in a seasonal cycle of primary production data was split into seasons. In Figure 5.5 the black dots represent the $\overline{FU}$ per time-bin. The dotted lines indicate the lower and upper bound on the mean, respectively$L_{\overline{FU}}$, $U_{\overline{FU}}$.

The top graph shows the $\overline{FU}$ over all seasons. The graphs blow show data for each season per 5-years bins. For all seasons between 1930 and 1949 the North Pacific is dark blue with a $\overline{FU}$ of 2.2. During the next years, 1950-54 the water is greening to a $\overline{FU}$ of 4.1.

The next 25 year the ocean is bluing again slowly until the 1975-79 period. Hereafter, a period of greening (1989-84), a period of bluing (1985-94) and a last period of greening can be recognized (1995-99). Concerning "the all season" colour of the North Pacific it is the period 1990-94 that shows the bluest colour with a $\overline{FU}$ of 1.7.

As shown in Figure 5.5 the period 1950-54 concerning the North Pacific's colour can marked as a remarkable period as for winter, spring and autumn the highest $\overline{FU}$ values (4 to 5) are encountered. For the summer this period of highs occurs during 1950-1965 with a maximum $\overline{FU}$≈4 during 1955-59. All seasons more or less show the same features.

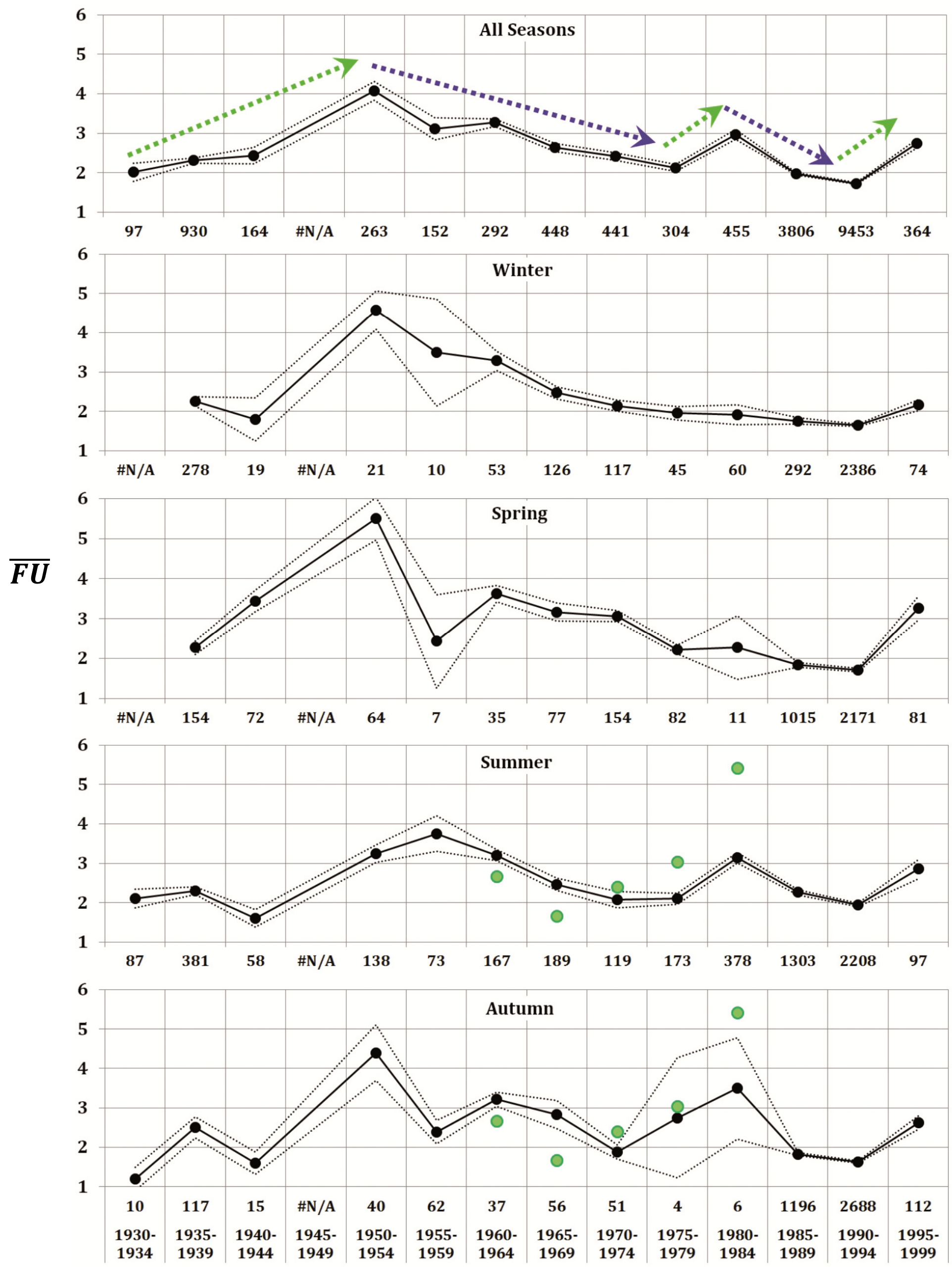

Figure 5.5 - Seasonal North Pacific means $\overline{FU}$ (black dots with connecting line), per lustrum including the number of observations, collected between 1930 and 1999 (#N/A means no or omitted data). The dotted lines indicate the lower and upper bound on the mean, respectively $L_{\overline{FU}}$ and $U_{\overline{FU}}$. In general, a trend, the greening of the water between 1930 and 1954, can be detected for all seasons. After the fifties the colour is slowly bluing, hereafter a greening period with a high in the 1980-1984 period and a low in the 1990-1994 period. Then the greening starts again. Per 5 years averaged total chlorophyll-a (Venrick *et al*. [14]) are shown as green dots in the summer and autumn graph. The integrated chlorophyll-a collected during May-October varies between 12 and 24 mg.m^2.

Looking at the highs in the periods 1950-54 and 1980-84 of the seasonal curves shown in Figure 5.5 we can conclude that within a relative short period of five years the ocean can green significantly while the reversed process, the transition greenish blue to blue, takes a longer time.

Venrick *et al.* [14] mentioned, in their 1987 *Science* publication, that a significant increase of integrated chlorophyll-a in the water column during May-October in the central North Pacific Ocean could be observed during 1968-85. This is in full agreement with our findings. The summer graph of Figure 5.5 shows an increase in colour from blue to blue-green in the period 1975-84. The autumn graph shows that ocean already starts to green significantly during the lustrum 1970-74. Ocean colour is strongly related to the chlorophyll *i.e.* an increase in chlorophyll means greening. Furthermore the “all seasons” graph of Figure 5.5 shows a contiguous blueing and greening during 1985-94 and 1995-99 respectively.

Antoine *et al*. [15], in search for long term trends in ocean colour, globally compared Coastal Zone Colour Scanner data (CZCS, 1979-86) with Sea-viewing Wide Field-of view Sensor (SeaWiFS, 1989-2002) data. One of the outcomes, a ratio of the logarithm of SeaWiFS to CZCS data, was an overall increase of the world ocean average chlorophyll concentration of 22%, although mainly found in inter-tropical areas. In contrast they found in oligotrophic gyres a declining of the chlorophyll concentration. Their findings mean a greening of the inter-tropical areas and a bluing of the oligotrophic gyres.

When we compare their presented annual North Pacific chlorophyll ratio average, of the area presented in Figure 5.3, we indeed see a bluing. Although small, comparing the 1980-84 and 1995-99 period (Figure 5.5, all seasons) the here presented result is similar to the results described by Antoine *et al*. One must bear in mind that comparing intermediate periods between 1980 and 2000 the bluest North Pacific oligotrophic water is found in the 1990-94 period, as mentioned before.

In 2001 Karl *et al*. [29] presented results on long-term changes in plankton community structure and productivity in the North Pacific subtropical gyre. One of their graphs, showing the standing stock chlorophyll concentration over the period 1965 to 2000 shows a maximum in euphotic zone depth-integrated chlorophyll concentration during 1980-84 and is conformed through our findings; a short greening of the North Pacific.

CONCLUSIONS AND RECOMMENDATIONS

We have presented Forel-Ule observations collected over seventy year in the North Pacific from which the oldest observations date back to 1930. It is one of the very few long-term oceanographic datasets archived by NOAA-NODC. The data was averaged in 5-year intervals (lustrum) between 1930 and 1999. To characterise colour changes and to identify inter-lustrum patterns 17171 observations located over 500 km off-coast were analyzed to establish the mean Forel-Ule colour for all season and per season. It was found that concerning its colour the North Pacific can vary significantly between blue and greenish-blue covering the Forel-Ule scale colours 1 to 6. Interestingly, it was found that this variation is only partly due to a yearly repetitive variation in the biological activity over the seasons.

Averaged over all seasons the greenest values with a $\overline{FU}$ = 4.1 were found during the years 1950-54, with a second high of $\overline{FU}$ = 3 in the period 1980-1984. The bluest ocean was encountered during 1990-94. Hereafter the ocean trends to green again. A remarkable long period of bluing took place between 1950-54 and 1975-79.

A significant increase in total chlorophyll-a in the water column during summer in the North Pacific between 1968 and 1985 as described by Venrick *et al*. is confirmed by the outcome of our research.

Ocean colour (biological activity), in this case the Forel-Ule colour, is an essential climate variable. Future work will focus on the link between (climate) forcing factors that control the changes in colour, e.g. by historical Forel-Ule scale analysis of other world oceans and merging of Forel-Ule data sets with satellite derived ocean colour data.

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CHAPTER 6 - MERIS-BASED OCEAN COLOUR CLASSIFICATION USING THE FOREL-ULE SCALE

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ABSTRACT

Multispectral information from ocean colour sensors is traditionally used to retrieve the concentration of pigments of phytoplankton and those associated with suspended sediment and dissolved organic matter. The retrieval algorithms generally, with some exceptions, only use part of the spectral information; they depend on calibration information that is a function of local environmental conditions (temperature, nutrients and light). In this paper we present a simple algorithm that uses normalized multi-band reflectance information in the visible part of the spectrum obtained by MERIS, a satellite-mounted spectrometer of the European space agency. This information is converted to a discrete set of numbers with the help of uniform colourimetric functions. The algorithm is demonstrated by transforming a number of MERIS Level-2 normalized reflectance images to Forel-Ule colour index images. The Forel-Ule scale is a sea colour comparator scale, indexed from 1 to 21. The scale covers all possible sea colours between indigo blue (the open ocean), brownish-green (coastal water) and 'cola' brown (humic-acid dominated water). Data based on this scale have been collected since the late nineteenth century. The reasons to reintroduce the indexation of seawater according to the Forel-Ule method are: 1) to classify oceans and coastal waters through a numerical value between 1 and 21, instead of a classification by the spectral radiance/reflectance signature of seawater; and 2) to create the possibility to compare historic ocean colour data with present-day satellite ocean colour data .

Keywords: Ocean Colour, MERIS, Forel-Ule, colourimetry.

INTRODUCTION

Satellite sensors to map the colour of oceans and seas synoptically have been used now for 3 decades. It would be of great interest to couple historically collected ocean colour data, that have obtained over a much longer time span, with satellite-derived ocean colour data for hindcasting purposes in order to detect really long-term trends. At the end of the nineteenth century a method to classify the colour of the sea by means of a colour comparator scale was described by Forel and Ule [1], [2]. The scale became known as the Forel-Ule (*FU*) scale. Scale observations have been performed ever since, and the technique has generated hundreds of thousands of data collected globe-wide over more than a century. Behrenfeld *et al.* have suggested [Nature 2006; [3]] that satellite measurements of ocean colour could provide a means of quantifying ocean productivity on a global scale, linking its spatial variability to environmental factors known to govern primary production. The operational characteristics of the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) enabled the detection of global ocean colour trends over huge areas of Earth. SeaWiFS was brought into space in the summer of 1997, so we cannot speak of a global trend analysis because observations now cover no more than a decade. Interestingly, analysis of surface colour variation over time in the North Pacific revealed a difference between the trends observed in situ [4] with data obtained by the satellite sensor [5].

With the launch, in 2002, of the MEdium Resolution Imaging Spectrometer (MERIS, European Space Agency), that measures water leaving reflectance in fifteen spectral bands with high signal-to-noise, it became possible to collect water-leaving reflectance not only in oceans but also in coastal waters [6]. In this article it is shown that this instrument opens the possibility to calculate the chromaticity coordinates of sea and ocean water colour and accordingly the Forel-Ule number. By comparing an unknown (*x, y*) chromaticity coordinate set belonging to a MERIS pixel with one of the twenty-one (*x, y*) chromaticity coordinate sets belonging to the Forel-Ule scale [7] a new MERIS water quality product, a Forel-Ule indexed image, becomes available. Based on this product, ocean colour trends can be constructed that reach back to over hundred years ago.

METHODS

In this section, the conversion of the normalized water-leaving reflectance in nine MERIS bands into a discrete *FU*-number is explained in three steps: Step 1: Calculation of the tristimulus values *X, Y*, *Z* by calculating the convolution of the CIE 1931 2° Colour Matching functions (CMF's) and the normalized water-leaving reflectance. Step 2: Calculation of the (*x, y*) chromaticity coordinates by the ratio of X or Y tristimulus value and the sum of the tristimulus values. Step 3: Determination of the *FU*-scale number by comparison, of the calculated (*x, y*) chromaticity coordinates in a Cartesian coordinate system, with the 21 unique chromaticity coordinates belonging to the *FU*-scale.

MERIS NORMALIZED REFLECTANCE

MERIS is a 68.5° field-of-view push-broom imaging spectrometer. It measures the solar radiation reflected by the ocean at a ground spatial resolution of 260 m × 290 m in 15 spectral bands. The bands are programmable in width and position, in the visible and near infrared wavelengths. MERIS allows global coverage of the Earth in 3 days. The radiation reflected by the ocean is atmospherically corrected to derive the normalized water leaving reflectance (a MERIS Level 2 product) [8]. The atmospheric correction applied assumes that the water totally absorbs the incoming sunlight in the NIR, and includes a correction for those sediment loaded waters where this assumption fails. The normalized water-leaving reflectance (dimensionless) $[\rho_W]_N$ is defined as

$$[\rho_W]_N(\lambda) = \frac{[L_W]_N(\lambda)}{F_0(\lambda)} \tag{6.1}$$

where $[L_W]_N$ is the normalized water-leaving radiance [9][10][11] and F_0 is the extraterrestrial solar irradiance.

$[\rho_W]_N$ (λ) is limited to the visible spectrum, covering the first nine MERIS bands all with a bandwidth of 10 nm except for band 8 with a bandwidth of 7.5 nm (Table 6.1) [12]. To classify the sea and ocean on its colour $[\rho_W]_N$ (λ) is used to calculate a single numerical value, *i.e.*, the *FU*-number per MERIS image pixel.

Table 6.1 - The central wavelengths of the first nine MERIS spectral bands. All bands have a width of 10 nm, with exception of band 8 (7.5 nm).

MERIS band	*Wavelength (nm)*	MERIS band	*Wavelength (nm)*
1	412.5	6	620
2	442.5	7	665
3	490	8	681.25
4	510	9	708
5	560		

FOREL-ULE INDEXATION

STEP 1: CALCULATION OF THE TRISTIMULUS VALUES

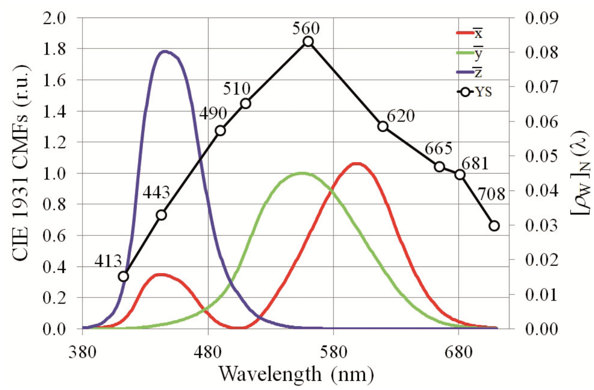

Figure 6.1 - The CIE 1931 20 Colour Matching functions for $\overline{x}$ (red), $\overline{y}$ (green) and $\overline{z}$ (blue) determined per nanometer. The black line represents a nine band ((open circles)) example spectrum (Yellow Sea) of MERIS normalized water-leaving pixel reflectance [ρw]*N* (λ).

Tristimulus values are the amounts of three primaries that specify a colour stimulus, 'derived' parameters from the RGB colours [13] and are noted as *X, Y* and *Z*. The CIE 1931 [14] standard colourimetric observer 2 degree colour matching functions (CMFs) $\overline{x}$ (red), $\overline{y}$ (green) and $\overline{z}$ (blue) presented in Figure 6.1 serve as weighting functions for the determination of the tristimulus values of the MERIS normalized water-leaving reflectance $[\rho_W]_N$ by the Eq. 6.2a, 6.2b and 6.2c;

$$X = \int [\rho_W]_N(\lambda)\overline{x}(\lambda)d\lambda \tag{6.2a}$$

$$Y = \int [\rho_W]_N(\lambda)\overline{y}(\lambda)d\lambda \tag{6.2b}$$

$$Z = \int [\rho_W]_N(\lambda)\overline{z}(\lambda)d\lambda \tag{6.2c}$$

The MERIS normalized water-leaving reflectance $[\rho_W]_N$ (λ_n) for n=1,...9, is re-sampled through linear interpolation over λ_i, where i = 412,... 710 and $\lambda_i = \lambda_0 + i\Delta\lambda$ ($\Delta\lambda$ = 1nm), to achieve the highest precision in the calculation of the tristimulus values, according to Eq. 6.3.

$$[\rho_W]_N(\lambda_i) = [\rho_W]_N(\lambda_n) + \left(\frac{\lambda_i - \lambda_n}{\lambda_{n+1} - \lambda_n}\right)\left([\rho_W]_N(\lambda_{n+1}) - [\rho_W]_N(\lambda_n)\right) \tag{6.3}$$

The CIE 1931 CMFs ($\bar{x}$, $\bar{y}$ and $\bar{z}$) were applied per 1 nm interval. The integration operations (Eq. 6.4a, 6.4b and 6.4c) to obtain the tristimulus value *X, Y* and Z, are performed through the Riemann sum approximation of the integrals;

$$X = \sum_{i=412}^{710} [\rho_W]_N(\lambda_i)\bar{x}(\lambda_i)\Delta\lambda \quad (6.4a)$$

$$Y = \sum_{i=412}^{710} [\rho_W]_N(\lambda_i)\bar{y}(\lambda_i)\Delta\lambda \quad (6.4b)$$

$$Z = \sum_{i=412}^{710} [\rho_W]_N(\lambda_i)\bar{z}(\lambda_i)\Delta\lambda \quad (6.4c)$$

STEP 2: CALCULATION OF THE CHROMATICITY COORDINATES

Subsequently the chromaticity coordinates *x, y* and *z* are calculated from the ratio of each of the tristimulus values and the sum of the values according Eq. 6.5a, 6.5b and 6.5c.

$$x = \frac{X}{X+Y+Z} \quad (6.5a)$$

$$y = \frac{Y}{X+Y+Z} \quad (6.5b)$$

$$z = \frac{Z}{X+Y+Z} \quad (6.5c)$$

As $x+y+z = 1$, and therefore $z = 1-x-y$, the third coordinate offers no additional information and only two coordinates (by convention *x* and *y*) are used to represent the colour in a so-called chromaticity diagram. The so-called white point W has the chromatic coordinates $x=y=z=1/3$ (Figure 6.2). The ratio of the vectors W to a particular point P (*a*) and W to the spectral locus (*a*+*b*), gives the colour saturation (*a*/*a*+*b*) or the intensity of the colour in P. In this way the chromaticity coordinates (x_M, y_M) for every MERIS pixel is calculated. In the next step the (x_M, y_M) is converted to a *FU*-number.

