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1 **Review of constituent retrieval in optically deep** 2 **and complex waters from satellite imagery**

3
4 Daniel Odermatt^{1,*}, Anatoly Gitelson², Vittorio Ernesto Brando³, Michael Schaepman¹

5
6 ¹Remote Sensing Laboratories, University of Zurich, Switzerland

7 ²School of Natural Resources, University of Nebraska, Lincoln, Nebraska, United States

8 ³CSIRO Land and Water, Environmental Earth Observation Programme, Canberra,
9 Australian Capital Territory 2601, Australia

10
11 * Corresponding author. Tel.: +41 446356517; fax: +41 446356846.

12 E-mail address: daniel.odermatt@geo.uzh.ch

13 14 **Abstract**

15 We provide a comprehensive overview of water constituent retrieval algorithms and
16 underlying definitions and models for optically deep and complex (i.e. case 2) waters
17 using earth observation data. The performance of constituent retrieval algorithms is
18 assessed based on matchup validation experiments published between January 2006 and
19 May 2011. Validation practices range from singular vicarious calibration experiments to
20 comparisons using extensive in situ time series. Band arithmetic and spectral inversion
21 algorithms for all water types are classified using a method based scheme that supports
22 the interpretation of algorithm validity ranges. Based on these ranges we discuss groups
23 of similar algorithms in view of their strengths and weaknesses. Such quantitative
24 literature analysis reveals clear application boundaries. With regard to chlorophyll
25 retrieval, validation of blue-green band ratios in coastal waters is limited to

26 oligotrophic, predominantly ocean waters, while red-NIR ratios apply only at more than
27 10 mg/m³. Spectral inversion techniques – although not validated to the same extent –
28 are necessary to cover all other conditions. Suspended matter retrieval is the least
29 critical, as long as the wavelengths used in empirical models are increased with
30 concentrations. The retrieval of dissolved organic matter however remains relatively
31 inaccurate and inconsistent, with large differences in the accuracy of comparable
32 methods in similar validation experiments. We conclude that substantial progress has
33 been made in understanding and improving retrieval of constituents in optically deep
34 and complex waters, enabling specific solutions to almost any type of optically complex
35 water. Further validation and intercomparison of spectral inversion procedures is
36 however needed to learn if solutions with a larger validity range are feasible.

37

38 **1 Introduction**

39 Optically deep and complex waters are referred to as case 2 waters, as opposed to
40 phytoplankton dominated case 1 waters of the open ocean (Morel and Prieur, 1977).
41 The variety within case 2 waters is large, because concentrations as well as specific
42 inherent optical properties of chlorophyll (*CHL*), total suspended matter (*TSM*) and
43 coloured dissolved organic matter concentrations (*CDOM*) are subject to potentially
44 large and independent variations. Satellite sensors such as SeaWiFS, MODIS, and
45 MERIS are currently being used to deliver ocean color data, attaining the requirements
46 necessary for ocean biogeochemistry and climate research (Dierssen, 2010; McClain,
47 2009). Alas, universally applicable algorithms for the retrieval of water constituents
48 from case 2 waters are not known (IOCCG, 2006, 2009). Specific algorithms are thus
49 optimized and validated for commonly understood but ill-defined water types, e.g.
50 turbid (Gitelson et al., 2007) or clear water (Belzile et al., 2004). Other authors address

51 trophic classes (Cheng Feng et al., 2009; Dekker and Peters, 1993; Iluz et al., 2003), for
52 which several diverging definitions exist (Bukata et al., 1995; Carlson and Simpson,
53 1996; Chapra and Dobson, 1981; Nürnberg, 1996; Wetzel, 1983). Trophic thresholds
54 vary however with ecosystem specific limitations to primary productivity, while the
55 validity of remote sensing algorithms is determined only by the variability in optical
56 properties.

57 Carder et al. (1999) and Morel (1980) distinguish empirical and analytical methods for
58 water constituent retrieval, and in-betweens with the epithet “semi-“. Empirical
59 algorithms are derived by statistical regression (Kabbara et al., 2008; Mahasandana et
60 al., 2009) or endmember selection (Tyler et al., 2006), which implies effective data
61 optimization but limited transferability (Austin and Petzold, 1981). Analytical
62 algorithms are based on simplified solutions of the radiative transfer equation. This
63 usually requires approximations or calibration with empirical coefficients (Carder et al.,
64 1999), while statistical regression often leads to solutions that coincide with properties
65 known from physical models (e.g. normalizing band ratios (Gitelson, 1992)), explaining
66 the epithet “semi-” from either side. Either type of algorithm is usually applied as a
67 band arithmetic solution for one constituent at a time, although empirical solutions can
68 also be found by other approaches (Gonzalez Vilas et al., 2011; Tyler et al., 2006).

69 In contrast, spectral inversion procedures match spectral measurements with bio-optical
70 forward models by means of inversion techniques. The spectral inherent optical
71 properties (IOPs, (Preisendorfer, 1961)) of all three constituents are thereby retrieved at
72 once from one spectral apparent property (AOP). Several inversion techniques are
73 applied for this procedure, whereby the investigated AOP is matched with simulated
74 AOPs from bio-optical forward models, i.e. either analytical relationships (Albert and
75 Mobley, 2003; Gordon et al., 1975; Lee et al., 2002; Maritorena et al., 2002; Park and

76 Ruddick, 2005) or numerical radiative transfer models (Bulgarelli et al., 1999; Jin and
77 Stamnes, 1994; Mobley, 1989; Zhai et al., 2010).
78 By comprehensively reviewing the literature from 2006 to May 2011, we discuss in this
79 paper recent studies reporting matchup validation results for water constituent retrieval
80 in case 2 waters from satellite imagery using band ratio or spectral inversion algorithms.
81 Accuracy assessments for band ratio or spectral inversion algorithms based only on in
82 situ measurements, e.g. Kostadinov et al. (2007)), Moore et al. (2009) or Shanmugam
83 (2010) or simulated datasets, e.g. Qin et al. (2007) are not discussed. We apply a
84 quantitative review approach on validation experiments published from 2006 to May
85 2011, although the algorithms used thereby may date further back. A temporally more
86 comprehensive, qualitative review in line with earlier work by Dekker et al. (1995) has
87 very recently been published by Matthews (2011).
88 We group the paper in 7 sections, where the relevance of IOPs and AOPs in models and
89 algorithms are discussed first, followed by a description of band arithmetic and spectral
90 inversion algorithms. Recent validation experiments for either approach are then
91 summarized and quantitatively analyzed for their range of applicability.