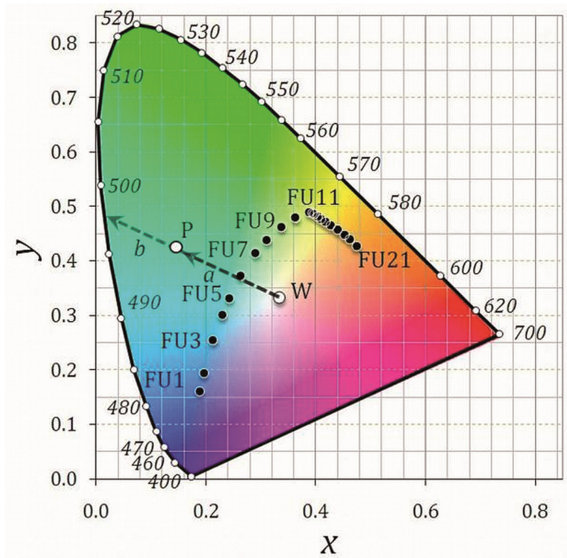

Figure 6.2 - The CIE1931 chromaticity coordinates, based upon transmission measurements, of the *FU*-scale colours 1 to 21 (black circles) including the white point W where xW = yW = 1/3). The outer curved boundary is the spectral locus (demarking the outer range of human perception), with wavelengths shown in nanometers.

STEP 3: DETERMINATION OF THE *FU*-SCALE NUMBER

The chromaticity coordinates of the original *FU*-scale, as calculated by Wernand and van der Woerd in 2010 [7], are presented in Table 6.2 and graphically shown in the chromaticity diagram of Figure 6.2.

In a Cartesian coordinate system the angle between two vectors can be calculated through the arctangent (Eq. 6.7). In this study the angle determining the *FU*-number is calculated in MATLAB software with the ATAN2 function (four-quadrant inverse tangent). The MATLAB ATAN2 function calculates the angle (in radials) between the vector to a point with certain *FU* coordinates (*x, y*) and the positive x-axis, giving higher angles in an anti-clockwise direction (Figure 6.3) and negative angles in a clockwise direction. The radials are then multiplied by 180/pi to get angles (α_i) in degrees (see Eq. 6.6 to Eq. 6.11).

For example, α_i in Figure 6.3 is the angle matching *FU*-number *8*. An example of the chromaticity coordinates, relative to the white point W, where $x_W = y_W = 1/3$, derived from the normalized spectral reflectance of a MERIS-pixel is indicated by a yellow dot in Figure 6.3 ($x_M - x_W = -0.15$, $y_M - y_W = 0.1$) In this study the angles were accordingly converted to degrees (modulus π).

$$i \in [1,21] \qquad (6.6)$$

$$\alpha_i = \arctan\left(y_i - y_W, x_i - x_W\right) \text{modulus}\ \pi \tag{6.7}$$

Table 6.2 - The chromaticity coordinates(*x, y*) of the *FU*-scale numbers [7].

No.	x	y	No.	x	y	No.	x	y
FU1	0.189	0.161	*FU8*	0.311	0.439	*FU15*	0.410	0.478
FU2	0.196	0.194	*FU9*	0.337	0.463	*FU16*	0.418	0.472
FU3	0.213	0.255	*FU10*	0.363	0.480	*FU17*	0.427	0.466
FU4	0.229	0.301	*FU11*	0.388	0.490	*FU18*	0.440	0.458
FU5	0.242	0.331	*FU12*	0.394	0.488	*FU19*	0.453	0.448
FU6	0.263	0.373	*FU13*	0.397	0.486	*FU20*	0.462	0.440
FU7	0.290	0.415	*FU14*	0.404	0.482	*FU21*	0.473	0.429

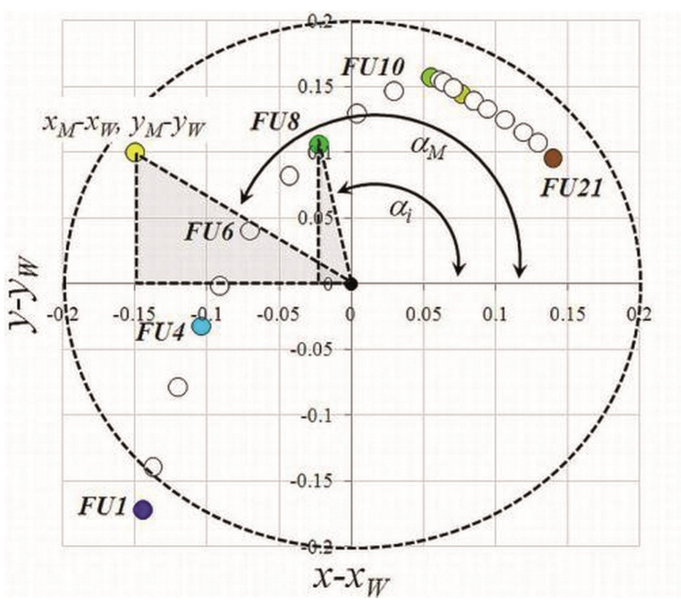

Figure 6.3 - A chromaticity diagram with known chromaticity coordinates relative to the white point of the scale colours *FU*1 to *FU*21 are shown in dots. An example of the chromaticity coordinates ($x_M - x_W$ = -0.15, $y_M - y_W$ = 0.1), again relative to the white point, derived from the normalized spectral reflectance of a MERIS-pixel is marked with a yellow dot. This pixel can be labelled *FU*6, after applying Eq. 6.9 deriving the angle α_M and consulting the lookup table 3. As an example the angle α_i (102.05, see Table 3), determining the position of *FU*8, is given.

For MERIS pixels with unknown *FU*-numbers boundaries distinguishing the various *FU* numbers need to be defined. The colour transition angle α_{iT} under which a scale number transition takes place, i.e. an *FU*-colour changes from one into the other can be defined according to Eq. 6.8.

$$\alpha_{iT} = \frac{(\alpha_i + \alpha_{i+1})}{2} \tag{6.8}$$

Both, α_i and α_{iT} are presented in Table 6.3.

Table 6.3 - Determination of the *FU*-number belonging to a MERIS pixel with known (*x, y*) chromaticity coordinates is achieved with the help of a given angle α_i. Apply a simple loop for *i*=1 to 21 and the logical function If $\alpha_M > \alpha_T$ is true for the first time reaching the angle α_{iT}=133.96^0 in accordance with a *FU*-number of *6*.

i	α_i^{0}	α_{iT}^{0}	For *i=1* to *21* If $\alpha_M > \alpha_{iT}$ Then *FU* =	*i*	α_i^{0}	α_{iT}^{0}	For *i=1* to *21* If $\alpha_M > \alpha_{iT}$ Then *FU* =
1	229.94	227.68	*1*	12	68.49	67.93	*12*
2	225.41	219.27	*2*	13	67.36	65.98	*13*
3	213.13	205.19	*3*	14	64.60	63.35	*14*
4	197.25	189.20	*4*	15	62.11	60.37	*15*
5	181.15	165.71	*5*	16	58.62	56.64	*16*
6	150.26	133.96	*6*	17	54.65	52.09	*17*
7	117.66	109.85	*7*	18	49.53	46.75	*18*
8	102.05	95.14	*8*	19	43.96	41.82	*19*
9	88.24	83.38	*9*	20	39.67	36.98	*20*
10	78.53	74.62	*10*	21	34.28		*21*
11	70.71	69.60	*11*				

The *FU*-number for a given MERIS pixel M with chromaticity coordinates $x_M - x_W$ = 0.15 and $y_M - y_W$ = 0.3 (yellow point in Figure 6.3) can be determined as follows: First the angle α_M is calculated according to Eq. 6.9:

$$\alpha_M = \arctan(y_M - y_W, x_M - x_W)\,\text{modulus } 2\pi \tag{6.9}$$

where

$$\alpha_M \in \left[0, \frac{3}{2}\pi\right] \tag{6.10}$$

So that in case α_M is negative

$$\alpha_M = \alpha_M + 360 \tag{6.11}$$

In Figure 6.3 $\alpha_M = 146^0$ and can now be compared with the twenty-one values of α_{iT} given in Table 6.3. A simple loop for i=1 to 21 (Table 6.3, column 4) will generate a *FU6* belonging to the MERIS pixel M ($x_M - x_W$, $y_M - y_W$).

DATA

Figure 6.4 - MERIS data were extracted from ESA's MERCI database. The North Sea (1), the Red Sea (2 and 3), the Yellow Sea (4) and the Sea of Japan (5) were chosen for their different sea colour properties.

To test the determination of the *FU*-colour from satellite data, the method was applied to five MERIS images acquired over the areas shown in Figure 6.4. The areas were chosen for their different sea colour properties and are the North Sea (1), the Red Sea (2, 3), Yellow Sea (4) and the Sea of Japan (5). The images were extracted from ESA's on-line database, the MERIS Catalogue and Inventory (MERCI) [15]. MERIS Reduced Resolution (RR) geophysical products (Tabel 6.4) contain, amongst other products, a total of 14 spectral images of normalized band reflectance. A Reduced Resolution image has 4 × 4 less points (pixels) than the same image in Full-Resolution. A RR-pixel represents an area of 1040 m × 1160 m.

Table 6.4 - The acquired MERIS Reduced Resolution images extracted from the MERCI database covering the North Sea (1), Red Sea (2 and 3), Yellow Sea (4) and the Sea of Japan (5).

Sea	Area	Product name	Start time UTC	End time UTC
North Sea Wadden Sea	1	MER_RR_2PQBCM20060504	04-MAY-2006 10:11:24	04-MAY-2006 10:18:01
Red Sea north	2	MER_RR_2PQBCM20031222	22-DEC-2003 07:56:09	22-DEC-2003 07:59:29
Red Sea south	3	MER_RR_2PQBCM20031223	23-DEC-2003 07:26:02	23-DEC-2003 07:29:22
Yellow Sea	4	MER_RR_2PPBCM20090211	11-FEB-2009 02:27:39	11-FEB-2009 02:34:16
Sea of Japan East Hokkaido	5	MER_RR_2PQBCM20040614	14-JUN-2004 01:07:24	14-JUN-2004 01:14:01

RESULTS

In order to classify natural waters as close as possible to their natural (paper/screen) sea colour, an exclusive *FU*-scale legend has been designed. The legend shown in Figure 6.5 represents the *FU*-colours as close as possible. For the reproduction of the *FU*-legend and for future comparison of sea water colour maps it is recommended to use the RGB values presented in Table 6.5.

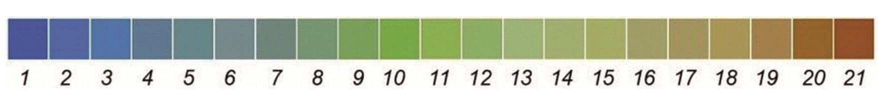

Figure 6.5 - The colours of the special designed *FU*-scale legend are chosen as close as possible to natural (paper/screen) sea colours and are composed of a combination of known RGB coordinates.

Table 6.5 - RGB values for the reproduction of the *FU*-legend.

FU nr.	R	G	B	*FU nr.*	R	G	B
1	33	88	188	*12*	148	182	96
2	49	109	197	*13*	165	188	118
3	50	124	187	*14*	170	184	109
4	75	128	160	*15*	173	181	95
5	86	143	150	*16*	168	169	101
6	109	146	152	*17*	174	159	92
7	105	140	134	*18*	179	160	83
8	117	158	114	*19*	175	138	68
9	123	166	84	*20*	164	105	5
10	125	174	56	*21*	161	77	4
11	149	182	69				

First, in the next section '*MERIS Forel-Ule maps*', MERIS images are converted into *FU*-maps and thereafter, in section '*Ground truth Forel-Ule maps*', the maps are validated by means of ground truth *FU*-observations, which were interpolated through an Inverse Distance Weighted (IDW) technique [16], [17].

MERIS Forel-Ule maps

For all five MERIS RR- images the (*x, y*) chromaticity coordinates per pixel were converted into a *FU*-number using Eq. 6.3 to 6.9. Converted images will be further referred to as *FU*-maps. Examples of *FU*-maps are presented in Figures 6.6, 6.7 and 6.8. The $[\rho_W]_N$ spectral signatures at the locations marked with a red circle in the maps are presented in Figure 6.9 and their matching *FU* numbers are provided in Table 6.6. In the figures land is marked grey, clouds are marked white and 'no data' is shown up in black.

The first *FU*-map shown in Figure 6.6, acquisition date of 4 May 2006, covers the North Sea, the Baltic and the Wadden Sea. The Wadden Sea, a tidal flat area north of Holland and Germany, and west of Denmark (also in Figure 6.6), was optically sampled from the RV '*Navicula*' 2.5 hour prior to the MERIS image acquisition time**.** The surface radiance L_{sfc}, sky radiance L_{sky} and incoming solar irradiance E_s were measured simultaneously using TRIOS hyper-spectral radiometers [18]. It should be noted that the ground truth spectral data of the Wadden Sea was calculated as remote sensing reflectance $R_{RS} = L_w/E_s$, where L_w is the water-leaving radiance L_{sfc}-ρ L_{sky} and E_s is the downward irradiance just above the sea surface [19]. However, to a good approximation $[\rho_W]_N \approx \pi R_{RS}$ [20], [21]. From the remote sensing reflectance R_{RS}, the *FU*-number was calculated to be *15* at the position in the red circle. The MERIS pixel within the red circle (Wadden Sea) has a calculated *FU*-value of 14, which is in good agreement with the ground truth *FU*-value concerning possible adjacency effects of tidal flats within the pixel. Furthermore, the Wadden Sea shows values of *FU9* to *FU18*.

Table 6.6 - The MERIS- image acquisition areas with season and year of acquisition and the geographical position of the pixel for which (*x, y*) chromaticity coordinates were converted into a *FU*-number. The positions are marked with a red circle in Figure 6.6, Figure 6.7 and Figure 6.8. For the Wadden Sea two *FU*-numbers were calculated; the first number is calculated from a MERIS pixel and the second (marked GT) is calculated from a ship-borne remote sensing reflectance measurement.

Acquisition Area	North Sea NS	Wadden Sea WS	Red Sea *RS1*-north	Red Sea *RS2*-south	Yellow Sea YS	Sea of Japan SJP	East of Hokkaido
Season	Spring 2006	Spring 2006	Winter 2003/4	Winter 2003/4	Winter 2008/09	Summer 2004	Summer 2004
LAT	52°48'11" N	53°33'52'' N	24°30'55" N	15°30'55" N	33°06'20" N	40°03'08" N	42° N
LON	2°41'08" E	6°37'49'' E	36°32'28" E	41°00'37" E	123°00'22" E	135°02'39" E	145° E
FU	*6*	*14* / GT *15*	*2*	*8*	*11*	*2*	*9*

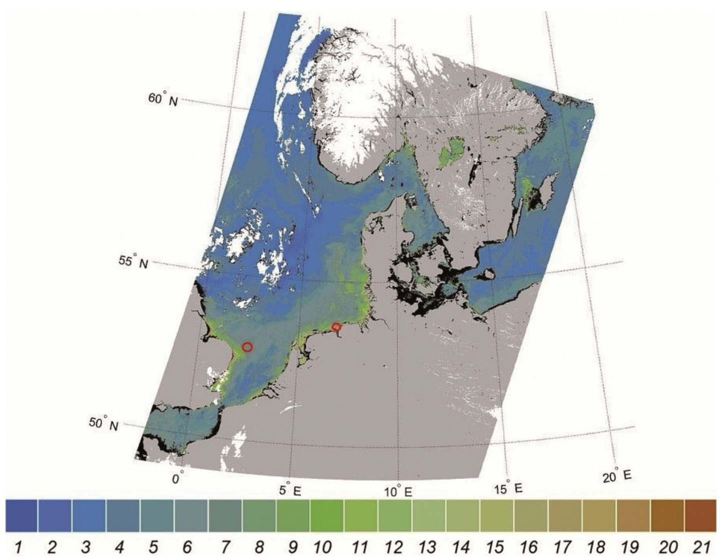

Figure 6.6 - The spring *FU*-map of the turbid North Sea (4 May 2006) shows *FU*-values ranging from 3 to 9 (red circle west *FU*6). The Wadden Sea area within barrier islands north of Holland and west of Denmark shows values between *FU*9 and *FU*18. The area within the red circle indicates a pixel value of *FU*=14, close to the ground truth equivalent of *FU*15.

The colour of the North Sea varies between *FU3* and *FU9*. The colour within the left red circle situated between the Thames and Humber estuaries was established at *FU6*. The central North Sea shows values of *FU3* to *FU4* with occasionally *FU2* (very blue water, oceanic).

Figure 6.7 shows a winter *FU*-map of both northern- and southern Red Sea of respectively 22 and 23 December 2003. The colour of the northern Red Sea is mainly *FU2* to *FU3* with maximum values of *FU5*. The southern part, more shallow compared to the northern part shows a possible plankton bloom starting south of 17.5^0 north with values of *FU8* (red circle) to *FU11*. The water flowing through the narrow strait of Bab-al-Mandab into the Gulf of Aden (area at the most south-eastern point on the map) shows much bluer values *FU2* to *FU4*.

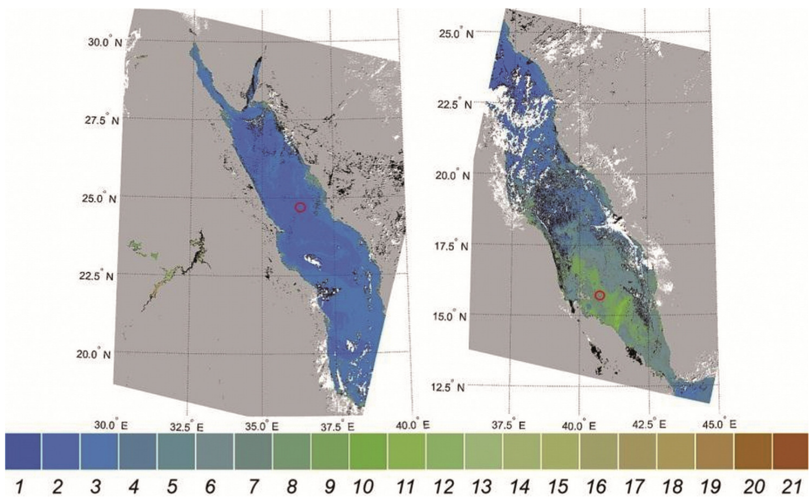

Figure 6.7 - The winter *FU*-map of the Red Sea, dated 22 (left) and 23 December 2003 (right) shows that open water of the northern part is mainly bluish *FU*1 to *FU*2 (in red circle *FU*2) and near coast values are around *FU*3. The southern part, much more shallow than the northern part, shows more greenish coloured water (in red circle *FU*=8). South of 17.5 North *FU*-values are encountered up to a maximum of *FU*11 possibly caused by enhanced plankton abundance.

Figure 6.8 shows a *FU*-map of the Yellow Sea (left) and the Sea of Japan (right) acquired respectively 11 February 2009 and 14 June 2004. The outflow of the Yangtze River (south of red circle left image) shows high *FU*-values between *FU7* up to real brownish colours of *FU*19. Unfortunately the area close to the river output is marked as a No Data area. Within the red circle a value of *FU*9 is calculated. The Sea of Japan shows values of *FU2* to *FU3* (within red circle *FU2*). Remarkable is the relative green area east of Hokkaido (*FU9* marked by the red circle east) with values up to *FU10*. To verify phytoplankton abundance the MERIS level2 chlorophyll product was consulted. Satellite derived Chlorophyll-*a* at the image acquisition date show at the same image concentrations of over 2mg.m^{-3} East of Hokkaido and concentrations of >0.1< 0.5mgm^{-3} in the Sea of Japan.

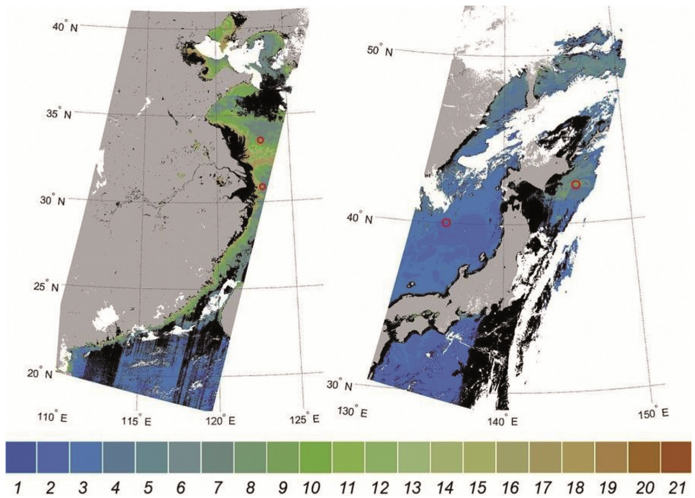

Figure 6.8 - The winter *FU*-map of the Yellow Sea, acquisition date 11 Feb. 2009 (left) and the summer *FU*-map of the Sea of Japan, acquisition date 14 Jun. 2004 (right). The Yellow Sea is mainly greenish brown with *FU*7 up to *FU*17 (*FU*9 in the lower red circle and *FU*11 in the upper red circle). Black indicates the lack of data. The Sea of Japan, a 'blue sea', shows summer values of around *FU*2 to *FU*3 (in red circle *FU*2). East of Hokkaido phytoplankton abundance greens the water to *FU*10 (*FU*9 within the red circle east). In this part of the eastern North Pacific MERIS level2 chlorophyll-a data indicate concentrations over 2mgm^{-3}.

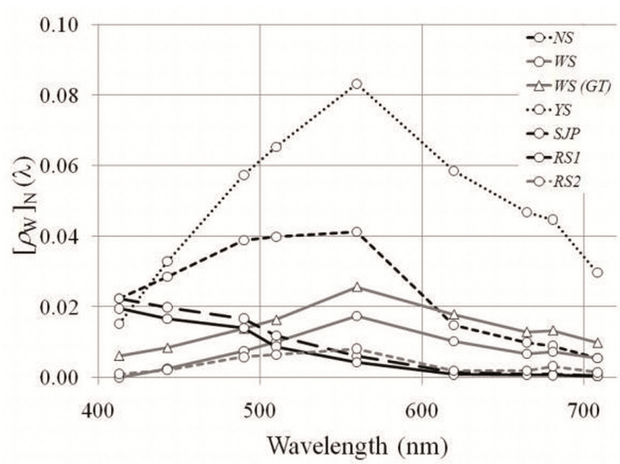

Figure 6.9 - Example of the pixel values of MERIS normalized water-leaving reflectance spectra of the North Sea (*NS*), Wadden Sea (*WS*), Yellow Sea (*YS*), Sea of Japan (*SJP*) and the northern and southern Red Sea (resp. *RS1* and *RS2*). Notice the similarity in shapes of the Wadden Sea spectra; *WS* is a MERIS normalized water-leaving reflectance spectrum and *WS (GT)* is the remote sensing reflectance spectrum at ground truth.

GROUND TRUTH FOREL-ULE MAPS

Except for a single spectral measurement performed in the Dutch Wadden Sea, no ground truth spectral data or *FU*-observations were available at the image acquisition dates. We can ask ourselves, how realistic are the here presented *FU*-maps?

For a more general validation of the satellite derived *FU*-maps, databases containing globally collected ship-borne *FU*-observations were consulted. From the oceanographic and meteorological database, archived by the United States National Oceanographic Data Centre (NOAA-NODC) [22], and from the ocean colour database at the Royal Netherlands Institute for Sea Research *FU*-observations were extracted for the sea areas. To validate the North Sea *FU*-map (Figure 6.6) data was extracted only for June 2001, as no data was available for the spring season. To create maps comparable to the maps shown in Figure 6 to Figure 8, data were interpolated according to an Inverse Distance Weighting interpolation technique.

For the North Sea 12 *FU*-observations were collected in June 2001. Data is shown in Figure 6.10 and the exact date, time and geographical position is tabulated in Table 6.7. The *FU*-observations vary between *FU3* in the north to *FU10* in the north east. Near the red circle shown in Figure 6.10 interpolated values of *FU5* to *FU7* can be determined. In the red circle the MERIS derived *FU*-number is *FU*6. Comparing the MERIS map of Figure 6.6 with the map, accomplished trough IDW interpolation, of Figure 6.10 and bearing in mind the difference in dates of data acquisition, the outcome of satellite derived *FU*-map of the North Sea can be called realistic.

Table 6.7 - *FU*-observations performed in the North Sea in June 2001 were used to produce a colour IDW colour map used for the validation of a MERIS derived *FU*-map of the North Sea.

Date	12/06/01		13/06/01		14/06/01	
Time	06.34	16.53	06.07	17.04	05.30	17.08
Station	802	808	812	818	822	827
Lat	53.6248	52.8757	53.3738	53.3755	53.1958	53.3338
Lon	3.5010	3.4992	3.4745	3.4725	2.2260	2.4825
FU	*10*	*8*	*12*	*9*	*5*	*4*
Date	15/06/01	16/06/01			17/06/01	17/06/01
Time	16.36	06.27	12.56	14.35	05.17	12.02
Station	838	843	846	847	853	858
Lat	53.4532	52.7332	53.4167	53.6667	53.6583	53.4992
Lon	3.4362	3.3333	2.8333	2.8333	3.6833	3.6843
FU	*7*	*7*	*6*	*3*	*7*	*9*

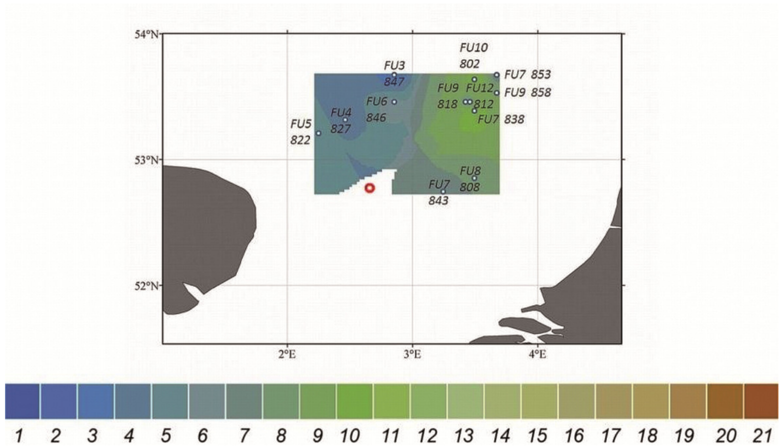

Figure 6.10 - A map of the North Sea: An IDW interpolation over 0.5 degrees with a grid size of 0.02 degrees of 12 ship-borne *FU* -observations collected in June 2001. The *FU*-observations vary between *FU*3 and *FU*10. Close to the red circle situated between the Thames and Humber estuaries values are between *FU*4 and *FU*5.

For the IDW map of the Red Sea presented in Figure 6.11 only 52 observations were available, which were collected during the winters of 1895 to 1898. Note the blue to green colour separation between northern and southern part, also visible on MERIS map of Figure 6.6.

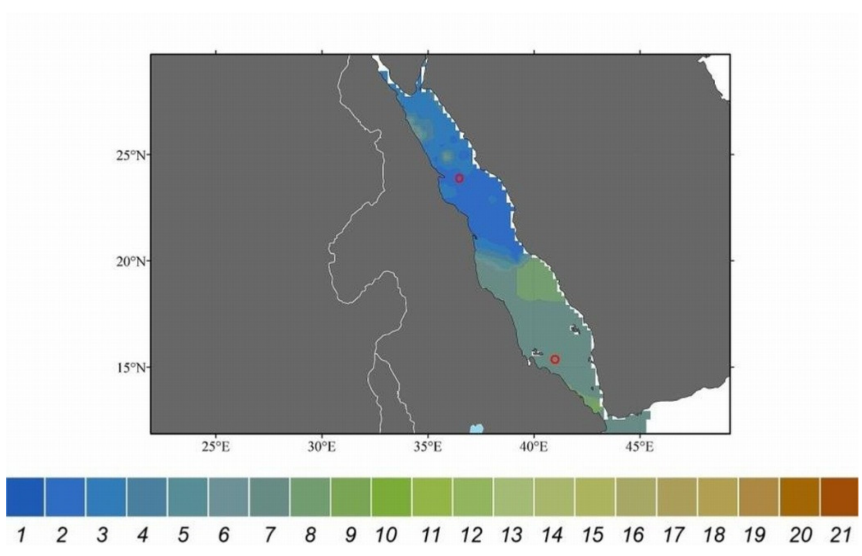

Figure 6.11 - The Red Sea: An IDW interpolation, over 2 degrees with a grid size of 0.2 degrees, of 52 *FU* in-situ observations collected during the winters of 1895 to 1898. Within the northern red circle *FU*=2 and within the southern red circle *FU*=7. This colour boundary can also be observed 100 years later in the MERIS map of Figure 6.7.

Comparing the MERIS winter *FU*-maps of the north and south Red Sea of Figure 6.7 with the winter IDW *FU*-map of Figure 6.11, similar patterns can be recognized despite a time cap of over a century between data acquisition. It seems that the colour of the Red Sea did not change significantly over time, although we cannot say anything about intermediate colour changes between 1899 and 2002. Within the red circles the MERIS *FU*-map (Figure 6.7) shows *FU2* for the northern location and *FU8* for the southern location and the IDW *FU*-map (Figure 6.11) shows a similar *FU2* for the northern location and a similar *FU8* for the southern location.

An IDW colour map for the Yellow Sea was composed out of 2882 *FU*-observations collected during the winters of 1930 to 1999 and is shown in Figure 6.12. The Yellow Sea shows *FU*-numbers of *FU*4 at open sea to values of *FU*20 in front of the outflow of the Yangtze River. Both, the MERIS map of Figure 6.8 and the IDW interpolation of Figure 6.12 show similar colour patterns. The red circles in the MERIS map indicate *FU*9 in the lower and *FU*11 in the upper red circle. In the IDW map respectively *FU*12 and *FU*14 are indicated. A possible explanation of the bluing of the water (bluer colours show up in the 2008/9 map) is the reduced outflow of Yangtze water into the Yellow Sea due to the hydroelectric Three Gorges Dam, which became operational in 2003. The effect is a reduced upwelling, less cooler and less nutrient-rich water reaches the sea surface, and thus productivity, resulting in less green water [23], [24]. No Data is marked black in the MERIS Yellow Sea map of Figure 6.8, therefore high *FU* values close to the Yangtze River can not be validated.

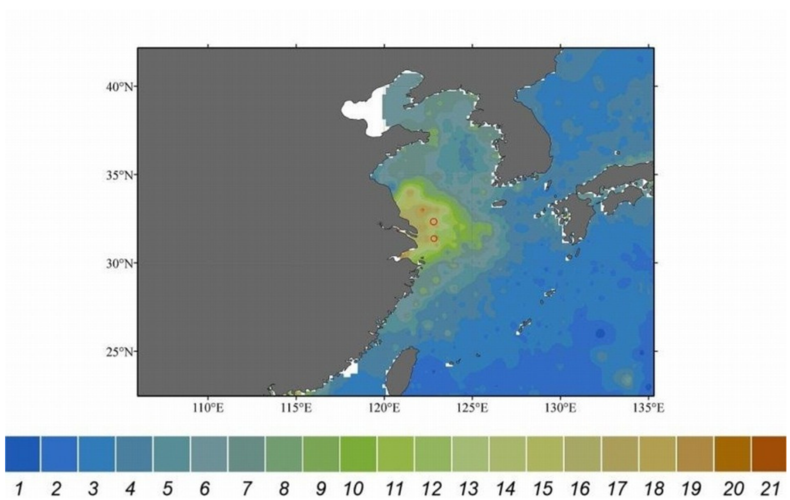

Figure 6.12 - Yellow Sea: An IDW interpolation over 2 degrees of 2882 *FU in-situ* observations collected during winter between 1930 and 1999. The grid size is 0.2 degrees. Within the red circles the colour is *FU12* (lower, in front of the Yangtze outflow) and *FU14* (upper). Near coast *FU*-numbers are as high as *18* to *20*.

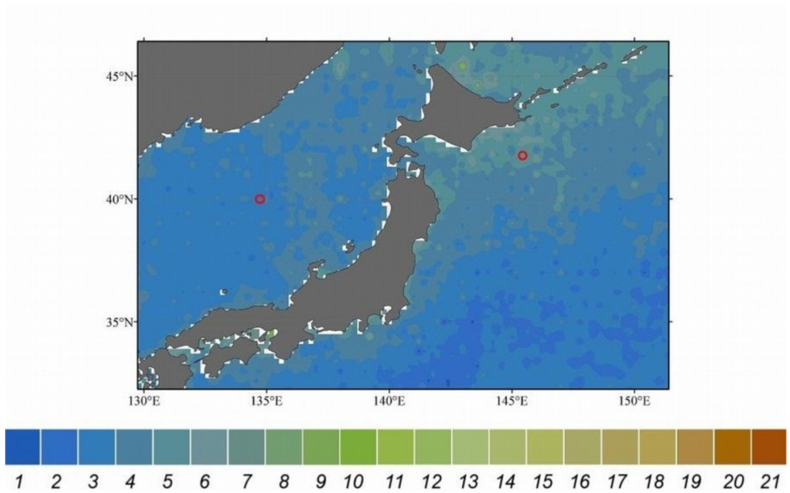

Figure 6.13 - Sea of Japan: An IDW interpolation over 2 degrees of 13392 *FU* in-situ observations collected during summer between 1930 and 1999. The grid size is 0.2 degrees. The sea colour varies in summer between *FU*2 to *FU*4. The colour marked with a red circle in the central Sea of Japan is *FU*2. East of Hokkaido colours vary between *FU*5 and *FU*7. The eastern red circle marks a *FU*7 value.

Based on 13,392 observations collected in the Sea of Japan and around Japan during the summers of 1930 to 1999, an IDW interpolation of *FU* is shown in Figure 6.13. The Sea of Japan shows colours varying between *FU2* and *FU4* similar to the findings of the summer MERIS map of Figure 6.8. Within the red circle both the MERIS-map and the ground truth *FU*-map show a value of *FU*-2. The North Pacific east of Hokkaido shows, like the MERIS *FU* map, greener seawater East of Hokkaido with interpolated values of *FU5* to *FU7* marked by the eastern red circle.

DISCUSSION AND CONCLUSIONS

In this paper an algorithm is presented that allows retrieval of the Forel-Ule sea colour from the MERIS satellite sensor. The Forel-Ule colour can be seen as the colour standard closest to the real colour of water. The elegance of our algorithm is that it converts multispectral observations to one simple number that is only dependent on a well-known universal set of colourimetric functions. The classification of sea water is simplified by means of a numerical value between 1 and 21, instead of a classification by a normalized water-leaving spectral reflectance signature, or the concentrations of the dominant optical constituents.

The approach is demonstrated by the processing of multispectral observations of oceans and coastal waters made by the MERIS ocean colour sensor, to *FU*-maps that cover colour classes between indigo blue, green and brown. Five different seas were selected worldwide; ocean colour data were processed to obtain *FU*-maps. The maps show very detailed patterns and gradients, mainly in the near coastal zone as expected by the more outspoken hydrographical gradients there. When the MERIS maps of sea and ocean colour distribution were compared with ground truth Forel-Ule observations mapped in the same season, similar patterns and *FU* numbers were observed, even when *FU*'s of more than a century ago were processed. This supports the validity of our approach. We expect that with a more thorough validation, MERIS satellite Forel-Ule mapping can be coupled to historic Forel-Ule observations for long-term trend analysis. The new 'MERIS level 2 product' proposed by us may well become a new standard for the classification of the colour of seas and oceans.

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CHAPTER 7 - TRENDS IN OCEAN COLOUR AND CHLOROPHYLL CONCENTRATION FROM 1889 TO PRESENT

Submitted to Progress in Oceanography

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ABSTRACT

Most analyses of the influence of global warming on the ocean's surface are based on satellite-derived oceanographic products for temperature change and, as to biological characteristics, for ocean colour and its derivative, chlorophyll concentration. Globe-wide ocean colour observations by satellites started in 1978 with the launch of the Coastal Zone Color Scanner. The record of chlorophyll changes over time has never been established over the period before this year for lack of a good alternative to satellite-based measurements. In this paper, we draw attention to and provide evidence of the usefulness of the Forel-Ule (*FU*) scale observation record, a time series that goes back all the way to the late 19th century. We have revisited this largely unexplored database in order to provide information on changes in chlorophyll at the ocean's surface over the period that climate change became effective. The *FU* scale has hardly been used since hyper-spectral satellite-borne instrumentation has become available. Yet, as we argue here, exploration of the historical Forel-Ule observation archive is a serious method to assess the impact of 'global change' on the ocean's biota, because it is a good representation. Changes of ocean surface chlorophyll can be reconstructed with confidence over the last century. The most complete *FU* record has been established in the North Atlantic, in terms of coverage over space and in time, and this data base has been used to test the validity of colour changes, and therewith chlorophyll changes, over timescales of up to 10 decades. Bio-optical models of ocean colour indicate that the Forel-Ule index is a chlorophyll proxy for the open ocean. We present statistical analyses of sea and ocean colour changes related to the long-term cycle of biological activity that is governed by natural phenomena, but possibly also by human influences, such as the release of greenhouse gases. The results of our analysis suggest that since the early 20th century, chlorophyll concentrations have decreased in the Indian Ocean and have fluctuated in

the Pacific; they increased in the Atlantic Ocean, the Mediterranean, the Chinese Sea, and in the seas west and north-west of Japan. No *global* trend of a uniform increase or decrease in chlorophyll concentration, and therefore phytoplankton abundance, has been identified.