92

93 **2 Relevance of IOPs in models and algorithms**

94 Regarding IOPs, the volume scattering function $\beta(\psi)$ is the elementary property for the
95 integration of the scattering and backscattering coefficients b and b_b , respectively, over
96 scattering angle ψ . Measurements of $\beta(\psi)$ (Chami et al., 2006; Freda et al., 2007; Freda
97 and Piskozub, 2007; Lee and Lewis, 2003; Petzold, 1972; Sokolov et al., 2010; Sullivan
98 and Twardowski, 2009) are normalized to the scattering phase function $\tilde{\beta}(\psi)$. Several
99 models of $\tilde{\beta}(\psi)$ have been proposed to approximate these measurements (Fournier and
100 Forand, 1994; Fournier and Jonasz, 1999; Haltrin, 2002; Mobley et al., 1993). Their

101 effect on calculated reflectance quantities is up to 20% (Chami et al., 2006; Gordon,
102 1993; Mobley et al., 2002; Morel et al., 2002; Morel and Gentili, 1996). The ratio of
103 molecular to total scattering, η , is a major proxy for the shape of $\beta(\psi)$, since molecular
104 $\tilde{\beta}_W$ is less anisotropic than particulate $\tilde{\beta}_{TSM}$ (Morel, 1974; Smith and Baker, 1981).
105 The absorption coefficient a in contrast is omnidirectional, but influences the intensity
106 and anisotropy of reflectance through the single scattering albedo ω_0 (Gordon and
107 Brown, 1973; Gordon et al., 1975; Morel and Prieur, 1977) and the number of
108 subsequent scattering events of a photon before reaching the interface, N (Loisel and
109 Morel, 2001; Morel et al., 2002), respectively. An alternative term for the former is the
110 single backscattering albedo ω_b . The latter indicates the blurring of $\beta(\psi)$ in turbid water
111 (Pfeiffer and Chapman, 2008; Piskozub and McKee, 2011; Sydor, 2007).
112 The ability to account for variations in these IOPs is limited for band arithmetic
113 algorithms, while increasingly addressed by spectral inversion algorithms for radiative
114 transfer simulations (Doerffer and Schiller, 2007; Schroeder et al., 2007b; Van Der
115 Woerd and Pasterkamp, 2008) or specific semi-analytical models (Albert and Mobley,
116 2003; Park and Ruddick, 2005).

117

118 **3 Relevance of AOPs in models and algorithms**

119 The first widely used AOP is the bihemispherical irradiance reflectance R^- , which is
120 related to ω_b in the earliest semi-analytical models for case 2 water by means of the
121 linear coefficient f (Gordon et al., 1975; Morel and Prieur, 1977), which again varies
122 with illumination zenith angle θ_s^+ (Gordon, 1989; Kirk, 1991; Sathyendranath and Platt,
123 1997).
124 Subsequent experiments for case 1 (Morel and Gentili, 1991, 1993) and case 2 (Loisel
125 and Morel, 2001) waters focus on anisotropy of the underwater light field, described by

126 η , N and the anisotropy factor Q that relates diffuse upwelling irradiance E_u^- to
127 directional upwelling radiance L_u^- . It is found that the directional variations in f and Q
128 partly compensate each other, leaving the subsurface remote sensing reflectance R_{rs}^- less
129 sensitive to anisotropy effects than R^- (Morel and Gentili, 1993). Accordingly, semi-
130 analytical models that relate ω_b directly to R_{rs}^- by means of quadratic coefficients
131 became more popular (Gordon et al., 1988; Lee et al., 1998).
132 Correction for air-water interface and normalization of the resulting R_{rs}^+ to zenith
133 illumination and viewing geometry will then result in the normalized water-leaving
134 reflectance $[R_w]_N$ (Gordon et al., 1988; Gordon and Clark, 1981). The calculation of
135 $[R_w]_N$ from at-sensor radiances as well as estimation of the coefficients in semi-
136 analytical models require knowledge of atmospheric and aquatic parameters, which
137 have to be retrieved through iterative procedures (Gordon and Franz, 2008; Morel and
138 Gentili, 1996). Since such procedures are more computationally expensive for case 2
139 than for case 1 waters (Kuchinke et al., 2009a), approximations find wide use in both
140 cases, compromising the potential improvement due to such normalizations.

141

142 **4 Band arithmetic algorithms**

143 *CHL* retrieval band arithmetic algorithms make use of the pigment's primary and
144 secondary absorption maxima at 442 nm and 665 nm, respectively (Bricaud et al.,
145 1995), a reflectance peak around 700 nm due to the minimum sum of absorption of
146 phytoplankton, particulate and dissolved matter and water (Gitelson, 1992; Vasilkov
147 and Kopelevich, 1982; Vos et al., 1986) and its fluorescence emission band at 681 nm
148 (Gower et al., 1999).
149 The primary feature is superimposed by *CDOM* absorption (Bricaud et al., 1981), and
150 therefore widely used in case 1 waters, where *CDOM* and *CHL* correlate as *CDOM* is a

151 phytoplankton degradation product (Morel and Prieur, 1977). Sensor specific standard
152 algorithms for primary *CHL* absorption bands exist for all medium resolution ocean
153 colour spectrometers (Aiken et al., 1995; Clark, 1997; Morel and Antoine, 2007;
154 Murakami et al., 2006; O'Reilly et al., 1998). They are referred to as OC2, OC3 and
155 OC4 depending on the number of bands used.

156 Using the secondary feature is promoted by weak variations in the spectral properties of
157 all other parameters apart from the increasing absorption by water (Dall'Olmo et al.,
158 2003; Gitelson, 1992; Schalles et al., 1998). Its major limitation is the absence of the
159 feature in oligotrophic and some mesotrophic lakes (Guanter et al., 2010).

160 Fluorescence line height (FLH) and maximum chlorophyll index (MCI) algorithms are
161 linear baseline algorithms for $<30 \text{ mg/m}^3$ and $>100 \text{ mg/m}^3$ *CHL* ranges (Gower et al.,
162 2005). They can be applied either with or without atmospheric correction (Binding et
163 al., 2011; Matthews et al., 2010).

164 *TSM* and corresponding particle scattering is best quantified outside the *CHL* or *CDOM*
165 features (Binding et al., 2010). Regression with a single band is possible if an accurate,
166 possibly NIR L_w coupled atmospheric correction is applied (Stumpf et al., 2003). Multi
167 band algorithms are however also used on uncorrected at-sensor radiances (Koponen et
168 al., 2007). The choice of spectral bands in regression algorithms depends on the
169 corresponding concentrations ranges, whereas appropriate wavelengths shift from 550
170 nm towards the red and NIR portions of the spectral range for increasing *TSM* (Wang
171 and Lu, 2010). The increase in absorption of pure water towards the NIR will namely
172 require increasing *TSM* to ensure a sufficient reflectance signal (Ruddick et al., 2006),
173 while less absorbing portions of the spectrum are more suitable for low concentrations.

174 Empirical regression of in situ *TSM* with all eligible bands of a spectroradiometric
175 measurement is a simple way to test this hypothesis (Nechad et al., 2010), and provides

176 the flexibility to derive suitable algorithms even for Landsat TM instruments (Wang et
177 al., 2009; Zhou et al., 2006).
178 *CDOM* retrieval methods are restricted to short visible wavelengths, where absorption
179 of *CDOM* and *CHL* coincide (Babin et al., 2003; Ferreira et al., 2009) and inaccuracies
180 due to NIR derived atmospheric correction are largest (Hu et al., 2000). Accordingly,
181 most band arithmetic approaches relate *CDOM* to a ratio of sensitive bands at <600 nm
182 and normalization bands at >600 nm (Kallio et al., 2001). The choice of suitable sensors
183 is smaller than for the estimation of *CHL* and *TSM*, due to insufficient radiometric
184 accuracy of Hyperion (Giardino et al., 2007) and Landsat Thematic Mapper (Kutser et
185 al., 2005b) in the short wave domain of the spectrum.