Keywords: chlorophyll, phytoplankton, CDOM, ocean colour, twentieth century, Forel-Ule scale, data archaeology, climate, time series, World seas, Oceans

INTRODUCTION

Oceanographic data archaeology is, according to the physical oceanographer Bruce Parker [1], a critical requirement for climate and global change research. The colour of the sea (ocean colour), besides water transparency, salinity and temperature, is one of the few oceanographic parameters that have been recorded over a century [2]. Observations of the colour of the sea were performed with the Forel-Ule scale; they date back to the end of the 19th century. The Forel-Ule scale has been proven to be an adequate sea colour comparator with the capacity to spectrally discriminate 21 natural sea colours between indigo blue and 'cola' brown [3]. Changes in water colour are caused by a change in the composition of the optically active substances [4]: suspended particulate matter, pigments (chlorophyll-a, b and c and carotenoids) in algae [5], and dissolved organic matter [6]. The blue colour of oligotrophic oceans is caused by domination of selective absorption and scattering of the water molecules. Chlorophyll colours the water green (carotenoids even red, such as peridinin of the sometimes abundant dinoflagellates), and the presence of coloured dissolved organic matter (CDOM) will, in high concentrations, account for the absorption of most of the blue part of the incoming sunlight, resulting in brownish coloured water, close to the colour of tea.

An important aspect of climate research is nowadays the detection of ocean colour from space, with derived products such as water transparency; coloured dissolved organic matter absorption and chlorophyll concentration. Water transparency can be used to predict the depth of the upper ocean mixed layer [7], which plays a critical role in the flux of energy between atmosphere and ocean. Chlorophyll provides the best index of phytoplankton biomass for primary productivity studies, as was recently again confirmed by Huot *et al.* [8]. As a matter of fact, phytoplankton accounts for nearly half of Earth's total primary productivity [9], nowadays readily derived from satellite data [9] and long-term changes in ocean primary production may well have important consequences for the global carbon cycle [11]. Changing climate will affect marine life, and this, in turn, plays a crucial role in climate control [12].

One of the Essential Climate Variables listed by the World Meteorological Organization (WMO) to detect biological activity in the ocean's surface is ocean colour [13]. Since the late 1990s sophisticated imaging ocean colour satellite sensors, such as the Sea viewing Wide angle Field of view Sensor SeaWiFS, the MEdium Resolution Imaging Spectrometer MERIS and the Moderate Resolution Imaging Spectroradiometer MODIS, sample the ocean's colour. With revisit times of 1 to 3 days, a swath width of around 1,000 to 2,000 kilometres and a spatial resolution of 250 to 1,000 meters, the ocean has never been before optically sampled on such a substantial scale. The first ocean colour observations from space emerged in the late 1970s of the past century, with the launch of the experimental Coastal Zone Color Scanner (CZCS). Therefore satellite ocean colour monitoring on a regular bases only covers the latest three decennia [14].

With the introduction of photo-electric cells, in the early 1920s [15], the first underwater radiometers were constructed, although it would take another 50 years until under- and above water optical measurements were collected on a more regular base during oceanographic expeditions. With the arrival of sophisticated low-cost photo-detectors in the 1970s, several oceanographic institutes had their own dedicated optical instruments designed, from which most never passed the prototype stage. Due to the diversity in instrument design, with each a different number of spectral filters equipped and lacking general measuring protocols, no standard global ocean colour database could be established over those past years. Finally, next to SeaWiFS, the 1990s brought the oceanographic community off-the-shelf ocean colour devices with rigid measurement protocols [16] and a start was made to archive these multi- and hyper-spectral ocean colour data.

Since 1890, well before the introduction of the photo-electric cells, a colour comparator method was used to establish the colour of the sea, through Forel-Ule scale observations [17] [18]. The method and the colour comparator scale, which consisted of twenty-one tubes filled with mixtures of coloured chemical solutions, have been recently described by Wernand and Van der Woerd [3]. Besides Forel and Ule, the inventors of the scale, Krümmel [19], Luksch [20] and Von Drygalski [21], were amongst the first to use this colour comparator method at open sea. Krümmel performed observations during the plankton expedition of the Humboldt Society in 1889. At that time only the blue to blue-green part of the scale (scale numbers 1 to 11) was used to classify the colour of open water. An example of Krümmel's contoured sea colour map is shown in Figure 7.1. The data was collected in the Atlantic during the Plankton Expedition of 1889 and the colour of the sea was expressed as a percentage of a yellow potassium chromate solution added to a blue copper-sulphate solution. Luksch collected observations over eight years during the '*Pola*' expedition (1890-1898) in the Mediterranean, Aegean- and Red Sea and Von Drygalski performed observations during the Greenland Expedition of the Geographical Society of 1891-1893. Since 1890, the Forel-Ule scale became the most commonly used and most simple scale to determine, through comparison, the colour of seas, lakes and rivers.

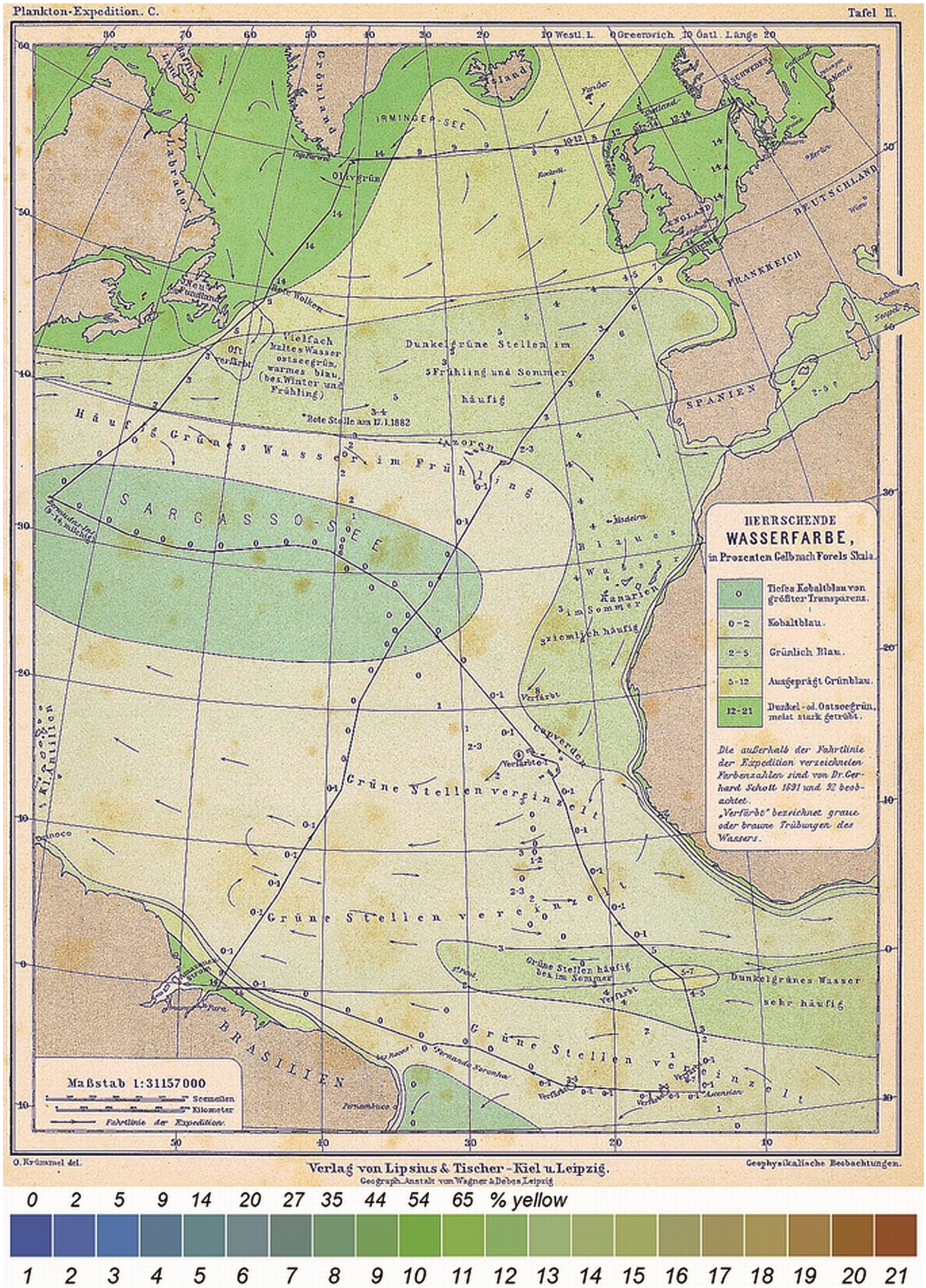


Figure 7.1 - Krümmel's contoured North Atlantic *FU*-map (1889). The sailing track of the steamship '*National*' is shown in black. The colour (Wasserfarbe) was indicated as a percentage of a yellow potassium chromate solution added to a blue copper-sulphate solution. The legend indicates the *FU*-scale colours 1 to 21.

Over the years only a limited number of geographical maps, based on interpolation of sets of Forel-Ule data, became available. The U.S. Navy Hydrographic Office published in the 1950s three atlases on marine geography, including Forel-Ule contours of the Sea of Japan [22], Korea [23] and Indochina [24]. A more comprehensive work in this field was conducted by Margaret Ann Frederick who presented her research in her 1970s master thesis ‘An Atlas of Secchi Disc Transparency Measurements and Forel-Ule Color Codes for the Oceans of the World’. In the thesis she presents contoured Forel-Ule maps for a number of seas and oceans [25]. Frederick had around 24,000 globally collected Forel-Ule observations to her disposal to create her contour maps on averaged sea colours, however, without any trend analysis. In a recent paper, Wernand and Van der Woerd [26] demonstrated that for the North Pacific Ocean significant decadal changes in all seasons can be detected between 1930 and 2000, based on an analysis of 17,171 *FU*-observations that are available for that ocean.

The aim of this paper is to improve the understanding of the links between climate and the marine ecosystems by an analysis of almost 'forgotten' global-wide collected ocean colour data. An analysis is presented of the temporal variation of ocean colour from 1889 untill the year 2000, based on a subset of 221110 globally collected *FU* observations. First the data selection and quality control procedures are described and a model is introduced that provides simple relations for the conversion from *FU*-scale number to Chlorophyll concentration. Subsequently the world-wide collected data are grouped in 28 seas and oceans and binned in 10 year intervals. The research focus is to detect and describe significant decadal variations in ocean colour and to establish if a significant trend on a timescale of a century is present for each of the 28 seas or oceans.

MATERIAL AND METHODS

The majority of *FU* observations was retrieved from oceanographic and meteorological databases archived by NOAA-NODC [27]. This dataset, extracted in 2007, contains, besides the *FU* index (coded 1 to 21), the ocean colour codes 31 to 37 that indicate a specific observed water colouring feature (see Table 7.1). Only data with an *FU* index were kept and three new attributes were added for each entry, indicating the meteorological season, the specific decade, and the sea area. The geographical naming follows the conventions of the U.S. Geological Survey (USGS) that is based upon the latitude and longitude at which the observation took place. This dataset contains 220440 observations collected from 1907 upto and including 1999.

From three historic expeditions, performed between 1889 and 1899, 670 observations were digitized and added to the NOAA-NODC dataset. The added *FU*-observations from before 1900 consisted of; 1) 89 observations from Krümmel's Plankton-Expedition in the North Atlantic in 1889, 2) 367 observations from Luksch '*Pola*' expeditions, collected from 1890 to 1898 in the Mediterranean, Aegean- and Red Sea and 3) 214 observations from Schott's German deep sea expedition on the steamer '*Valdivia*', collected from 1898 to 1899 in the North Sea, Atlantic, Indian Ocean, Red Sea and Mediterranean. During Von Drygalski's Greenland Expedition of the Geographical Society of 1891-1893, around 70 *FU* observations were collected in the North Sea, North Atlantic, Davis Strait and Baffin Bay. However, the bad quality of the printed map made it impossible to digitize these data.

Table 7.1 - Legend to the NODC colour codes.

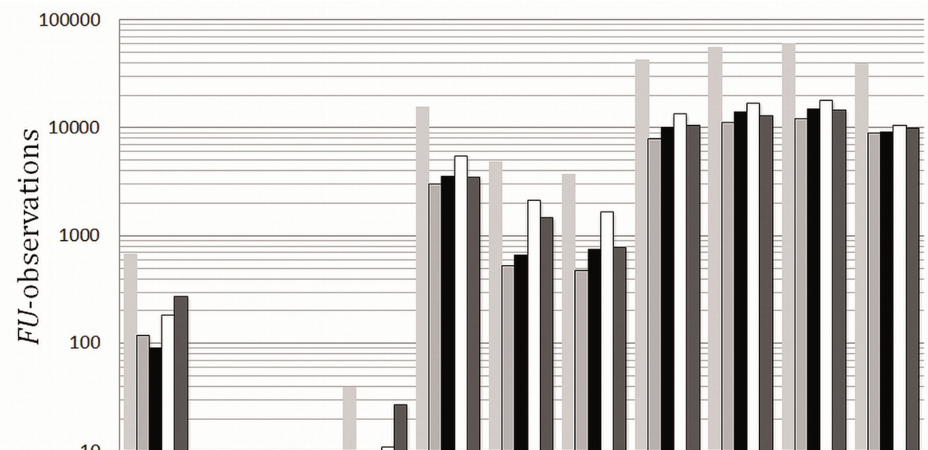
NODC code	Observed colour
1 to 21	Forel-Ule
31	Green
32	Blue
33	Grey
34	Red
35	Chalky
36	Brown
37	Luminescent

The re-formatted dataset is referred to as dataset-0 and contains 221110 *FU* globally collected observations of open water, lakes and rivers. Figure 7.2 shows a bar chart of the total number of *FU* observations collected within each decade and divided over the seasons. The 1889 to 1899 period, as an exception, covers eleven years to gain as much available information of the start period of ocean colour observation.

Subsequently, dataset-0 was differentiated into three geographical areas by applying Basin Masks (BM). The Basin Masks are used to filter out observations within land boundaries (lakes and rivers), and observations close (100 km or 500 km) to the coast. The Basin Masks were created and executed in ArcGIS 9.3 software [28] by means of the ArcGIS clip function.

First BM1 was created to extract data from dataset-0 free of observations within land boundaries like river and lake. This dataset is referred to as dataset-1 and contains 219839 sea observations.

Table 7.2 shows the distribution of the *FU*-observations per sea area with details on the total and seasonal numbers of *FU*-observations, also expressed as a percentage of the total. The definition of seasons follows the meteorological convention. In order to achieve a statistically significant trend analysis, only seas and oceans with more than one thousand *FU* observations were analysed in this paper. The selected oceans and seas are the Barents Sea, Bering Sea, East China Sea, Indian Ocean, Mediterranean, North- and South Atlantic, North- and South Pacific, Norwegian Sea, Pacific Coast, Philippine Sea, South China Sea, Sea of Japan, Sea of Okhotsk and the Yellow Sea.



	1889-1899	1900-1909	1910-1919	1920-1929	1930-1939	1940-1949	1950-1959	1960-1969	1970-1979	1980-1989	1990-1999
Total	670	1		39	15589	4798	3664	42327	55254	60036	38732
Winter	119			1	3022	531	480	7926	11364	12149	9023
Spring	92				3539	660	749	10227	13977	14998	9236
Summer	183	1		11	5512	2138	1657	13504	17010	18056	10557
Autumn	276			27	3516	1469	778	10670	12903	14833	9916

Figure 7.2 - The temporal distribution of the total number of 221110 *FU*-observations contained within dataset-0 for the period 1889 to 1999. Data is binned per season and per decade except for the first period of 11 years from 1889-99. Notice: the period 1900 to 1929 contain zero or a limited number of observations.

Second, BM2 was created to extract open sea observations from dataset-0, at a distance of more than 100 km off-coast, to avoid direct effects of anthropogenic pressure in the coastal zones like increased nutrient loading (eutrophication) or higher sediment loading by changes in land use or erosion, which would result in short-term and drastic colour changes, definitely influencing the open sea *FU* values. This dataset is referred to as dataset-2 and contains 61434 open sea observations. The last mask, BM3, was created to extract observations from dataset-0 at a distance of over 500 km from the coast to include the oceans, but at the same time avoid the influences of mixing with the differently coloured water of nearby seas. This dataset will be referred to as dataset-3 and contains 21971 open ocean observations.

An example of the shapes of the three data extraction masks is given in Figure 7.3. One must bear in mind that by clipping the data to the dimensions of the mentioned masks, the number of observations per sea area diminishes by roughly a factor of 4 in case of BM2 and a factor 10 in case of BM3. However, to establish a realistic colour of the bulk water of a sea or ocean, not influenced by its nearby coastal or surrounding seawater (with much higher *FU* numbers) this action is unavoidable. The data extraction masks, datasets name and the number of observations included in the dataset are summarized in Table 7.3.

Table 7.2 - The distribution of *FU*-observations contained within dataset-1. The table shows from left to right; the seas for which *FU* data was collected, its abbreviation, the total number of observations, the observations per season (Winter (W), Spring (Sp), Summer (S) and Autumn (A)) with the percentage of the total number of observations. Seas discussed in this article are in bold italic. Observations of the inland Caspian Sea (465 obs.) are filtered out using BM1.

Sea Area	Abr.	Total	W	W-%	Sp	Sp-%	S	S-%	A	A- %
Antarctica	AA	51	48	94.1	3	5.9	0	0	0	0
Atlantic Ocean	***AT***	**8161**	1318	16.2	1823	22.3	3090	37.9	1930	23.7
Arctic Ocean	ARO	1	0	0	0	0	1	100	0	0
Baltic	BAL	122	0	0	47	38.5	58	47.5	17	13.9
Barents Sea	***BAR***	**2651**	25	0.9	477	18.0	1741	65.7	408	15.4
Baffin Bay	BFB	5	0	0	0	0	4	80	1	20
Black Sea	BL	110	1	0.9	31	28.2	28	25.5	50	45.5
Bay of Biscay	BOB	17	2	11.8	3	17.6	7	41.2	5	29.4
Bering Sea	***BS***	**1750**	14	0.8	56	3.2	1645	94.0	35	2
Caribbean Sea	CB	700	179	25.6	158	22.6	210	30.0	153	21.9
Chukchi Sea	CS	50	0	0		0	50	100	0	0
East China Sea	***ECS***	**3432**	638	18.6	859	25.0	1122	32.7	813	23.7
Gulf of Alaska	GAK	279	1	0.4	75	26.9	179	64.2	24	9
Gulf of Mexico	GM	110	3	2.7	28	25.5	27	24.5	52	47.3
Greenland Sea	GRS	21	0	0	4	19.0	13	61.9	4	19.0
Indian Ocean	***INO***	**3446**	971	28.2	711	20.6	552	16.0	1212	35.2
Kara Sea	KRA	97	0	0	0	0	53	54.6	44	45.4
Mediterranean	***MED***	**1080**	163	15.1	155	14.4	366	33.9	396	36.7
North Sea	NS	56	4	7.1	9	16.1	22	39.3	21	37.5
Norwegian Sea	***NWS***	**1524**	27	1.8	277	18.2	1121	73.6	99	6.5
Pacific Coast	***PC***	**1842**	303	16.4	461	25.0	522	28.3	556	30.2
Pacific Ocean	***PAC***	**34611**	6281	18.1	7417	21.4	11077	32.0	9836	28.4
Philippine Sea	***PHS***	**106557**	24931	23.4	27115	25.4	27873	26.2	26638	25.0
Red Sea	RS	166	51	30.7	61	36.7	0	0	54	32.5
South China Sea	***SCS***	**3055**	760	24.9	889	29.1	813	26.6	593	19.4
Sea of Japan	***SJP***	**39198**	6432	16.4	10399	26.5	13371	34.1	8996	23
Sea of Okhotsk	***SOK***	**1393**	18	1.3	261	18.7	897	64.4	217	15.6
Yellow Sea	***YS***	**9354**	2244	24	1952	20.9	3323	35.5	1835	19.6
Total		**219839**	44414	20.2	53271	24.2	68165	31	53989	24.6

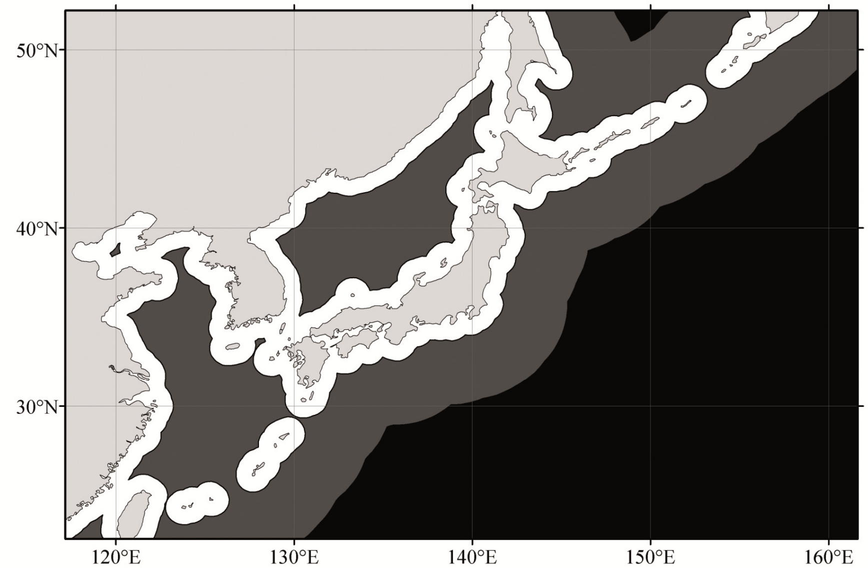


Figure 7.3 - Example (around Japan) of three defined masks to extract *FU*-observations; in white the BM1 mask starting at the land/sea boundary spreading over the whole sea with on top of this layer, in dark grey, BM2 starting at a distances of >100 km off land and on top of this layer BM3, a layer in black, starting at a distance of 500 km off land.

Table 7.3 - The number of *FU*-observations per dataset unmasked and obtained by the use of 3 data-extraction masks. Off-coast indicates the areas where *FU*-data were collected.

Mask	-	BM1	BM2	BM3
FU-Dataset	Dataset-0	Dataset-1	Dataset-2	Dataset-3
Off-Coast	+ lakes/rivers	0 km	>100 km	>500km
No. of Obs.	221110	219839	61434	21971

From dataset-1, a global map of the *FU*-colour distribution was established through an Inverse Distance Weighted interpolation [29], [30]. IDW interpolation explicitly implements the assumption that data collected at scattered points that are close to one another are more alike than those that are further apart. The IDW determines cell values by calculating a linearly weighted combination of nearby *FU*-observations. The weight is calculated by taking the inverse of the distance between the cell and *FU*-observation, raised to a power (usually equal to two). This power option controls the significance of known points on the interpolated values, based on their distance from the output point.

Datasets-2 and -3 are statistically analysed per sea area and per decade. Data were binned per decade to eliminate any influence of a yearly cycle in the colour of the sea. The results for the selected seas and oceans (given in bold-italic in Table 2) are described in section 3. The results of the statistical analyses for the other seas, extracted by means of the BM2 mask, are tabulated and presented in Annex A. The mean *FU* values of a sea ($\overline{FU}$), with upper- $U_{\overline{FU}}$ and lower $L_{\overline{FU}}$ bounds on mean, is calculated as follows. Consider a sample made up of *n* *FU*-observations denoted by (FU_1, FU_2, ..., FU_n). The arithmetic mean of this dataset, $\overline{FU}$, is defined as [31]:

$$\overline{FU} = \frac{1}{n} . \sum_{i=1}^{n} FU_i \qquad (7.1)$$

The standard deviation S(n-1) of this sample is defined as

$$S(n-1)^2 = \frac{1}{n-1} \sum_{i=1}^{n} (FU_i - \overline{FU})^2 \qquad (7.2)$$

S is needed to calculate the standard error of the mean ($SE_{\overline{FU}}$):

$$SE_{\overline{FU}} = \sqrt{\frac{S(n-1)^2}{n}} \qquad (7.3)$$

The lower bound on mean, corresponding to the lower bound of the confidence interval of the mean is defined by

$$L_{\overline{FU}} = \overline{FU} - SE_{\overline{FU}} . z \qquad (7.4)$$

where we have taken z = 1.96 for a confidence interval of 95% [32]. The upper bound on the mean ($U_{\overline{FU}}$), is calculated accordingly (sign changes to +).

MODELLING

An *FU* colour change from a lower to a higher scale index indicates a greening of seawater, caused by the presence of light-absorbing substances like chlorophyll or CDOM. In order to simulate the relation of chlorophyll or CDOM and the *FU* index, the HydroLight-EcoLight [33] bio-optical modelling software was adopted. This model is solves the radiation-transfer equations of light in natural waters and computes radiance or irradiance distributions and derived quantities, like remote sensing reflectance R_{RS} and *FU* [34]. By varying the model's input parameters, like chlorophyll, CDOM or mineral concentrations, a relation can be established between concentrations and R_{RS} or the *FU* index. HydroLight-EcoLight employs mathematically sophisticated invariant imbedding techniques to solve the radiative transfer equation. Details of this solution method can be found in Mobley's book on *Light and Water* [35] and in his 'Comparison of numerical models for the computation of underwater light fields' [36]. Both models, HydroLight and EcoLight, generate the same output. With the difference that HydroLight computes the full 3D-radiance distribution, whereas EcoLight computes only irradiances.

Two simulation runs were made to establish the influence of either chlorophyll or CDOM on the colour of seawater, *i.e.*, on the remote sensing reflectance R_{RS} and on the *FU* number. For modelling the oceanic waters, the new IOP model "NEW" case 1, integrated in the modelling software, was used. This model is based on a combination of i) the results of modelled particle absorption as given by Bricaud *et al.* 1998 [37] and ii) the results of modelled particle absorption more recent publication by Morrison and Nelson [38] and Vasilkov *et al*. [39]. The "NEW" case 1 two-component IOP model consists of pure water [40] (component 1) and chlorophyll bearing particles with co-varying CDOM and detritus (component 2). One of the model's output parameters is the remote sensing reflectance $R_{RS}(\lambda)$, which was automatically convoluted with CIE1932 curves into a chromaticity coordinate set *x, y* and accordingly into a *FU* scale number (see [3] for more details). In this way, a relation between chlorophyll and *FU* could be established for oceanic waters that is used in the trend analysis to convert *FU* back into a chlorophyll concentration.

For seas the Case 2 water generic four-component IOP model was used, where component 1 is pure water, component 2 represents chlorophyll bearing particles, component 3 is CDOM (given as absorption in m^{-1} at 440 nm, a_{440}), not co-varying with chlorophyll bearing particles and component 4 represents the mineral particles. To simulate the chlorophyll- and mineral concentration in open sea water, they were set respectively to $0.1 mgm^{-3}$ and 0 or $0.2 gm^{-3}$. The CDOM absorption (a_{440}) was varied between 0.01 and $1.0 m^{-1}$. Again, the calculated remote sensing reflectance $R_{RS}(\lambda)$ was convoluted with CIE1932 curves into a chromaticity coordinate set *x, y* and into a *FU* scale number [3]. In Table 7.4 the EcoLight model parameters, including the scattering and absorption properties of the constituents, are tabulated for both models.

Table 7.4 - Specifications for atmosphere, inherent optical properties and concentration ranges of the four components (C1 to C4) in the Ecolight model.

Ecolight IOP model specification	**C 1 pure water**	**C 2 chlorophyll (mgm^{-3})**	**C 3 CDOM (m^{-1})**	**C 4 minerals (gm^{-3})**
Case 1 - ocean chlorophyll dominated	Pope & Fry	0.1 to 40	Co-varying with component 2	-
Case 2 - ocean CDOM dominated	Pope & Fry	0.1	0 to 1	0 or 0.2
Specific absorption	-	mass specific a - apstarchl.txt	astar (waven) = 1.0* exp [-.0140*(waven - 440.)]	astarmin_calcareoussand
Specific scattering	-	b = 0.4070 X^(0.7950) * (660/waven)^(1.0000) (Loisel/Morel)	-	bstarmin_calcareoussand
Phase function	-	Morel small particles Case1 ≈ bb/b = 0.05	-	Morel Small Particle Case 1 ≈ bb/b = 0.05
Sky model	Normalised radiance by RADTRANX (Harrison and Coombes). Diffuse and direct sky by RADTRANX (Kasten and Czeplak)			
Parameters	Cloud Fraction = 0, Solar Zenith = 50^0, Press = 29.9 in.merc, Day of Year = mean earth-sun distance used, Air Mass Type = 1, Rel. Hum. = 80%, Wind Speed = $5ms^{-1}$, Visibly = 15km, Total Ozone = 300 Dobson units, Aerosol Opt. Thickness = 0.261			

RESULTS

Figure 7.4 and Figure 7.5 show the geographical positions of the observations extracted under respectively BM3 (>500km) and BM2 (>100km). Note that in Figure 7.4 the 500-km boundaries (in white) also are applied around islands in the major oceans, to avoid any terrestrial influence on the mean colour of the ocean. Clearly, the parts of the globe that are under-sampled are mainly found in the Southern Hemisphere.

For further analysis the Atlantic and Pacific were split into a northern (NA, NP) and an equatorial (EA, EP) part, indicated in both figures by red lines. The southern parts of both oceans were not analysed. From the South Atlantic no data were available for the period 1900 to 1959 and the remaining periods were highly under-sampled. For the South Pacific the period 1950 to 1999 contains observations, however, only the last two decades were reasonably sampled. The Indian

Ocean has been analysed in one part. The selected and analysed seas are limited to the Barents Sea, Bering Sea, East China Sea, Mediterranean, Norwegian Sea, Pacific Coast, Philippine Sea, South China Sea, Sea of Japan, Sea of Okhotsk, and Yellow Sea.

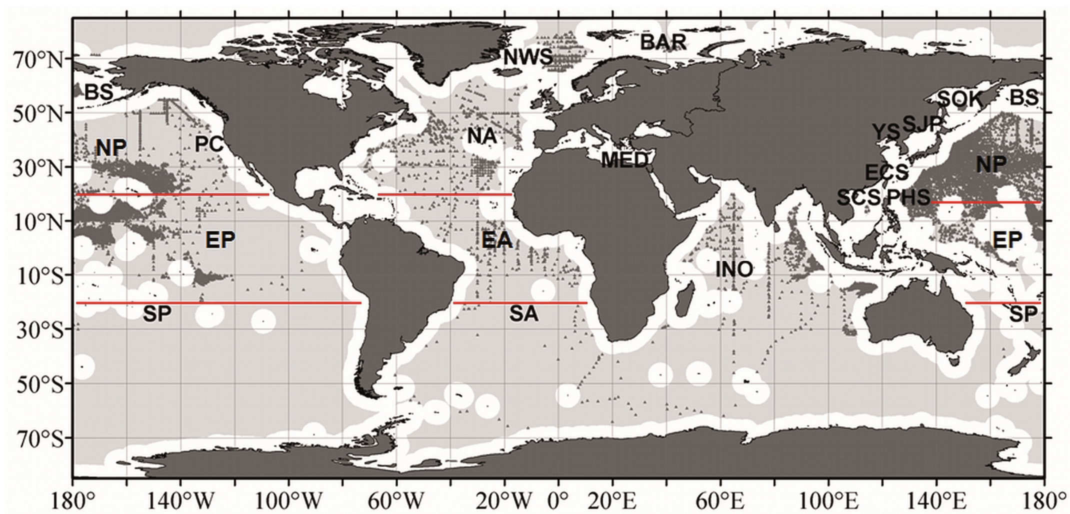


Figure 7.4 - The positions of the 21971 *FU*-observations extracted 500 km off-coast with the BM3 mask. Oceans and seas are indicated by abbreviations as mentioned in Table 7.2. Red lines indicate the division of north and equatorial regions.

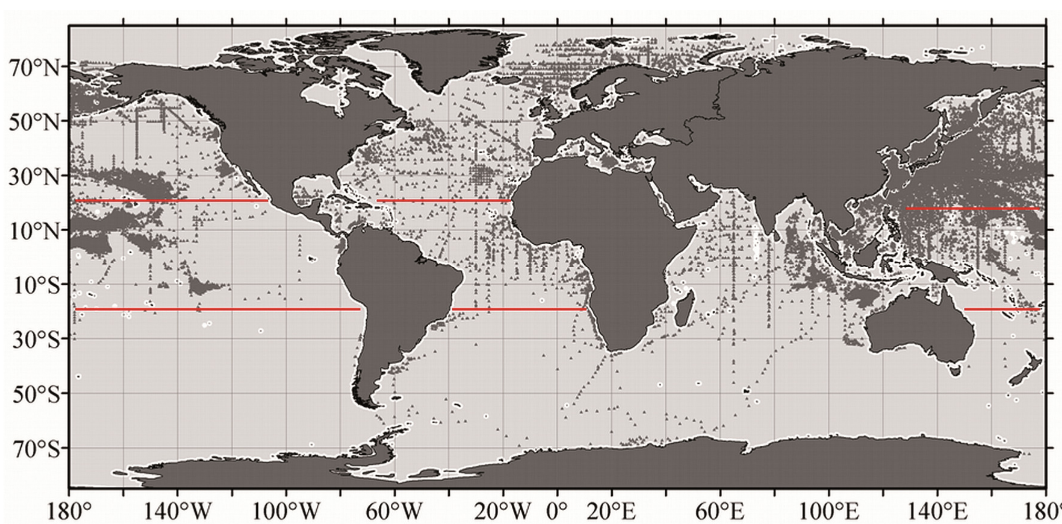
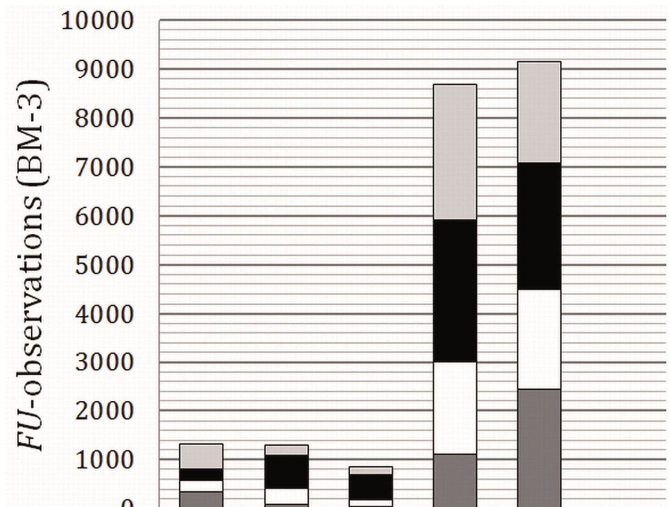


Figure 7.5 - The positions of 61434 *FU*-observations extracted 100 km off-coast with the BM2 mask. Red lines indicate the division of north and equatorial regions.

Although the Mediterranean has a limited number of 237 observations, it was found to be important to analyse this sea, for which data were already collected at the end of the 19th century. The statistical analysis is performed for each season and for all seasons.



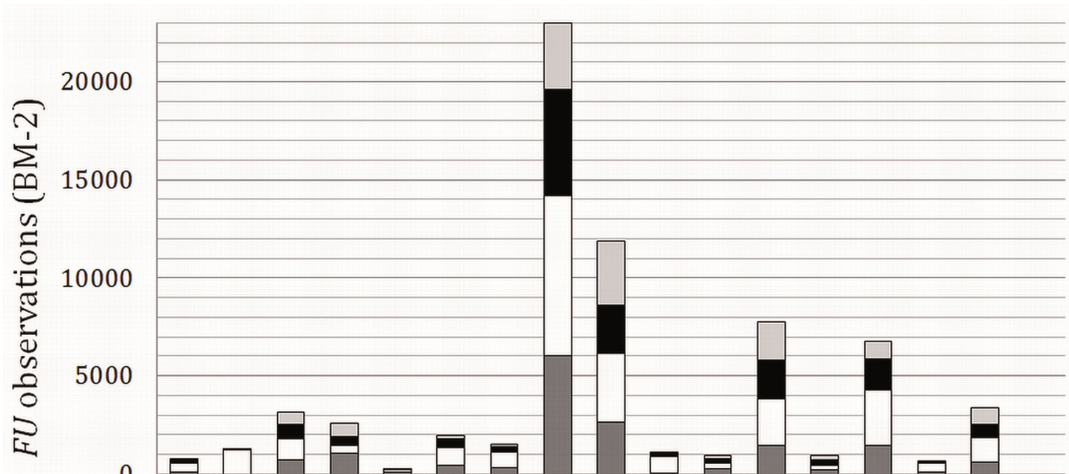
	INO	NA >20N	Eq.A >20S <20N	NP >20N	Eq.P >20S <20N	Sum
Selected	1314	1304	851	8681	9152	21302
n-Autumn	506	212	160	2769	2082	5729
n-Summer	237	666	521	2910	2572	6906
n-Spring	221	327	129	1889	2047	4613
n-Winter	350	99	41	1113	2451	4054

Figure 7.6 - The selected 21302 *FU*-observations extracted under the ocean mask BM3, binned per sea area and per season.

Figure 7.6 shows the number of available *FU* observations of the selected oceans extracted under BM3 (> 500 km off-coast). Because the statistical analysis is also performed for each season, the number of seasonally binned observations is also given. In Figure 7.7, these numbers are provided for all seas that were extracted under BM2 (> 100 km off-coast).

In order to understand the oceanic decadal trend analysis of chlorophyll, we first present the Ecolight modelling results of the conversion between *FU* and chlorophyll concentration (see 'FU modelling').

After that the statistical analysis of the oceans and seas of all observations from 1889 to 2000 is presented (see 'Century averaged ocean colour)) followed by a trend analysis of the same dataset, binned into decades, (see 'Decadal averaged regional chlorophyll and ocean colour').



	BAR	BS	ECS	INO	MED	NA >20N	Eq.A 20S-20N	NP >20N	Eq.P 20S-20N	NWS	PC	PHS	SCS	SJP	SOK	YS	Sum
Selected	709	1251	3129	2597	237	1952	1507	22963	11871	1084	926	7742	927	6740	595	3351	67581
n-Winter	6	6	586	712	33	159	135	3386	3270	24	159	1948	202	891	3	821	12341
n-Spring	174	37	776	457	13	428	239	5375	2480	184	234	2002	261	1552	48	681	14941
n-Summer	438	1196	1026	389	73	926	783	8160	3459	808	240	2315	254	2847	433	1222	24569
n-Autumn	91	12	741	1039	118	439	350	6042	2662	68	293	1477	210	1450	111	627	15730

Figure 7.7 - The selected 67581 *FU*-observations extracted under the basin mask BM2, binned per sea area and per season.