186

187 **5 Spectral inversion algorithms**

188 The constitution of spectral inversion algorithms is more heterogeneous than band
189 arithmetic algorithms, with differences in water, interface, atmospheric models and
190 inversion techniques. Spectral inversion algorithms perform a simultaneous retrieval of
191 IOPs and concentrations of the optically active constituents. One of the major
192 weaknesses of these algorithms is related to the appropriate parameterization of the IOP
193 spectral shapes (IOCCG, 2006).
194 Table 1 contains a list of recent studies reporting validation results for spectral inversion
195 algorithms in case 2 waters. NN inversion techniques are dominant, probably due to
196 their improved availability as MERIS level 2 products (Doerffer and Schiller, 2007) and
197 by BEAM plug-ins (Doerffer and Schiller, 2008a; Schroeder et al., 2007b). Other
198 inversion techniques include area minimization (Kutser et al., 2001), matrix inversion
199 (Brando and Dekker, 2003), downhill simplex (Heege and Fischer, 2004), least-squares
200 (Santini et al., 2010), spectral optimization (Kuchinke et al., 2009a) and Levenberg-

201 Marquardt optimization (Van Der Woerd and Pasterkamp, 2008). Only one application
202 of the SeaDAS semi-analytical algorithms (Carder et al., 1999; Lee et al., 2002;
203 Maritorena et al., 2002) is listed in Table 1. This is however to a large extent due to
204 their focus on retrieving IOPs rather than constituent concentrations.
205 Most algorithms are used together with specific atmospheric correction modules. The
206 use of standard level 2 reflectance products is only foreseen for two algorithms
207 (Schuchman et al., 2005; Van Der Woerd and Pasterkamp, 2008). The inversion
208 modules match atmospherically corrected R_{rs}^+ or R^- with Hydrolight simulated data
209 (Brando and Dekker, 2003; Doerffer and Schiller, 2007, 2008a; Santini et al., 2010; Van
210 Der Woerd and Pasterkamp, 2008), other numerical (Jerome et al., 1996; Pozdnyakov et
211 al., 2005) or semi-analytical (Heege and Fischer, 2004; Kuchinke et al., 2009a)
212 simulations. Findings from the validation experiments in Table 1 are discussed later.

213

214 *Table 1: List of matchup validation experiments with spectral inversion processed spaceborne data.*
215 *Concentration thresholds in bold letters indicate successful quantitative validation, italic letters indicate*
216 *successful quantitative falsification, and regular letters indicate missing validation. Expected minimum*
217 *R^2 for validation is 0.4 (CHL, CDOM, tripton) and 0.6 (TSM). Asterisks (*) indicate retrieval of tripton*
218 *instead of TSM; circles (°) indicate retrieval of inorganic suspended matter instead of TSM; plus signs (†)*
219 *indicate “dissolved organics” [mgC/l] instead of CDOM; carets (∧) indicate “colored detrital matter”*
220 *[m^{-1}] instead of CDOM. Concentrations in absorption units are given at 400 nm and, if originally given*
221 *in another wavelength, converted according to Smith and Baker (1981) with explicitly given spectral*
222 *exponents (Matthews et al., 2010; Santini et al., 2010) or an approximate 0.017 spectral exponent where*
223 *not specified (Binding et al., 2011; Giardino et al., 2010; Schroeder et al., 2007b; Van Der Woerd and*
224 *Pasterkamp, 2008). Algorithm references: ¹Doerffer and Schiller (2007), Moore et al. (1999); ²Doerffer*
225 *and Schiller (2008a, b); ³Schroeder et al. (2007a; 2007b); ⁴Pozdnyakov et al. (2005); ⁵Brando and*
226 *Dekker (2003); ⁶Heege and Fischer (2004). Strict and relaxed matchups chosen from Cui et al. (2010),*
227 *Kuchinke et al. (2009b) is omitted due to a lack of absolute in situ concentration values.*

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Experiment	Algorithm	<i>CHL</i> [mg/m ³]		<i>TSM</i> [g/m ³]		<i>CDOM</i> [m ⁻¹]	
		max	min	max	min	max	min
Binding et al. (2011)	NN algal ₂ ¹	70.5	1.9	19.6	0.8	7.1	0.5
Cui et al. (2010)	NN algal ₂ ¹	16.1	0.7	67.8	1.5	2.0	0.7
Minghelli-Roman et al. (2011)	NN algal ₂ ¹	9.0	0.0	-	-	-	-
Binding et al. (2011)	NN C2R ²	70.5	1.9	19.6	0.8	7.1	0.5
Giardino et al. (2010)	NN C2R ²	74.5	11.67	-	-	4.0	1.3
Matthews et al. (2010)	NN C2R ²	247.4	69.2	60.7	30.0	7.1	3.4
Odermatt et al. (2010)	NN C2R ²	9.0	0.0	-	-	-	-
Schroeder et al. (2007b)	NN FUB ³	12.6	0.1	14.3	2.7	2.0	0.8
Shuchman et al. (2006)	Coupled NN ⁴	2.5	0.1	2.7°	1.3°	3.5 ⁺	0.0 ⁺
Giardino et al. (2007)	MIM ⁵	2.2	1.3	2.1*	0.9*	-	-
Odermatt et al. (2008)	MIP ⁶	4.0	0.6	-	-	-	-
Santini et al. (2010)	2 step inversion	5.0	1.8	13.0*	3.0*	0.8	0.1
Van der Woerd and Pasterkamp (2008)	Hydropt	20.0	0.0	30.0	0.0	1.6	0.0

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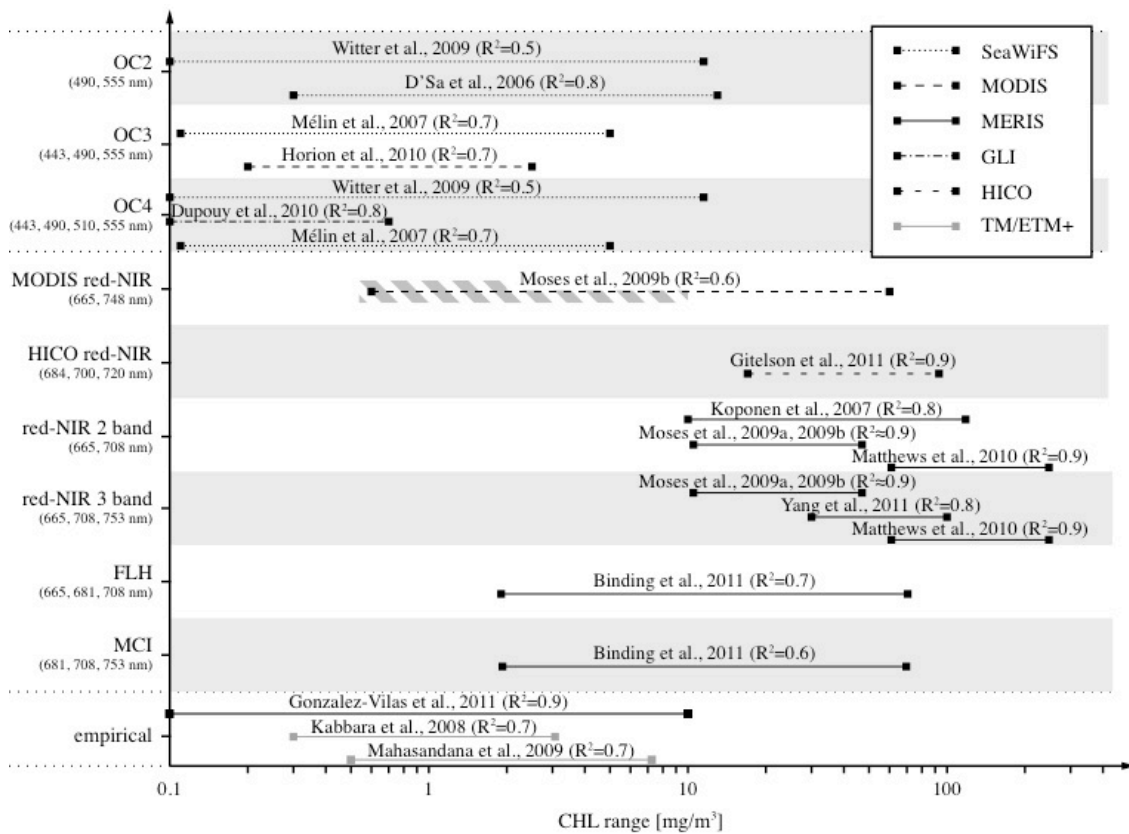
231 6 Validation experiments