FU MODELLING

The two-component case 1 water model was fed by varying chlorophyll concentrations, the four-component case 2 water model was fed by varying CDOM a_{440} between 0 and 1 m^{-1} with fixed values for components three and four mimicking open sea bio-optical values. For each run the EcoLight modelling software output parameters are the spectral remote sensing reflectance $R_{RS}(\lambda)$, as shown in Figure 7.8, and the *FU* number shown in Figure 7.9.

Figure 7.8a shows R_{RS} spectra generated by the case 1 model with varying chlorophyll, Figure 7.8b shows R_{RS} spectra generated by the case 2 model with varying CDOM absorption and chlorophyll and mineral concentrations set to 0. Figures 7.8c and 7.8d show R_{RS} spectra generated by the case 2 model with varying CDOM and chlorophyll set to 0.1mgm^{-3} and minerals set to 0 and to 0.2gm^{-3} respectively.

From Figure 7.9A we see that a change in chlorophyll concentration from 0.1 to 1mgm^{-3} results in a shift in *FU* index from 1 to 4. An exponential fit to the modelresults provides the following relation, with clorophyll in mgm^{-3}:

$$Chl = 0.061e^{0.666FU} \quad (7.5)$$

This relation takes into account that in the open ocean chlorophyll bearing particles are co-varying with CDOM and detritus, whereas detritus contributes only 5% to 20% to the non-water absorption coefficient [41]. Eq. 7.5 is used to transform the acquired $\overline{FU}$ into an average chlorophyll concentration per decade for oceanic regions.

For the seas, results will be presented as $\overline{FU}$ only, because they, compared to the open ocean, generally have more optically active constituents and therefore, no single relation between *FU* and Chl can be established. However, to demonstrate the influence of CDOM, on the *FU* scale index we present case 2 model results for 3 modelled parameter settings. The parameter settings are identical to the settings used to generate the results in Figures 7.8b, 7.8c and 7.8d.

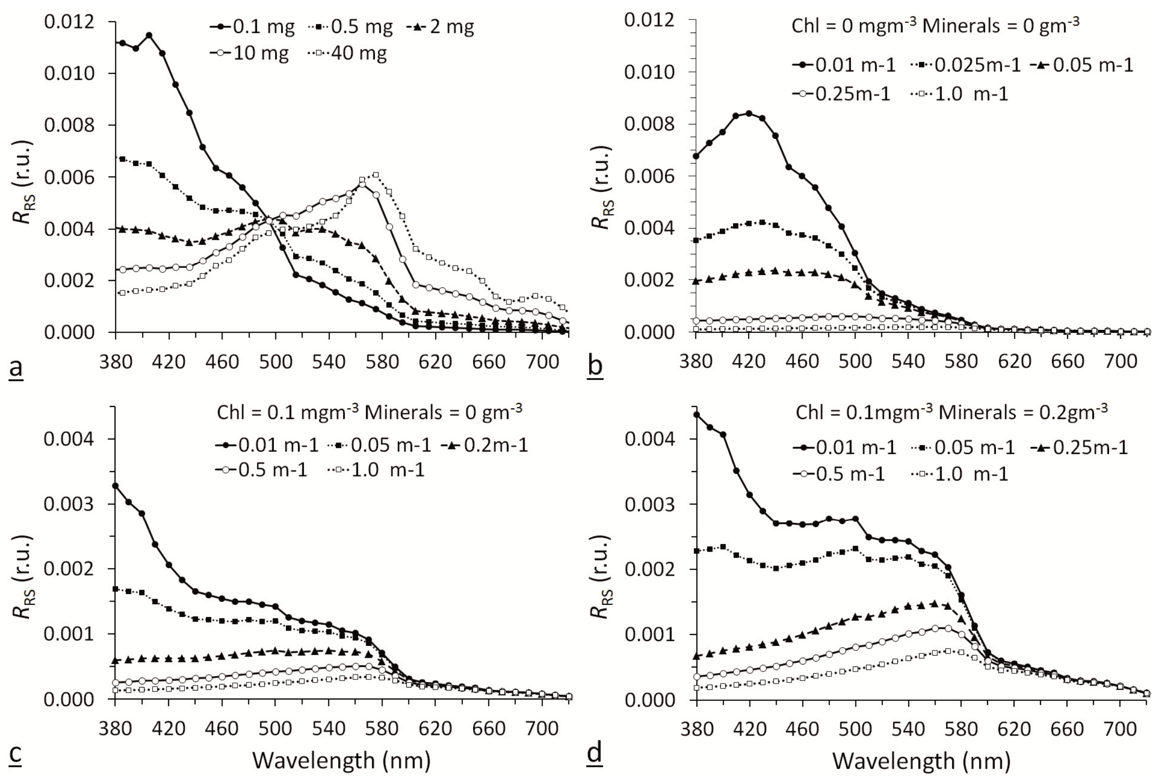


Figure 7.8 - Examples of the Ecolight modelled R_{RS} (sr^{-1}) for case 1 waters (panel a) and case 2 waters (panels b, c and d) with variable composition (see also Table 4). In panel (a) only the input chlorophyll concentration is varied between 0.1 and 40 mgm^{-3}. For case 2 waters the input $CDOM_{440}$ absorption (a_{440}) is varied between 0.01 and 1.00 m^{-1} with chlorophyll and mineral concentration of both 0 (panel b), fixed chlorophyll concentration of 0.1mgm^{-3} and a mineral concentration of 0 (panel c) and fixed chlorophyll concentration of 0.1mgm^{-3} and a mineral concentration of 0.2gm^{-3} (panel d). From these R_{RS} spectral signatures the chromaticity coordinate set and *FU* number were calculated.

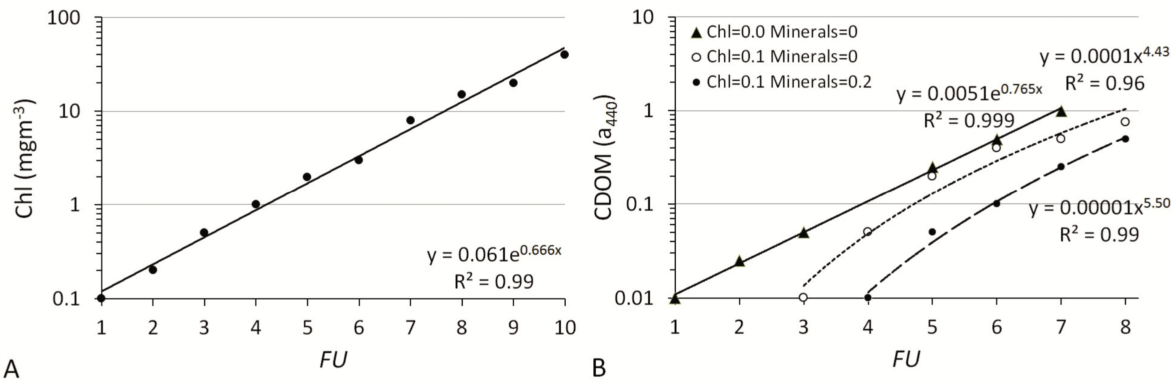


Figure 7.9 - Chlorophyll concentration and CDOM attenuation at 440 nm as a function of *FU*-number. The *FU*-numbers were derived from the Ecolight R_{RS} spectra. In the left panel (a), chlorophyll was varied from 0.1 to 40mgm^{-3} with a resulting span of *FU*1 to *FU*10. For case 2 waters (panel b), the relationship between CDOM and *FU* was calculated for three combinations of chlorophyll concentration (0 or 0.1mgm^{-3}) and mineral concentration (0 or 0.2gm^{-3}).

From Figure 7.9B we see that a change in CDOM absorption from 0.01 to 0.1 m^{-1} results in a shift over the first 4 *FU* scale colours in case that only CDOM, next to water itself, is the only absorber of light. Through an exponential fit $CDOM_{440}$ absorption can be calculated with a coefficient of determination R^2=0.999 according to

$$CDOM_{440} = 0.0051 * e^{0.765*FU} \tag{7.6}$$

Setting both the background chlorophyll concentration to 0.1mgm^{-3} and the mineral concentration to zero, the *FU* numbers change from *FU*=3 to *FU* ≈ 8 (open circles in Figure 7.9b), which implies that the fixed low chlorophyll concentration already colours the water to *FU*=3. This outcome is somewhat different from the case 1 modelling results, shown in Figure 7.9A, where the same chlorophyll concentration corresponds to *FU*=1. However, we must bear in mind that in the case 1 model, different from the case 2 model, CDOM is co-varying with chlorophyll. Through a power law fit $CDOM_{440}$ absorption can be calculated with a coefficient of determination R^2=0.96 according to

$$CDOM_{440} = 0.0001 * FU^{4.43} \tag{7.7}$$

In the last set of results of the case 2 Ecolight model, the background chlorophyll concentration was set to 0.1mgm^{-3} and the mineral concentration was set to 0.2gm^{-3}. For *FU* numbers between 4 and 8 the $CDOM_{440}$ absorption can be calculated with a coefficient of determination R^2=0.99 according to

$$CDOM_{440} = 0.00001 * FU^{5.50} \tag{7.8}$$

The above CDOM-*FU* relations are presented to help with the interpretation and comparison of a derived $\overline{FU}$ in seas for which more background knowledge of the area specific inherent optical properties are available.

In the following we show the significance, *i.e.* the accuracy and applicability, of the here presented *FU* scale observations by visualizing i) an overall (1889-1999) monthly $\overline{FU}$ and by ii) visualizing an overall monthly chlorophyll concentration using Eq. 7.5. An example of the applicability of the binned *FU* scale observations and their conversion to chlorophyll concentration is given in Figure 7.10.

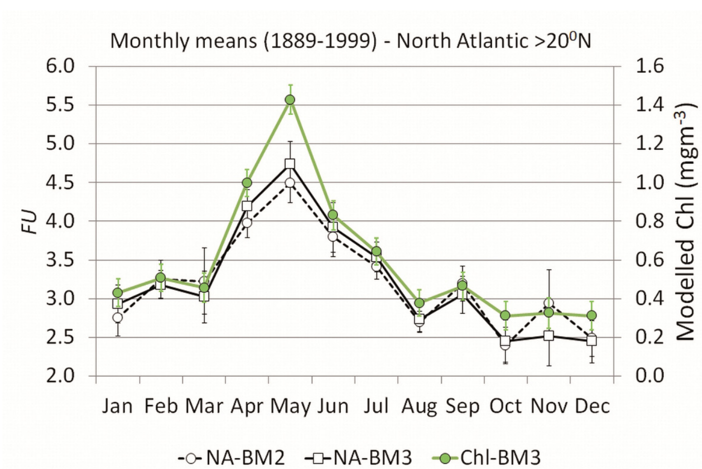


Figure 7.10 - Representation of North Atlantic monthly $\overline{FU}$ and chlorophyll. The BM2 (circles) and BM3 (squares) extracted *FU* data with error bars show the same pattern and reveal the North Atlantic spring bloom. On the secondary axes, indicated with green line/circles, the modelled chlorophyll (see Eq. 7.4) with error bars is shown.

North Atlantic data, collected between 1899 and 1999, were extracted under the BM3 and BM2 mask to reveal possible divergence between both datasets, as the latter could be effected by coastal phenomena influencing the colour of the sea. The number of observations extracted under BM2 accounts for twice the number extracted under BM3. The data were converted to chlorophyll by Eq. 7.5 and the monthly $\overline{FU}$ and chlorophyll were calculated. A similar result was found for both the analysed datasets, with an identified *FU* maximum (spring bloom) in May. Calculated chlorophyll (BM3) shows a concentration of around 1.4mgm^{-3} in May, which is in good agreement with North Atlantic bloom values mentioned in literature [42].

From the above described findings, we conclude that *FU* is a good proxy for chlorophyll in the open ocean. Besides water itself, chlorophyll, *i.e.* phytoplankton, gives the ocean its colour [43]**.** However, we must bear in mind that next to chlorophyll the non-covarying CDOM, through absorption, can have a similar influence on the colour of the sea and therefore on *FU*.

CENTURY AVERAGED OCEAN COLOUR

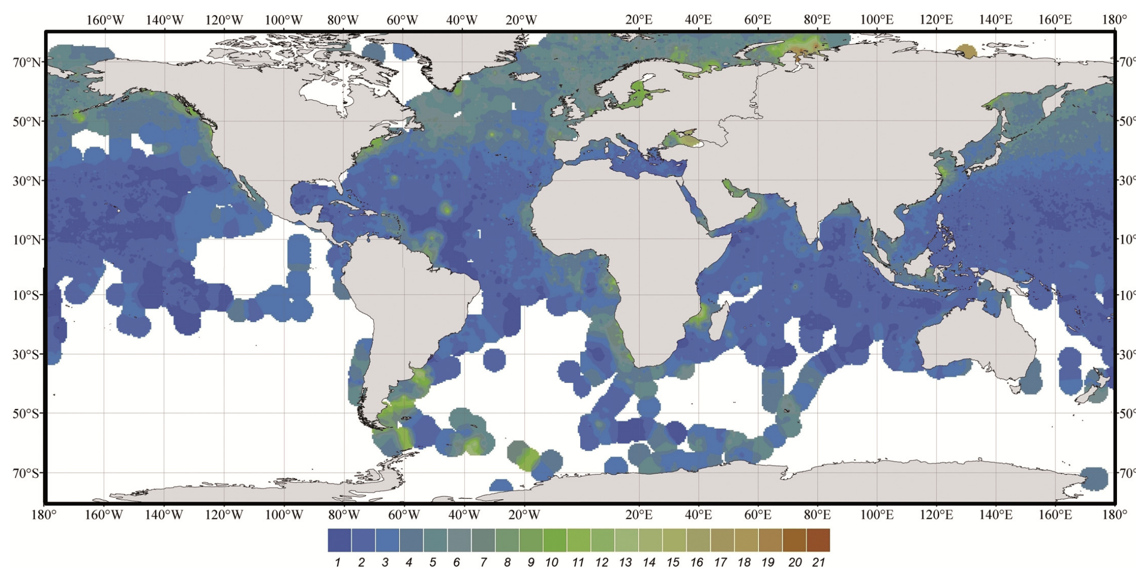


Figure 7.11 - An global IDW interpolation of BM1 clipped *FU* observations. The weight is set to a power of 2. The search radius is set to 4 degrees with an output grid size of 0.5 degrees. Data collection period covers 1889 to 1999.

To establish a global view of the *FU* data collected between 1889 and 1999, all observations contained within dataset-1 were interpolated according to the IDW technique. The Inverse Distance Weight function was set to a power law of index 2**.** The search radius, that limits the number of *FU* observations used for calculating each interpolated *FU* value, was set to respectively 2.5 and 4 degrees with an output grid size of 0.5 degrees. The difference between results of interpolation using a search radius of 2.5 and 4 degrees turned out to be negligible, although for under-sampled seas the applied interpolation technique results in *FU* values for areas where no observation were performed. A map of IDW interpolated *FU* values, with a search radius of 4 degrees, is presented in Figure 7.11. The southern oceans, highly under-sampled, are shown in white.

A first analysis of Figure 7.11 shows that the lowest *FU* numbers are found in the Equatorial Pacific and the Indian Ocean (*FU*<2) and in the Equatorial Atlantic (*FU*<3). Note the extreme high *FU* values (16 to 21) east of the Ob and Yenisei estuaries in the Kara Sea (75^0N, 70^0E), most likely caused by extremely high CDOM values [44] . Also in the Baltic, where CDOM is the major light absorber [45], *FU* numbers of around 14 are encountered. The Atlantic shows increasing *FU* values (up to *FU*=5) towards higher latitudes caused by the influence of more extensive phytoplankton blooms.

Table 7.5 - Results of the statistically analysed observations collected in selected oceans and seas between 1889 and 1999. Presented in the columns below the ocean/sea abbreviation is the number of observations followed by respectively the mean $\overline{FU}$ with lower- $L_{\overline{FU}}$ and upper bound $U_{\overline{FU}}$ on mean for all seasons and per season. The two masks under which data was filtered are indicated in the second row.

	Sea	***BAR***	***BS***	***ECS***	***INO***	***MED***	***NA***	***EA***	***NP***	***EP***	***NWS***	***PC***	***PHS***	***SCS***	***SJP***	***SOK***	***YS***
	Mask -BM	**2**	**2**	**2**	**2**	**2**	**3**	**3**	**3**	**3**	**2**	**2**	**2**	**2**	**2**	**2**	**2**
All	n	709	1298	3129	1314	237	1304	851	8681	9152	1084	926	1238	1092	7025	595	3352
	$\overline{FU}$	**5.8**	**4.8**	**4.4**	**1.7**	**2.6**	**3.5**	**2.5**	**2.4**	**1.6**	**5.1**	**2.3**	**2.5**	**2.9**	**3.5**	**4.3**	**4.2**
	$L_{\overline{FU}}$	5.7	4.7	4.3	1.7	2.5	3.4	2.5	2.4	1.6	5.0	2.2	2.4	2.8	3.5	4.2	4.2
	$U_{\overline{FU}}$	6.0	4.8	4.5	1.8	2.7	3.6	2.6	2.4	2.0	5.2	2.4	2.5	2.9	3.5	4.4	4.3
N-Winter S-Summer	n	6	6	586	350	33	99	41	1113	2451	24	159	2722	238	936	3	821
	$\overline{FU}$	**3.7**	**5.8**	**5.4**	**1.6**	**3.2**	**2.9**	**2.6**	**2.3**	**1.6**	**3.4**	**2.3**	**2.5**	**3.2**	**3.4**	**4.7**	**4.8**
	$L_{\overline{FU}}$	2.6	4.2	5.1	1.6	2.9	2.8	2.2	2.2	1.6	2.8	2.1	2.4	3.0	3.4	1.8	4.6
	$U_{\overline{FU}}$	4.8	7.5	5.7	1.7	3.5	3.1	3.1	2.3	1.7	4.0	2.5	2.5	3.4	3.5	7.5	5.0
N-Spring S-Autumn	n	174	39	776	221	13	327	129	1889	2047	184	234	3340	305	1623	48	681
	$\overline{FU}$	**6.7**	**4.3**	**4.6**	**1.8**	**3.3**	**4.3**	**2.3**	**2.6**	**1.4**	**4.8**	**1.9**	**2.7**	**2.7**	**4.0**	**5.2**	**5.0**
	$L_{\overline{FU}}$	6.2	4.0	4.4	1.7	2.0	4.1	2.1	2.5	1.4	4.5	1.8	2.7	2.6	4.0	4.8	4.8
	$U_{\overline{FU}}$	7.2	4.7	4.8	1.9	4.6	4.5	2.4	2.7	1.5	5.1	2.0	2.8	2.8	4.1	5.5	5.2
N-Summer S-Winter	n	438	1241	1026	237	73	666	521	2910	2572	808	240	3991	301	2964	433	1223
	$\overline{FU}$	**5.4**	**4.8**	**3.8**	**1.7**	**2.7**	**3.4**	**2.6**	**2.9**	**1.6**	**5.2**	**2.6**	**2.3**	**2.8**	**3.3**	**4.3**	**3.6**
	$L_{\overline{FU}}$	5.2	4.7	3.7	1.6	2.5	3.2	2.5	2.9	1.5	5.1	2.3	2.2	2.6	3.2	4.2	3.5
	$U_{\overline{FU}}$	5.6	4.8	3.9	1.8	3.0	3.5	2.7	3.0	1.6	5.3	2.8	2.3	3.0	3.3	4.4	3.7
N-Autumn S-Spring	n	91	12	741	506	118	212	160	2769	2082	68	293	2328	248	1502	111	627
	$\overline{FU}$	**6.6**	**5.7**	**4.2**	**1.8**	**2.3**	**2.8**	**2.5**	**1.6**	**1.7**	**5.1**	**2.5**	**2.4**	**2.8**	**3.4**	**4.1**	**3.8**
	$L_{\overline{FU}}$	6.3	4.7	4.1	1.7	2.1	2.6	2.3	1.8	1.6	4.7	2.3	2.4	2.7	3.4	3.9	3.6
	$U_{\overline{FU}}$	7.0	6.6	4.4	1.9	2.4	3.0	2.7	1.9	1.7	5.5	2.7	2.5	3.0	3.5	4.3	4.0

From all data, extracted under either BM3 or BM2, the mean $\overline{FU}_{1889\text{-}1999}$ per sea area with lower- $L_{\overline{FU}}$ and upper bound $U_{\overline{FU}}$ on mean (Eq. 7.1 to 7.4) were calculated. Results of this analysis are presented in Table 7.5. The used data extraction basin masks are indicated.

The results of Table 7.5 show, similar to the IDW interpolation of Figure 7.11, that the Equatorial Pacific and Indian Ocean are the bluest oceans of our globe with a mean $\overline{FU}$ of 1.6 and 1.7, respectively. With the results of Table 7.5 one can classify and rank the oceans and greater seas in terms of their mean $\overline{FU}$ colour, presented in Figure 7.12. This figure shows that in the 20th century the North Atlantic Ocean has been the greenest ocean of our planet, while the Barents Sea was the greenest open sea of all.

In order to support these classifications, with recently collected global data (> the year 1999), Figure 7.13 shows examples of an entire MODIS mission composite (4 July 2002 to 30 Jun 2010) for the CDOM index [46] and chlorophyll-*a* concentration.

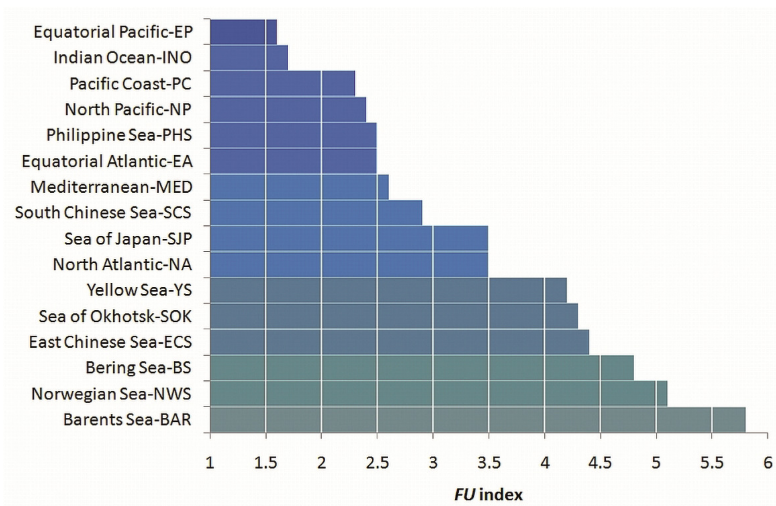


Figure 7.12 - Representation of the oceans and seas identified and arranged in terms of their $\overline{FU}$ colour as calculated from all available observations extracted under BM2 or BM3 (see Table 7.4). The Barents Sea is the most greenish sea (bottom) and the Equatorial Pacific is the most bluish ocean (top).

Note: In case 1 waters a 'mean' relationship exists between the CDOM content and the chlorophyll concentration, anomalies in this relation, for both case 1 and case 2 waters are given by this so-called CDOM index Φ [46].

In the hyper-oligotrophic Equatorial Pacific gyre [47], located within the greater white box, we see a Φ<1 and very low chlorophyll concentrations, that are expected in blue oligotrophic oceans (around 0.02mgm^{-3}). Within the smaller white box, indicating the Barents Sea, we see a CDOM index around 3.5 and chlorophyll values around 5mgm^{-3} colouring the sea green. Areas with an increasing CDOM index and or increasing chlorophyll concentration (Figure 7.13) are generally compatible with an increasing $\overline{FU}$ index (Figure 7.11).

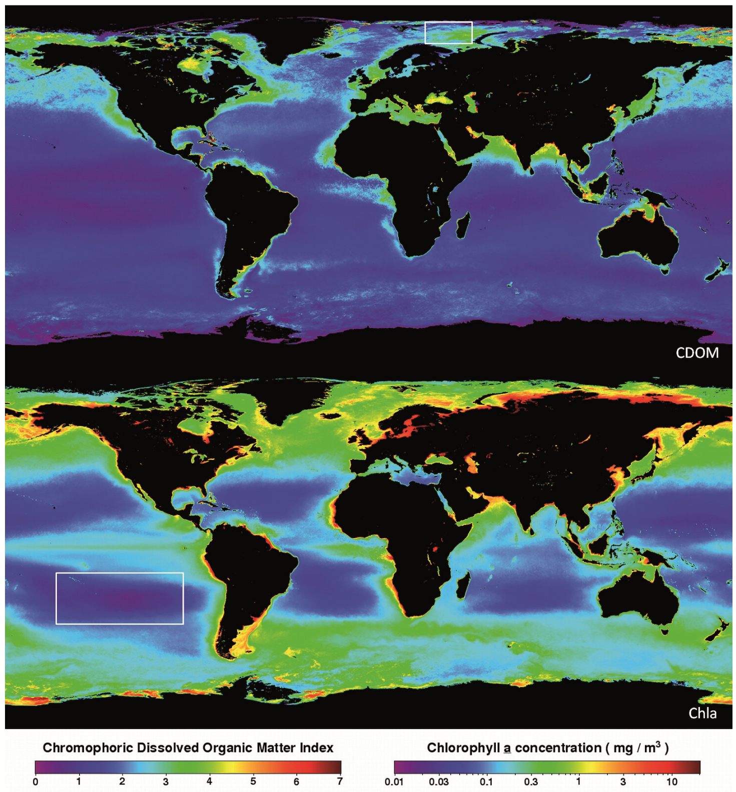


Figure 7.13 - An entire MODIS mission composite map of the CDOM Index and chlorophyll-a concentration (4 July 2002- 30 Jun 2010). The map shows a CDOM index<0.5 with the lowest oceanic chlorophyll concentrations of ≈ 0.02mgm^{-3} in the South Pacific (white box left). The small white box at the top indicates the open water of the Barents Sea with a CDOM index ≈ 3.5 and chlorophyll concentrations ≈ 5mgm^{-3}. Source: level 3 browse, http://oceancolor.gsfc.nasa.gov/

DECADAL AVERAGED REGIONAL CHLOROPHYLL AND OCEAN COLOUR

To establish the influence of the Basin Mask on the decadal trend analysis for open ocean water, we compared the results of dataset-2 (BM2) and dataset-3 (BM3). Because the conversion from *FU* index to chlorophyll concentration does depend on the CDOM absorption, only oceanic waters with a CDOM index Φ<2.5 were converted with Eq. 7.5. See also the global CDOM composite in Figure 7.13.

For the remaining seas, as indicated in bold in table 7.2, we applied the trend analyses on BM2 extracted data. For all presented data, per sea or per ocean, the overall trend covers the whole period of data collection. The least-squares regression lines, indicated by a full blue or green line, indicate either a bluing or greening of the ocean/sea under investigation.

For the oceans bluing/greening means decrease/increase in chlorophyll, for the rest of the sea this can mean a decrease/increase in $\overline{FU}$, which can either mean a decrease/increase in chlorophyll or CDOM or a combination of both.

In the next paragraphs, for the sea areas shown in Table 7.5, the results of our statistical analysis (Eq. 7.1 to 7.5) are presented per decade per sea area. In some cases, the BM2 extracted data is enclosed within the boundary of a neighbouring sea or ocean, hence a second data selection was needed, executed with the ArcGIS data selection tool, to exclude overlapping data. The total number of extracted *FU* observations per sea or ocean can therefore be slightly different from the number of observations given in Table 7.2 and Figure 7.7. Data extracted under the BM3 mask concern only the oceans, data extracted under the BM2 mask concern both oceans and world seas.

Oceans

In Figure 7.14 the results of the statistical analysis are presented for the Atlantic and Pacific Ocean and in Figure 7.15 for the Indian Ocean, per decade between 1889 and 1999. The $\overline{FU}$ (Eq. 7.1 to 7.4) has been converted to a chlorophyll concentration according to Eq. 7.5 with lower and upper bound (95% confidence interval). The left part of both figures are based on data extracted under the BM2, the right part of the figure are based on data extracted under BM3. The number of observations per decade is indicated below each graph. The trend line with regression coefficients, where *y* is the chlorophyll concentration in mgm^{-3} and *x* is the Decadal Number DN (1889-99=1, 1990-99=11), and the coefficient of determination R^2 and the statistical significance *p* are indicated below the trend line at the bottom of each graph.

The Northern- and Equatorial Atlantic show a similar greening trend for both BM2 and BM3. In the last decade of the 19th century the average NA surface chlorophyll concentration amounts to 0.18mgm^{-3}, whereas last decade of the 20th century shows a value of 0.5mgm^{-3}. The overall trend shows an average growth (BM2, BM3) of 0.046mgm^{-3} per decade. The EA shows a smaller averaged chlorophyll growth of 0.029mgm^{-3} per decade.

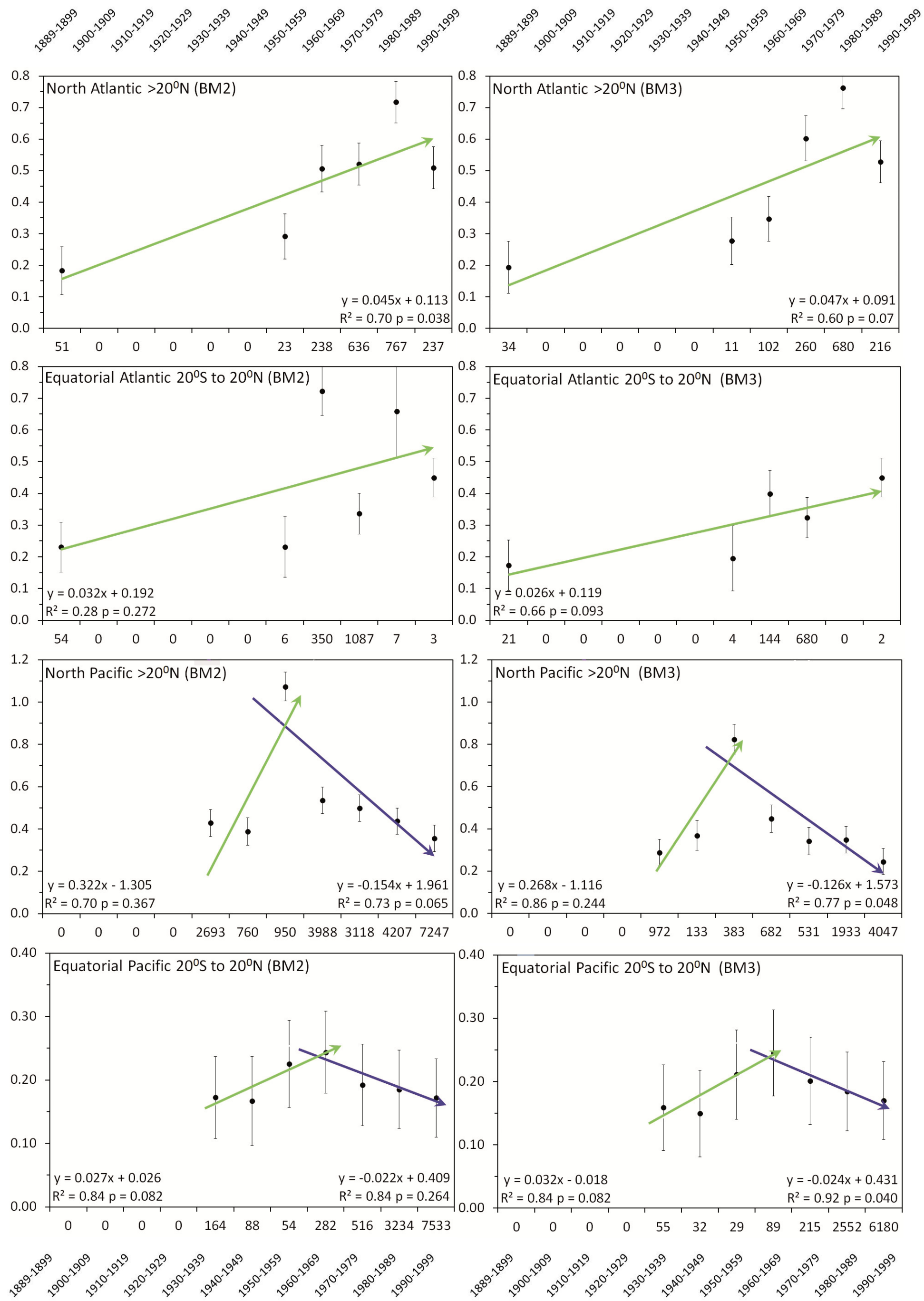


Figure 7.14 - Ocean trends: Scatter plots showing the temporal evolution in chlorophyll (mgm^{-3}) per decade over the period 1889-1999. The number of *FU* observations that were used to calculate the mean chlorophyll concentration per decade is provided below each point. Superposed lines are least-squares regression lines that indicate a bluing (blue trend line) or greening of an ocean (green trend line). Regression coefficients, with the coefficient of determination R^2 and p are indicated at the bottom of each graph.

Note the difference in the chlorophyll concentration for data extracted closer to the coast (BM2, resulting in higher concentrations) and for data extracted over 500 km off-coast (BM3).

For the North Pacific we found similar patterns for both BM2 and BM3, a greening period between 1930-39 and 1950-59 followed by a bluing period (a decline in chlorophyll) until 1999. In a relative short period chlorophyll increased over a factor 3 over 3 decades (1930-59) and decreased over the following 5 decades with a factor 4 until it reached the overall decadal chlorophyll minimum of $\approx 0.25 mgm^{-3}$. Slightly lower chlorophyll concentrations are found for the BM3 extracted data.

For the Equatorial Pacific we found similar patterns for both BM2 and BM3, a greening period between 1930-39 and 1960-69, followed by a bluing period (a decline in chlorophyll) until 1999. Chlorophyll reached its maximum in 1960-69, a decade later than the maximum observed in the North Pacific. The modelled EP surface chlorophyll concentrations are the lowest found in our analysis and vary during the whole period between 0.15 and $0.25 mgm^{-3}$. The average rate of EP chlorophyll growth and decline is established at $\pm 0.025 mgm^{-3}$ per decade.

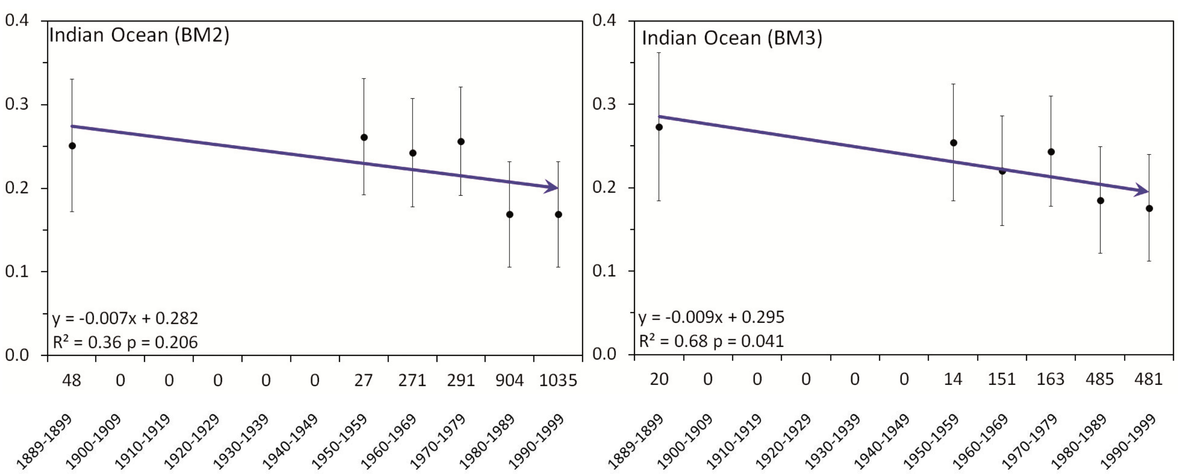


Figure 7.15 - Ocean trends: Scatter plots showing the temporal evolution in chlorophyll (mgm^{-3}) per decade over the period 1889-1999. The number of *FU* observations that were used to calculate the mean chlorophyll concentration per decade is provided below each point. Superposed lines are least-squares regression lines that indicate a bluing (blue trend line) or greening of an ocean (green trend line). Regression coefficients, with the coefficient of determination R^2 and p are indicated at the bottom of each graph.

The results for the Indian Ocean, presented in Figure 7.15, show a bluing ocean for both BM2 and BM3 data. With an R^2 of 0.36 for BM2 the relation is marginal which might be caused by the influence of higher chlorophyll concentrations closer to the coast. However, the BM3 data BM3 and show a more significant (R^2 of 0.68 with a p = 0.041) decline in chlorophyll of 0.1 mgm^{-3} between 1889 and 1999. A maximum value of 0.3 mgm^{-3} was found in the first analysed decade.

SEAS

For all analysed seas (see Table 7.3) the decadal $\overline{FU}$ values and trend lines are presented in Figure 7.16 and Figure 7.17. The trend line regression coefficients, where *y* is the *FU* number and *x* is the decadal number (DN), plus the coefficient of determination R^2 and the statistical significance *p* are indicated below the trend line at the bottom of each graph. In general BM2 was used as data extraction mask. The $\overline{FU}$ values are not converted into chlorophyll concentrations (Eq. 7.5) in waters with a CDOM index Φ>2.5 (Figure 7.13), which occurs in most of the seas. In these seas a change in CDOM as well as chlorophyll can cause shifts in sea colour.

Figure 7.16 shows for both the northern Barents and Bering Sea a bluing trend. The Barents Sea, the greenest open sea of our planet, shows a dramatic bluing with a factor of -0.78 $\overline{FU}$ per decade from ≈ 8.6 (1940-49) to ≈ 4.7 (1990-99). From 1950 to 1999 the Bering Sea is bluing with a factor of -0.27 $\overline{FU}$ per decade from ≈ 5.7 to ≈ 4.4. The Norwegian Sea, situated below the Barents Sea, has an average decadal $\overline{FU}$ value of 5.1±0.2 and shows no significant colour change.

The Mediterranean was geographically split into a western and eastern part, based on the known existence of an east-west oligotrophy gradient at 15^0 East [48] [49] [50]. In total 824 *FU* observations (BM1) between 1889 and 1999 were collected. From these only 237 observations (BM2) were analysed. Our analysis shows that the western part is slightly greener compared to the eastern part, in line with published results; $\overline{FU}_{MED.West}$= $\overline{FU}_{MED.East}$+ 0.8.