232 Recent ISI journals (2006-2011) comprise about 50 published papers reporting water
 233 constituent retrieval from satellite imagery for optically deep and complex waters,
 234 among which about three quarter apply band arithmetic algorithms. Applied selection
 235 criteria are the availability of coinciding validation data, concentration ranges and
 236 statistical quality measures, namely R².

237

238 6.1 Chlorophyll-a retrieval

239 All recent band arithmetic *CHL* retrieval applications are depicted in Figure 1, with
 240 corresponding sensors and concentration ranges. The three previously described major
 241 groups are distinguished; green/blue ratios defined for OC algorithms, red-NIR band
 242 ratios and further empirical algorithms.



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Figure 1: Overview of recently (2006-2011) published ISI journal papers on the separate retrieval of chl-a from satellite imagery using matchup-validated semi-analytical and empirical algorithms. Hatched areas indicate disputed application ranges. The red-NIR 3 band application by Chen et al. (2011) is omitted since the variation range retrieved from Hyperion (21-27 mg/m³; R²=0.6) is too small to display.

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The OC2-OC4 algorithms are successfully applied to retrieve 0-10 mg/m³ CHL in optically complex water. They are however considerably less accurate than red-NIR ratios at high CHL, which coincides with theoretical concerns that their use is limited to Open Ocean. This is because independently varying CDOM disturb the correlation between such short wavelengths and the primary CHL absorption feature. From top to bottom in Figure 1, study areas are Lake Erie (OC2 and OC4), the Mississippi Delta (OC2), Lake Tanganyika (OC3) and the Northern Adriatic Sea (OC3 and OC4), and a lagoon in New Caledonia (OC4). Several of these examples indicate that the observed water optical properties resemble those in case 1 water to some extent. Mélin et al. (2007) mention that two thirds of their observations refer to case 1 water, and Horion et al. (2010) assume explicitly that even Lake Tanganyika is case 1. The data by D'Sa et

260 al. (2006) follow a shifted but correlated mixture of constituents as found for case 1
261 water (Morel and Maritorena, 2001), which can be accounted for by regional adjustment
262 as done by Witter et al. (2009). Dupouy et al. (2010) present a turbidity index for the
263 preselection of applicable data points. Atmospheric correction algorithms provide R_{rs}^+
264 and $[R_w]_N$ output for application of the OC algorithms (Gordon and Voss, 2004; Gordon
265 and Wang, 1994; Siegel et al., 2000; Stumpf et al., 2003; Toratani et al., 2007). Further
266 OC applications to optically complex waters lack quantitative matchup validation (Gons
267 et al., 2008; Wang et al., 2011; Werdell et al., 2009).

268 NIR-red algorithms using 2 or 3 bands are validated using MERIS data for up to 250
269 mg/m^3 *CHL* in Zeekoevlei (Matthews et al., 2010), and suitable for the 10-100 mg/m^3
270 interval represented by the Dnieper River, the Sea of Azov, the Gulf of Finland, Lake
271 Dianchi and Kasumigaura, as in vertical order in Figure 1. *CHL* $<10 \text{ mg/m}^3$ is only
272 observed in Moses et al. (2009a; 2009b). Their calibration data and root mean square
273 errors (RMSEs), as well as previous simulations (Dall'Olmo and Gitelson, 2006)
274 indicate a minimum applicability threshold at 10 mg/m^3 *CHL*. Although lower *CHL* is
275 successfully retrieved from field spectroscopy measurements (Gitelson et al., 2009).
276 Enhancement of NIR-red algorithms by *CDOM* and tripton derived coefficients from a
277 look-up-table may even extend the applicable range, but are only validated for waters
278 with high *CHL* (Yang et al., 2011). Advantages in the use of either 2 or 3 bands are
279 inconsistent (Moses et al., 2009a; Moses et al., 2009b). Larger differences in accuracy
280 occur through different atmospheric correction methods. The MERIS bright pixel
281 procedure (Moore et al., 1999) performs considerably better than the C2R atmosphere
282 module (Doerffer and Schiller, 2008b) in Moses et al. (2009b). Other procedures are
283 SCAPE-M (Guanter et al., 2010) for MERIS (Yang et al., 2011) and FLAASH (Cooley
284 et al., 2002) for Hyperion (Chen et al., 2011), which imply the use of either R_{rs}^+ or R^-
285 for *CHL* retrieval. Matthews et al. (2010) demonstrate that NIR-red algorithms can even

286 be used with uncorrected data at the top of atmosphere (TOA). The same applies to
287 MCI, which outperforms FLH, the MERIS Algal_2 and C2R algorithms at the remote
288 measurement of an algae bloom event in the Lake of the Woods (Binding et al., 2011).
289 Accuracy restrictions for low *CHL* are however similar as for the 2 and 3 band NIR-red
290 algorithms as far as RMSE (5.7 and 7.3 mg/m³ for MCI and FLH, respectively) is
291 concerned. FLH was also found inapplicable to oligotrophic water in the Laurentian
292 Lakes, raising concerns over the fluorescence signal to noise ratio under unfavourable
293 atmospheric conditions (Gons et al., 2008).

294 The empirical studies by Kabbara et al. (2008) and Mahasandana et al. (2009) consist of
295 regression models for Landsat-7 ETM+ and Landsat-5 TM. They prove the feasibility
296 of *CHL* estimation with high-resolution sensors, but need parameterization for each
297 single image. In contrast, Gonzalez Vilas et al. (2011) train NNs for preclassified
298 MERIS observations and in situ measured concentrations without the application of an
299 explicit bio-optical model. Their approach achieves high accuracy and temporal stability
300 at the expense of regional restriction.