BM1 and BM2 related $\overline{FU}$ both show a significant greening between 1889 and 1999. The results for the BM2 dataset are plotted in Figure 7.16. The Mediterranean has been significantly greening over 11 decades with a increase of 0.17*FU* per decade (*FU* = 0.17DN + 1.11 with a R^2 = 0.80 p = 0.042). Interestingly, this growth rate is similar to the results found for the North Atlantic with a raise of 0.19*FU* per decade (*FU* = 0.19DN + 1.39 with a R^2 = 0.76 p = 0.025). As a indication of the potentially related changes in biomass, the *FU* was converted into chlorophyll (see Table 7.6). With a $\overline{FU}$=1.4 during 1889-99 and a $\overline{FU}$=3.4 during 1990-99 chlorophyll increased over 11 decades from 0.15 to 0.6 mgm^{-3}.

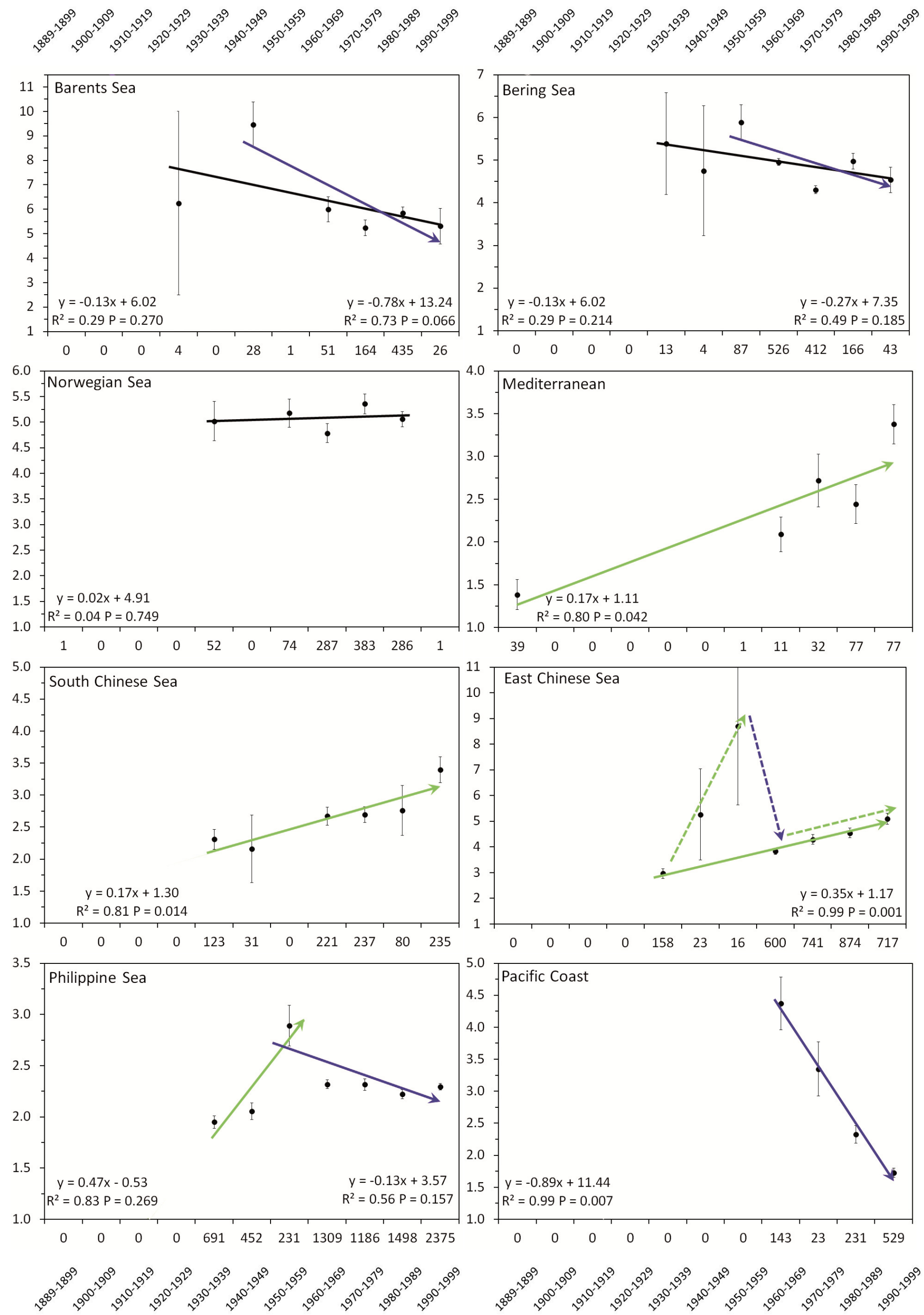


Figure 7.16 - Sea trends: Scatter plots showing the temporal evolution of $\overline{FU}$ per decade over the period 1889-1999. The number of *FU* observations that were used to calculate the mean is provided below each point. Superposed lines are least-squares regression lines that indicate a bluing (blue trend line) or greening of a sea (green trend line). A sea with no significant trend is indicated by a black line. Intermediate changes in the decadal $\overline{FU}$ are indicated by a dashed line. Regression coefficients, with the coefficient of determination R^2 and p are indicated at the bottom of each graph.

The South- and East Chinese Sea both show a greening between 1930 and 1999, the East Chinese Sea being slightly greener. Anomalies are identified in the periods 1940-49 and 1950-59, however values are based upon a limited number of observations compared to the rest of the periods.

The Philippine Sea shows a greening trend for the period 1930-59, adjacently followed by a bluing trend until 1999. Similar to the results of the North Pacific as shown in Figure 7.14 the chlorophyll and $\overline{FU}$ inflection points are identified in the period 1950-59.

Data of the Pacific Coast concerns data of open seawater although the name of the area implies else. No other sea discussed in this paper showed such a major change in colour, from $\overline{FU}$=4.4 to 1.7 over the relative short period 1960-99. This sea is bluing with a decline of -0.89*FU* per decade (FU = -0.89DN+11.4, R^2=0.99, p=0.007).

The results of the remaining seas; Yellow Sea, Sea of Japan and the Sea of Okhotsk are shown in Figure 7.17. The central Yellow Sea (>100km off-coast) is not as yellow as its name would suggest. The colour of this sea can be marked as stable; the first observations were collected between 1930 and 1939 and have $\overline{FU}$=4.3, slightly (within error bars) more than in the last decade b1990 to 1999 showing a $\overline{FU}$=4.2.

For the Sea of Japan an overall greening is found between 1930 and 1999 with an anomaly found in the under-sampled period 1950-59. Between 1960 and 1999 this sea is greening even more rapidly.

The Sea of Okhotsk, a bluish-green sea, interconnected with the Sea of Japan shows an overall major greening between 1930 and 1999 with an inter-decadal undulating pattern in $\overline{FU}$ not seen in other seas.

Table 7.6 - The Mediterranean $\overline{\boldsymbol{FU}}$ values per decade with modelled chlorophyll concentrations, assuming an oligotrophic (case 1) classification. Chlorophyll has been probably overestimated due to the presence of CDOM. Over the period 1900 to 1959 no *FU* observations were available. Chlorophyll values increased from the first to last decade by a factor of 4.

Decade	1889-1899	1900-1959	1960-1969	1970-1979	1980-1989	1990-1999
$\overline{FU}$	1.4	-	2.1	2.7	2.4	3.4
chlorophyll (mgm^{-3})	0.15	-	0.25	0.37	0.31	0.58

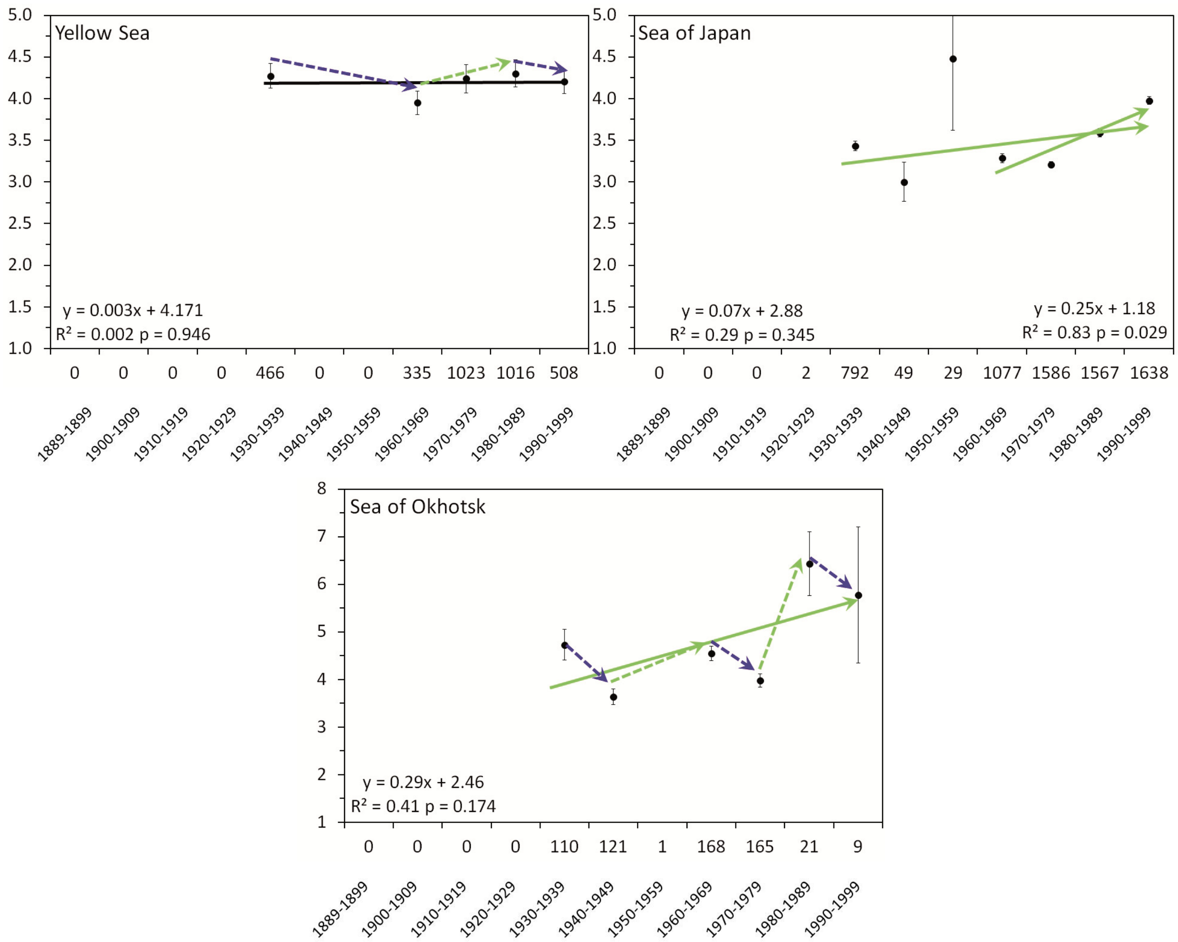


Figure 7.17 - Sea trends: Scatter plots showing the temporal evolution of $\overline{FU}$ per decade over the period 1889-1999. The number of *FU* observations that were used to calculate the mean is provided below each point. Superposed lines are least-squares regression lines that indicate a bluing (blue trend line) or greening of a sea (green trend line). A sea with no significant trend is indicated by a black line. Intermediate changes in the decadal $\overline{FU}$ are indicated by a dashed line. Regression coefficients, with the coefficient of determination R^2 and *p* are indicated at the bottom of each graph.

DISCUSSION AND CONCLUSIONS

We conclude that the ocean colour dataset containing Forel-Ule observations, established over the period 1889 to 1999, is of high quality and offers a unique insight in the temporal changes of colour at the surface in the 20th century for oceans and seas word-wide. The Forel-Ule colour comparator scale has been identified as an objective scale to compare and classify ocean colour. The simplicity of the *FU* scale constructions and the robustness of the protocols provide a well-calibrated and stable measurement by the human eye [3].

The Forel-Ule classification of natural water started in the late nineteenth century and can be marked as one of the oldest oceanographic records, next to salinity, temperature and water transparency records. In no way these valuable ocean colour records can be replaced by other data, and it is not acceptable to simply reject historic datasets or methods that are relatively unknown by classifying them as 'subjective' and this has happened in the case of Secchi disc records [51].

The Forel-Ule classification accuracy is supported by the analysis of the North Atlantic dataset, covering the period 1889 to 1999. The monthly cycle of Forel-Ule ocean colour and derived chlorophyll results are fully in line with the monthly cycles established by satellite ocean colour sensors and other measurements found in literature. Also for the Northern Pacific the *FU*-based seasonal changes compare well with the values of chlorophyll changes reported for this region [26].

Modelling of the expected water colour, based on the state-of-the-art radiation transfer code (EcoLIght), using a two-component and four-component model, has demonstrated how the concentration of chlorophyll or CDOM attenuation relate to the *FU* index. For the clearest oceanic waters (*FU*=1 to 5), where the algal pigments are the dominant absorbing factor (next to water), a simple exponential relation was found between the *FU* index and chlorophyll concentration. Thus significant changes in the average chlorophyll concentration per decade could be reconstructed (Figure 7.14). Although the *FU*-Chl relation can be improved by a better estimate of the CDOM index and specific inherent absorption by phytoplankton in each ocean, the observed variation in colour is real and indicates a change in biological activity.

Stimulated by the clear and significant changes in ocean colour that were found for the Pacific [26], all oceans and seas were analysed for temporal colour changes in the last century. We are well aware of the fact that in some seas the numbers of observations available and used for our analyses are low. At the same time, we have to bear in mind that these observations are the only existing old but valuable oceanographic data. All error bars are at the 2σ level and these error bars are used in the calculation of the significance of the linear trend analysis. For the oceans some trend relations might be due to chance (lowest p is 0.038), although it is clear that the option of a stable colour for each decade is not correct. For a number of seas the reported changes are very significant.

Our trend analysis indicates that the North Atlantic and Equatorial Atlantic have been greening. The increase in North Atlantic chlorophyll after the 1950's is consistent with the positive trends in Phytoplankton Colour Index (PCI) obtained by the Continuous Plankton Recorder (CPR) surveys over past 50 years [52] [53] [54]**.** Further evidence of a greening Atlantic is given by Edwards *et al*. as written down in the SAHFOS ecological status report of 2008 ('*there has been a large* *increase in phytoplankton since the late 1980s in most regional area of the North Atlantic'*) [55] and ('*certain calcareous taxa (foraminifera) are actually increasing between 1958 to 2000 in terms of abundance'*) [56].

Lowest open ocean (>500 km off-coast) chlorophyll values of ≈0.14 mgm^{-3} were found in the period 1889-1899. The North Atlantic chlorophyll shows a growth of 0.047 mgm^{-3} per decade. The Equatorial Atlantic greens less dramatically with an amount of 0.026 mgm^{-3} per decade.

Both the North- and Equatorial Pacific and the Philippine Sea all show an increase as well as an adjacent decrease in chlorophyll between 1930 and 1999. The Indian Ocean shows a continuing but slow decline in chlorophyll over the period 1889 and 1999. Bluing seas are the Barents Sea and the Bering Sea. The Pacific Coast shows an extreme and fast bluing over a relative short period between 1960 and 1999.

Like the Atlantic, the Mediterranean shows a greening trend over the whole of the analysed period. At the other side of the globe similar trends are found for the East- and South Chinese Sea, the Philippine Sea (similar to the North Pacific) and the Sea of Okhotsk. The Sea of Japan shows after a period of changing colours a more distinct and continues greening over the period 1960 to 1999. The Norwegian Sea and the Yellow Sea are, concerning decadal and long-term colour changes, less affected seas.

The above findings show that no global trend could be detected either in the ocean's colour or in its chlorophyll content. Our results lead to the conclusion that an ocean-wide phytoplankton decrease suggested by Boyce *et al*. [57] in *Nature* (2010) has not taken place. They reported a global decline of phytoplankton over the past century, in their opinion forced by an increase in sea surface temperature. However, differences in data filtering techniques may well have been the cause of their results, that are so different from the ones we present here. Boyce *et al*. based their conclusions on datasets from which only data obtained in waters <25 m deep or < 1 km from the coast were excluded. This means that their results, so very close to coasts, are biased by chlorophyll-rich eutrophic coastal zones. This will have an impact on trends in oligotrophic regions, where chlorophyll varies much less. In contrast to Boyce *et al.*, we have omitted data <100 km or 500 km from the coast.

Henson *et al*. [58] recently concluded that detection of climate change-driven trends in the satellite data record is confounded by the relatively short time series and large inter-annual and decadal variability in productivity. According to Henson *et al.*, recent observed changes in chlorophyll, primary production and the size of the oligotrophic gyres can not be explicitly ascribed to the impact of global climate change. They even suggest that time series of up to 40 years length are needed to distinguish possible global warming trends from natural variability.

Gregg and Conkright [42] reanalysed the CZCS global ocean chlorophyll product, using SeaWiFS compatible atmospheric correction methods, and made a first quantitative comparison of the decadal trends in global ocean chlorophyll over the periods 1979-1986 (CZCS) and 1997-2000 (SeaWiFS). They reported a decrease in global chlorophyll concentrations from the CZCS records to the present, of about 6% and found larger reductions in the northern high latitudes and an increase in chlorophyll in the low latitudes. Their conclusions are not in line with ours, but we must bear in mind that results are based upon the results of two relative short periods.

RECOMMENDATIONS

The dataset presented here contains 220,000 Forel-Ule observations, but 160,000 remain unexploited. It would be of great importance to investigate these latter ones, collected in coastal- and shelf seas (< 100 km off-shore) globe-wide to establish the possible influence of coloured near shore waters on open-ocean colour. Moreover, with a refinement of the model results presented here, it should be possible to classify water quality not only in the open ocean but also in seas, where CDOM is not co-varying with chlorophyll. In these seas, besides human influence, notably eutrophication by nutrient input of rivers and by sediment and CDOM load changes, play a role. However, we must bear in mind that such a refinement is not an easy task as chlorophyll- and CDOM absorption can have a similar influence on the sea and ocean colour and therefore on *FU*.

Future work should concentrate on explanation of driving forces behind the decadal trends in open-ocean colour presented here, and anomalies in the ocean colour record over long terms of up to a century. Hindcasting it is the only way to understand and predict changes in the ocean's ecosystem in its relation to climate change.

Ocean- and sea related long-term series are limited and a simple literature search shows that long-term generally means: between 5 and at most 30 years. It is therefore not only challenging but also necessary to combine archived long-term data series of basic water quality parameters such as Secchi disc depth, chlorophyll or phytoplankton abundance (Contineous Plankton Recorder colour index) to establish, inter-annual or inter-decadal means from which results can be coupled and compared to our results. Data of long-term time series, e.g., the Continuous Plankton Recorder Surveys in the North Sea and North Atlantic since 1948 (SAHFOS, UK), the Hawaii- and Bermuda Atlantic Ocean Time-Series (HOTS and BATS, both since 1988) and the California Cooperative Oceanic Fisheries Investigations (CalCOFI since 1949) should help to achieve this goal.

Finally, we like to make a plea, substantiated in the present paper, for the reintroduction of the *FU*-scale to classify the colour of seas and oceans. Ocean colour classification by means of a single numerical value instead of a hyper-spectral classification will facilitate the interpretation of long-term ocean colour data series and at the same time facilitate a connection between the present and the past. MERIS satellite Forel-Ule mapping can play a role here, through validation and coupling of historic observations to the present era of satellite-based monitoring.

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