301 The types of sensors used in the present experiments correlate clearly with the choice of
302 applications; SeaWiFS and MODIS for the OC algorithms and low *CHL* concentrations,
303 MERIS for the retrieval of high *CHL* by means of red-NIR band ratios and Landsat for
304 empirical algorithms. The advantage of MERIS' 681 nm and 708 nm bands over
305 comparable instruments that lack these bands is known (Gitelson et al., 2008; Gower et
306 al., 1999), and demonstrated for MODIS by Moses et al. (2009a). Gitelson et al. (2011)
307 use a set of hyperspectral HICO data to define optical band positions for a 3 band red-
308 NIR algorithm at even higher accuracy.

309 Appropriate atmospheric corrections that preserve the NIR reflectance peak and allow
310 for directional normalization to $[R_w]_N$ are another prerequisite and asset, respectively.

311 The SeaDAS toolbox for SeaWiFS and MODIS offers a large variety in this regard (Hu

312 et al., 2000; Ruddick et al., 2000; Stumpf et al., 2003; Vidot and Santer, 2005; Wang,
313 2007), whereas occasional failure in retrieving the NIR peak is reported for MERIS'
314 C2R atmospheric correction module (Guanter et al., 2010; Odermatt et al., 2010).

315

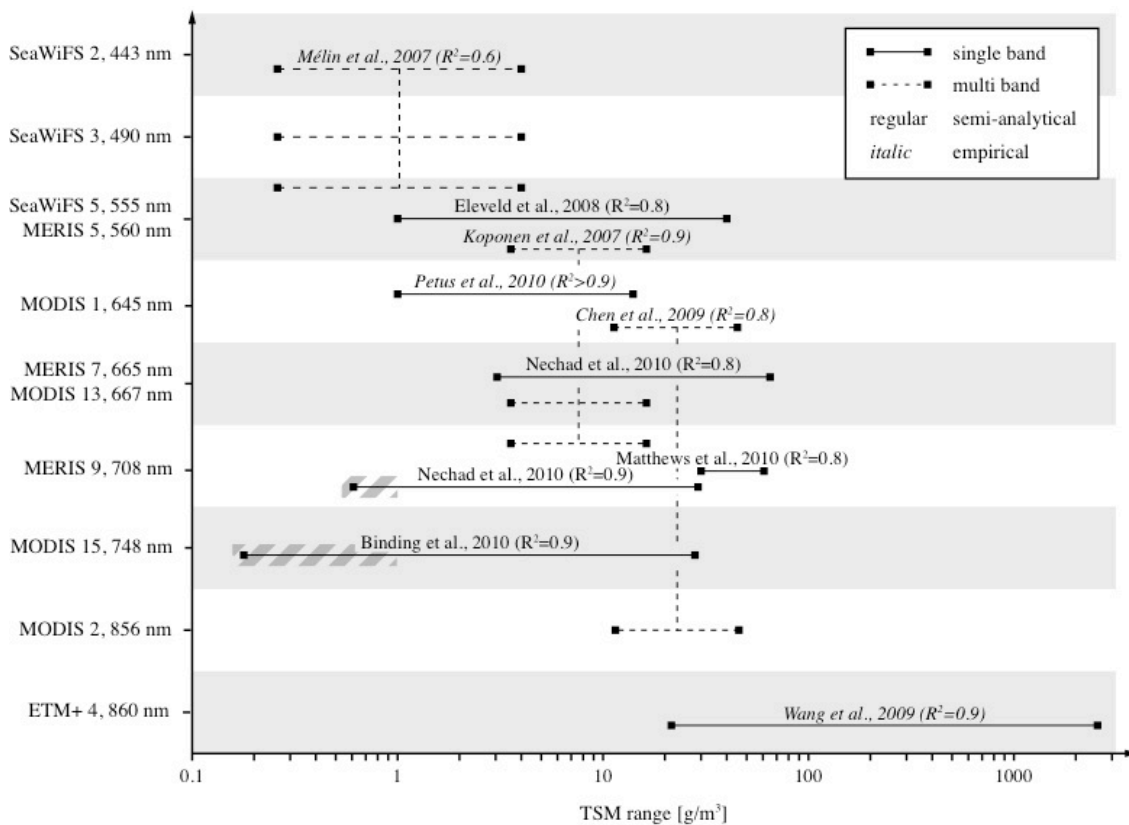
316 **6.2 Suspended sediment retrieval**

317 Recent *TSM* retrieval validation experiments are listed in Figure 2, for increasing central
318 wavelengths of chosen sensors and bands in vertical direction. The convergence in
319 frequently applied methods is not as evident as among the *CHL* algorithms in Figure 1.

320 The advantage of semi-analytical over empirical algorithms is a matter of adaptivity and
321 justification rather than accuracy. Application of semi-analytical algorithms implies a
322 physically sound procedure with defined R_{rs}^+ from atmospheric correction procedures
323 as mentioned for *CHL* (Moore et al., 1999; Ruddick et al., 2000; Stumpf et al., 2003).

324 Their configuration allows adjustment to other sensors or bands (Van der Woerd and
325 Pasterkamp, 2004), and comparison of atmospheric corrections (Matthews et al., 2010)
326 or reflectance models (Nechad et al., 2010). In contrast, empirical algorithms apart from
327 Petus et al. (2010) and Mélin et al. (2007) are applied to uncorrected at-sensor radiances
328 (Koponen et al., 2007) and physically undefined reflectance quantities (Chen et al.,
329 2009; Wang et al., 2009), leaving them unjustified for applications beyond the data they
330 are derived for. However, empirical algorithms are advantageous for evaluation
331 experiments as with the validation of *TSM* from geostationary MSG-SEVIRI data by
332 means of MODIS *TSM* (Neukermans et al., 2009).

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335 *Figure 2: Overview of recently (2006-2011) published ISI journal papers on the separate retrieval of*
 336 *TSM from satellite imagery by means of matchup-validated semi-analytical and empirical algorithms.*
 337 *Hatched areas indicate disputed application ranges. The retrieval of tripton from MERIS band 10 (754*
 338 *nm) at $R^2=0.3$ was omitted (Yang et al., 2011).*

339

340 An increase in spectral band position with observed *TSM* concentration range is found
 341 in Figure 2 as well as in several discussions (Fettweis et al., 2011; Wang and Lu, 2010;
 342 Zhang et al., 2010). Maximum sensitivity thresholds are estimated at 30 g/m^3 for
 343 SeaWiFS' 555 nm band (Eleveld et al., 2008) or around $150\text{-}200 \text{ g/m}^3$ for bands at <650
 344 nm (Fettweis et al., 2011; Wang and Lu, 2010). Only one recent quantitative validation
 345 experiment investigates such extreme turbidity, accordingly at 860 nm (Wang et al.,
 346 2009). In less turbid water, the accuracy variations for 8 MERIS bands between 620 and
 347 885 nm is only $R^2=0.89$ to 0.93 , and lower in absolute values but similar in variation for
 348 MODIS (Nechad et al., 2010). Multi band algorithms are recommended for low *TSM*
 349 concentrations due to the increasing superimposition by other constituents' optical
 350 properties (Nechad et al., 2010). In this regard, Nechad et al. (2010) suggest a 1 g/m^3

351 minimum threshold for single band algorithms, while Binding et al. (2010) mention that
352 their RMSE increases to 47% of mean concentrations below 5 g/m³. Matchups in clear
353 Adriatic coastal water, which is in two thirds of all matchups typically oceanic,
354 confirms the challenges in retrieval of low *TSM*, with a relatively low R² (Mélin et al.,
355 2007).

356

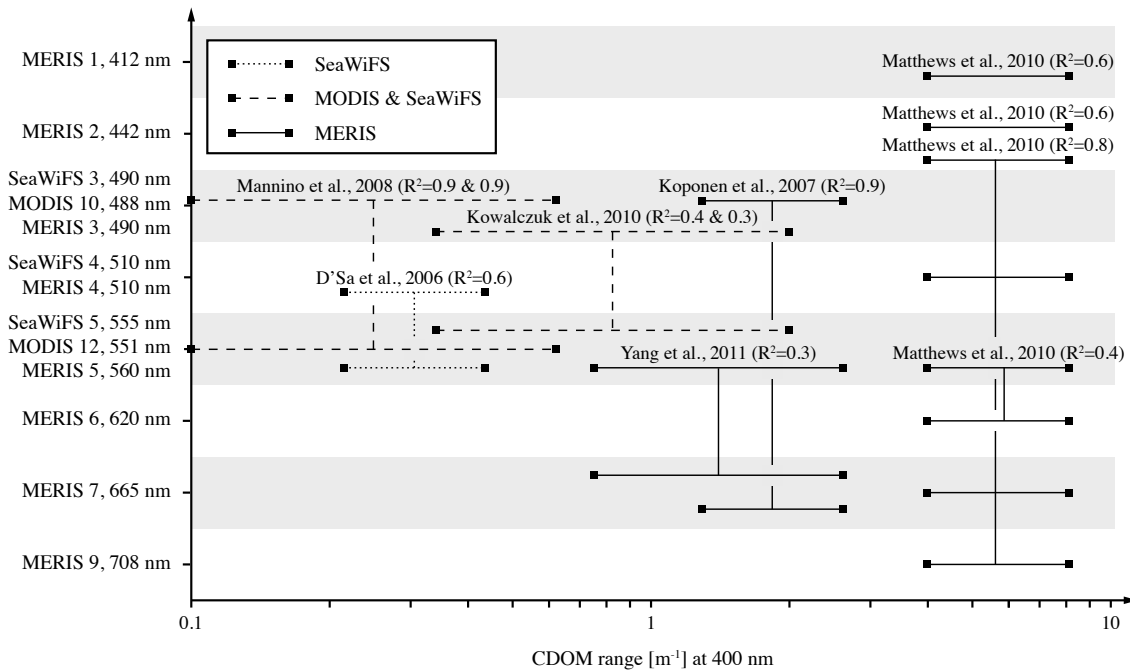
357 **6.3 Dissolved organic matter retrieval**

358 All *CDOM* retrieval band arithmetic algorithms in Figure 3 are from empirical
359 regression (D'Sa and Miller, 2003; Gitelson et al., 1993; Kallio et al., 2001; Kowalczyk
360 et al., 2005), in the case of Yang et al. (2011) by means of bio-optical simulations
361 (Ammenberg et al., 2002). The examples indicate that single band approaches and
362 bands at less than 490 nm are only applicable to extremely high concentrations and
363 correspondingly strong *CDOM* absorption variations as in Zeekoevlei (Matthews et al.,
364 2010). The two best correlations are calculated for band ratios that apply a 442-490 nm
365 band that is sensitive to both *CHL* and *CDOM* variations, and the *CHL*-sensitive 665
366 nm band of MERIS for normalization (Koponen et al., 2007; Matthews et al., 2010). In
367 both cases no atmospheric correction is applied, although *CDOM* in the Gulf of Finland
368 is already much less abundant than in Zeekovlei.

369 Ammenberg et al. (2002) uses the 665 nm band to normalize the 560 nm band rather
370 than the 442-490 nm bands, whereas both the interference with *CHL* absorption and the
371 *CDOM* signal are considerably weaker at 560 nm. The correlation of this ratio with
372 intermediate *CDOM* in Lake Dianchi and Lake Kasumigaura remains however
373 relatively low, in spite of the application of a look-up-table retrieved parameterization
374 (Yang et al., 2011). A recent validation exercise with ALI bands 2 and 3 at similar
375 spectral positions is only qualitative and thus not included in Figure 3 (Kutser et al.,
376 2009). Earlier studies have however demonstrated the potential of this band

377 combination for mapping *CDOM* in inland waters even at high spatial resolution

378 (Kutser et al., 2005a; Kutser et al., 2005b).



379

380 *Figure 3: Overview of recently (2006-2011) published ISI journal papers on the separate retrieval of*
381 *CDOM from satellite imagery by means of matchup-validated, arithmetic algorithms. Where necessary,*
382 *normalization to 400 nm is done with explicitly mentioned spectral exponents (Smith and Baker, 1981),*
383 *i.e. 0.0157 (Yang et al., 2011), 0.0161 (D'Sa et al., 2006) and 0.0188 (Matthews et al., 2010), or an*
384 *approximate average of 0.0215 (Mannino et al., 2008).*

385

386 The SeaWiFS and MODIS bands ratios recommended by Kowalczyk et al. (2005) and

387 D'Sa and Miller (2003) omit the red-NIR part of the spectrum as previously found for

388 the band arithmetic retrieval of *CHL* with these two instruments. The former was

389 validated with data of the Baltic Sea from both SeaWiFS and MODIS (the latter not

390 shown in Figure 3, $R^2=0.3$) and outperforms the *CDOM* output from SeaDAS semi-

391 analytical algorithms (Carder et al., 1999; Garver and Siegel, 1997; Maritorena et al.,

392 2002) in all cases (Kowalczyk et al., 2010). A SeaWiFS validation in the Mississippi

393 estuary achieves an even higher correlation at lower concentrations (D'Sa et al., 2006).

394 The two validation exercises are also the seasonally most representative ones given that

395 data matchups from several years and seasons are analyzed.

396

397 **6.4 Spectral inversion applications**

398 13 or a quarter of the selected publications in 2006-2011 ISI journals refer to spectral
399 inversion algorithms (Table 1), with several papers on new algorithms where validation
400 is only a subchapter (Santini et al., 2010; Schroeder et al., 2007b; Van Der Woerd and
401 Pasterkamp, 2008). The quantitative content is often less detailed than with band
402 arithmetic algorithms, hindering an estimate of their applicability as shown in Table 1.
403 The MERIS algal_2 product (Doerffer and Schiller, 2007) and *CHL* from C2R and its
404 boreal and eutrophic version (Doerffer and Schiller, 2008a; Koponen et al., 2008) have
405 been applied in several experiments. C2R is successfully validated for low to
406 intermediate concentrations ($<16 \text{ mg/m}^3$) (Cui et al., 2010; Minghelli-Roman et al.,
407 2011; Odermatt et al., 2010), while C2R and even its eutrophic water version are found
408 unsuitable for high *CHL* concentrations (Binding et al., 2011; Giardino et al., 2010;
409 Matthews et al., 2010). C2R's *CDOM* is found adequate in a eutrophic lagoon in the
410 Baltic Sea, where concurrent *CHL* is strongly underestimated (Giardino et al., 2010). In
411 contrast, *CDOM* in oligotrophic perialpine and Finish lakes is underestimated by both
412 C2R and its boreal version while *CHL* is adequate (Koponen et al., 2008; Odermatt et
413 al., 2010). C2R's atmospheric correction failed at retrieving the red-NIR reflectance
414 peak in several examples, while it outperforms other procedures with its accuracy at
415 blue and green wavelengths (Giardino et al., 2010; Odermatt et al., 2010; Odermatt et
416 al., 2008). *TSM* retrieved by the two NN is inapplicable to turbid water (Cui et al., 2010;
417 Matthews et al., 2010), but accurate at about $<15\text{-}30 \text{ g/m}^3$ (Koponen et al., 2008).
418 Validation of the FUB MERIS NN algorithm is successful and thorough at low to
419 intermediate concentrations of all constituents over a wide spatiotemporal range
420 (Schroeder, 2005; Schroeder et al., 2007b). Even lower constituent concentrations are
421 successfully retrieved from a single Hyperion image by means of matrix inversion

422 (Giardino et al., 2007). All other applications do not meet the requirements for
423 quantitative matchup validation. Ground truth comparisons are limited to spectral fits
424 (Van Der Woerd and Pasterkamp, 2008), frequency distribution (Kuchinke et al.,
425 2009b) and transect comparisons (Santini et al., 2010), or display occasional failure that
426 prevent sufficient correlations (Odermatt et al., 2008; Shuchman et al., 2006).

427

428 **7 Discussion**

429 The assessed quantitative validation experiments using band arithmetic algorithms
430 consist of comparisons of several methods where in situ data are acquired for exactly
431 this validation purpose. They are numerous enough to synthesize several general
432 conclusions based on individual findings and validation sites, e.g. the validity range for
433 red-NIR *CHL* algorithms, the suitability of OC algorithms for low and intermediate
434 *CHL*, the choice of *TSM* retrieval wavelengths according to expected concentrations
435 ranges or the *CHL* variation normalization strategies in *CDOM* retrieval algorithms.
436 A sufficient number of studies with spectral inversion algorithms are only available for
437 the MERIS NN algorithms. Only the algorithm by Schroeder et al. (2007b) has been
438 successfully validated using matchup correlations of all three constituents over several
439 image acquisitions and aquatic regions as given for many band arithmetic algorithms.
440 We presume two main reasons for this difference, namely availability and complexity.
441 The importance of the availability of algorithms is well represented by the frequent use
442 of retrieval algorithms and corresponding atmospheric correction procedures in SeaDAS
443 and BEAM. They lead to the use of OC algorithms, such as the most popular *CHL*
444 retrieval methods based on SeaWiFS and MODIS data, while NN algorithms are
445 evaluated in most experiments using MERIS data. The opposite cases are rare, although
446 not hindered by sensor or data properties. Consequently, the (semi-)operational use of

447 spectral inversion algorithms is mainly limited to their promoters unless other potential
448 users find easier available methods unsuitable, which may again indicate challenging
449 bio-optical conditions, complicating validation.

450 Crucial sensor and data properties are the red-NIR wavebands as used in MERIS, the
451 spatial resolution of Landsat and ALI instruments and the temporal resolution of MSG-
452 SEVIRI. In the first case, the red-NIR *CHL* retrieval experiments with MERIS
453 outnumber and outperform corresponding experiments for most other sensors, rendering
454 MERIS the preferred instrument for estimating *CHL* in meso- to eutrophic waters. In
455 the case of MSG-SEVIRI, TM, ETM+ and ALI, radiometric accuracy, bandwidths and
456 a lack of appropriate preprocessing tools complicate routine use, as established with
457 dedicated ocean color instruments. However, experimental evidence is given that either
458 of those instruments can be used for case 2 water constituent retrieval under certain
459 circumstances. Simpler methods are however mostly empirical, providing rapid access
460 to data and their correlations, but at the cost of being site specific and not expressing
461 any cause-effect relationship.

462 On the opposite side, complexity in constitution, application and validation of spectral
463 inversion procedures is clearly highest. They retrieve several aquatic and possibly
464 atmospheric parameters from a larger number of spectral bands. Failure at any point in
465 the procedure, i.e. the assumption of an inappropriate shape in *CDOM* absorption, may
466 propagate errors in the estimates of other parameters, complicating a coherent validation
467 or falsification. Band arithmetic algorithms on the contrary make use of known
468 relationships between one aquatic parameter and 1-3 spectral bands that are sensitive to
469 an optical property of the sought-after parameter or allow the normalization of other
470 variations. The validation or falsification of such relationships is straightforward and
471 reveals a good estimate of an algorithm's validity range.

472 For a comparison of the known validity ranges for band arithmetic algorithms (Figure 1
473 to Figure 3), we apply a scheme that helps to further categorize applications for case 2
474 waters. Natural variations in each constituent are separated in a low, intermediate and
475 high range. Low *CHL* is referred to as oligotrophic, and ranges up to 3 mg/m³, the
476 integer average from ecological classification schemes (Bukata et al., 1995; Carlson and
477 Simpson, 1996; Chapra and Dobson, 1981; Nürnberg, 1996; Wetzel, 1983). Previous
478 definitions of the second threshold between mesotrophic and eutrophic waters differ
479 from 5.6 to 20 mg/m³ and are supplemented with a hypereutrophic water in some
480 schemes (Table 2). According to these sources and Figure 1 we set the threshold to 10
481 mg/m³, which approximately limits the applicability of OC and red-NIR algorithms at
482 the top and bottom of their concentration range, respectively. *TSM* thresholds are set at
483 3 and 30 g/m³ due to the experimental ranges in Figure 2, corresponding water types are
484 referred to as clear, cloudy or turbid. An analogous portioning is carried out for *CDOM*
485 according to Figure 3, allowing the assignment of all collected validation experiments to
486 one or several variation spaces with regard to independent variations in the other two
487 constituents as in Figure 4 (e.g. *TSM* retrieval in clear and cloudy water at given *CHL*
488 and *CDOM* (Binding et al., 2010)).

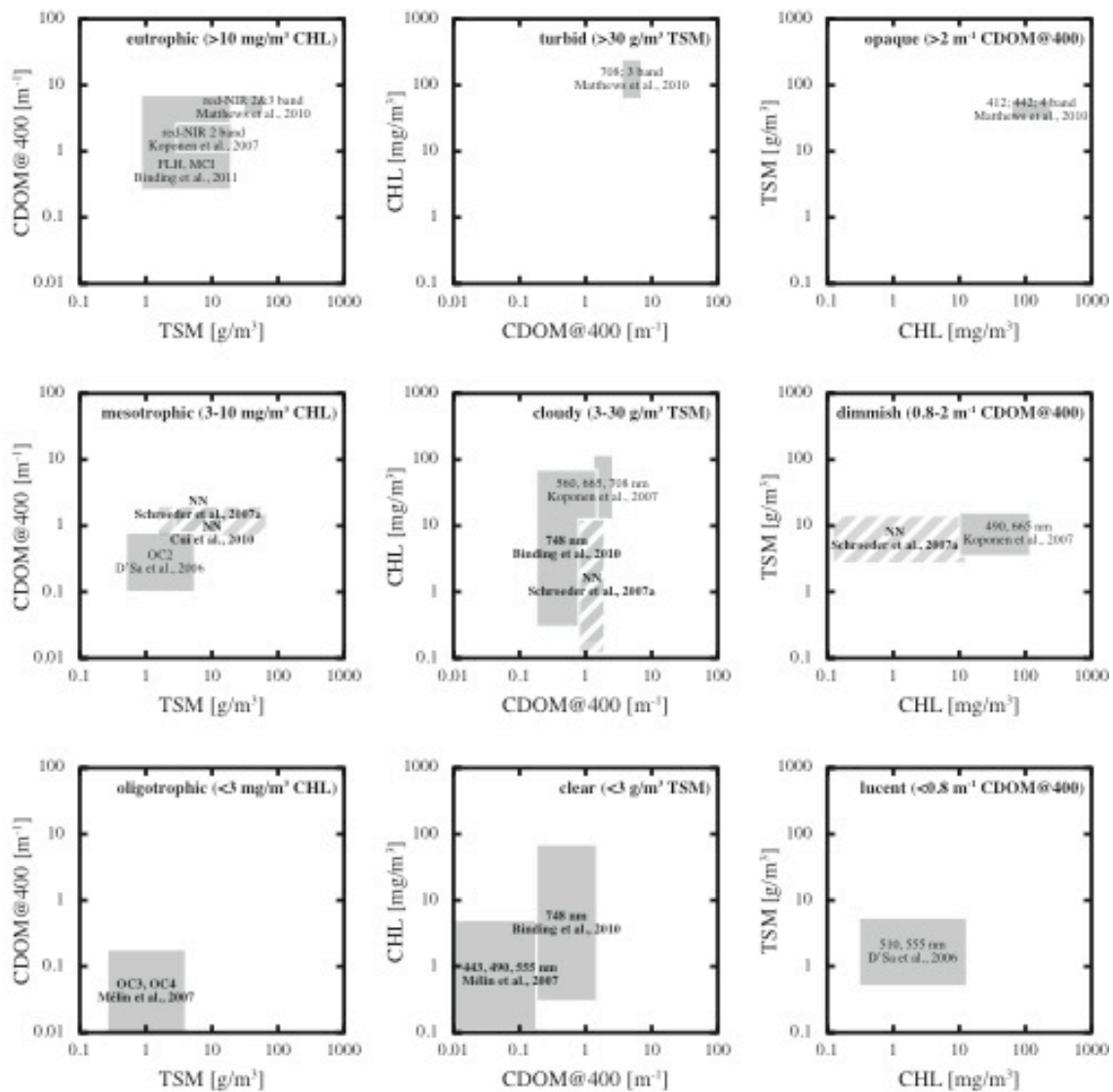
489

490 *Table 2:* Trophic levels for coastal and inland waters and corresponding *CHL* [mg/m³].

Author	Oligotrophic	Mesotrophic	Eutrophic	Hypereutr.
Chapra and Dobson (1981)	0-2.9	2.9-5.6	>5.6	n.a.
Wetzel (1983)	0.3-4.5	3-11	3-78	n.a.
Bukata (1995)	0.8-2.5	2.5-6	6-18	>18
Carlson and Simpson (1996)	0-2.6	2.6-20	20-56	>56
Nürnberg (1996)	0-3.5	3.5-9	9-25	>25

491

492



493

494 *Figure 4: Case 2 water classes for CHL (left column), TSM (center) and CDOM (right) concentrations,*
 495 *with high to low concentration classes from top to bottom, and the remaining two constituents varying in*
 496 *x- and y-direction of each box. Class names and concentration ranges are titled in each box. Algorithm*
 497 *validation ranges are indicated as boxes and labeled with corresponding retrieval methods or center*
 498 *wavelengths. Bold labels indicate validation experiments with >10 images, hatched areas indicate*
 499 *simultaneous retrieval of all constituents. Reading example: Binding et al. (2011) validate the FLH and*
 500 *MCI algorithms for CHL in eutrophic waters with 0.85-19.60 g/m³ TSM and 0.26-7.14 m⁻¹ CDOM.*

501

502 Published validation experiments as used in Figure 1 to Figure 3 are depicted in Figure
 503 4 if variation ranges of all three constituents are given, even if only individual
 504 constituents are retrieved. Only two spectral inversion experiments from Table 1 can be
 505 positioned. Schroeder et al. (2007b) present simultaneous retrieval of all parameters at
 506 an accuracy that is comparable to corresponding band ratio validations, while only *CHL*

507 is retrieved accurately in Cui et al. (2010), but variations in *TSM* and *CDOM* are also
508 given. The *CHL* retrieval column in Figure 4 shows the suitability of red-NIR
509 algorithms for eutrophic water, and the potential of OC algorithms for oligo- to
510 mesotrophic waters at relatively low *TSM* and *CDOM* variations. Several different
511 algorithms retrieve *TSM* accurately, but the relationship between sensitive wavelength
512 and concentration range (Figure 2) is no more visible. Relatively few experiments are
513 assigned to turbid water, probably because measuring in situ *TSM* is much less of an
514 effort than additional *CHL* and *CDOM*. The proof of successful *CDOM* retrieval is
515 however generally scarce, similar as with low *CHL* concentrations.

516 The directional reflectance properties of water are often neglected. Spectral inversion
517 algorithms that make use of directional radiative transfer simulations are the most
518 adequate solution, as they can account for all influencing parameters assuming a given
519 $\tilde{\beta}(\psi)$ (Doerffer and Schiller, 2008a; Giardino et al., 2007; Van Der Woerd and
520 Pasterkamp, 2008). Regarding classical analytical approaches, directional effects are
521 parameterized using coefficients (e.g. f , Q) that vary with constituent concentrations
522 (Morel and Gentili, 1991, 1993). Their estimation requires iterative optimization, which
523 needs an extension for band arithmetic analysis (Yang et al., 2011). More recent
524 analytical models are even parameterized with a specific geometry (Albert and Mobley,
525 2003; Park and Ruddick, 2005). A corresponding application example is given in
526 Nechad et al. (2010), where the retrieval of *TSM* from cloudy water using a classical
527 model (Gordon et al., 1988) is surprisingly better than a directional model (Park and
528 Ruddick, 2005). Nonetheless, an improvement is expected especially for water with less
529 particle scattering, i.e. higher η and lower N , and thus with higher anisotropy.

530 Atmospheric correction procedures that provide an accurate $[R_w]_N$ e.g. through iterative
531 procedures are thereby eligible alternatives to more extensively parameterized
532 reflectance models.

533 The prominence of band-ratio algorithms for the individual retrieval of CHL in case 2
534 waters reported in this study, warrants however a note of caution. It has been suggested
535 that changes on phytoplankton assemblages, as due to climate change, may shift
536 phytoplankton composition in response to altered environmental forcing (e.g. Montes-
537 Hugo et al., 2008). This process might uncouple *CDOM* and *TSM* concentrations from
538 phytoplankton stocks and lead to further uncertainty in the retrieval of individual
539 constituents, which is usually the case when using empirical algorithms, as opposed to
540 the consolidated retrieval by inversion algorithms (Dierssen, 2010).

541 Extending from the intercomparison of algorithms performance based on synthetic and
542 in situ data sets (IOCCG, 2006), a series of intercomparison and benchmark exercises
543 including application to satellite imagery and matchup analysis is recommended to shed
544 light on the comparability of water constituent retrieval algorithms and identify their
545 applicability constraints in the near future.

546

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552

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