Chapter 4

MODELLING THE BACKSCATTERING PROBABILITY OF MARINE PARTICLES IN CASE II WATERS

4.1. Background

In order to develop new methods to retrieve bio-geochemical or physical parameters of the marine environment from ocean colour data, either based on semi-analytic models or radiative transfer simulations, parameterisations of the inherent optical properties (IOPs) of the various constituents present in sea water are required. Such parameterisations are meanwhile rather well established for Case I waters [*Bricaud et al.*, 1981; *Bricaud et al.*, 1998; *Loisel and Morel,* 1998; *Zhang et al.*, 2003]. The constituents present in Case II waters are characterised by a larger variability as compared to Case I waters. This variability as well as the difficulties encountered with *in-situ* determination of bio-optical parameters are the main reasons for the actual lack of bio-optical models for Case II waters. During the COASTLOOC (Coastal Surveillance Through Observation of Ocean Colour) project [*Babin*, 2000], bio-optical models of the absorption of non-chlorophyllous particles and coloured dissolved organic matter (CDOM) as well as marine particles scattering were developed from measurements taken in European coastal waters. One objective of this study is to develop a bio-optical model of the back scattering probability of marine particles which shall allow to simulate the light field in Case II waters with the accuracy required for the development of retrieval schemes for oceanic constituents. The model was derived by optimising the agreement between radiative transfer simulations of the hemispherical reflectance just below the sea surface and the corresponding COASTLOOC data.

4.2. The COASTLOOC Data Set

The COASTLOOC [*Babin*, 2000] data set has been used to derive the model for the back scattering probability of marine particles presented in this study. The COASTLOOC data set relates the subsurface hemispherical reflectance at 13 wavelengths between 412 nm and 865 nm to a variety of IOPs and water constituents concentrations. Most of the 424 stations visited during COASTLOOC have been gathered in Case II waters, except for 93 stations located in Case I waters in the Atlantic Ocean and Mediterranean Sea. The locations of stations visited during all COASTLOOC cruises are shown in Figure 4.1. The measurements taken in the Adriatic Sea, Baltic Sea, English Channel and North Sea were used for the development of the backscattering model. The measurements at 196 of the 243 stations in these areas fulfilled the requirements in terms of completeness and accuracy. More information on COASTLOOC is given in Table 4.1.
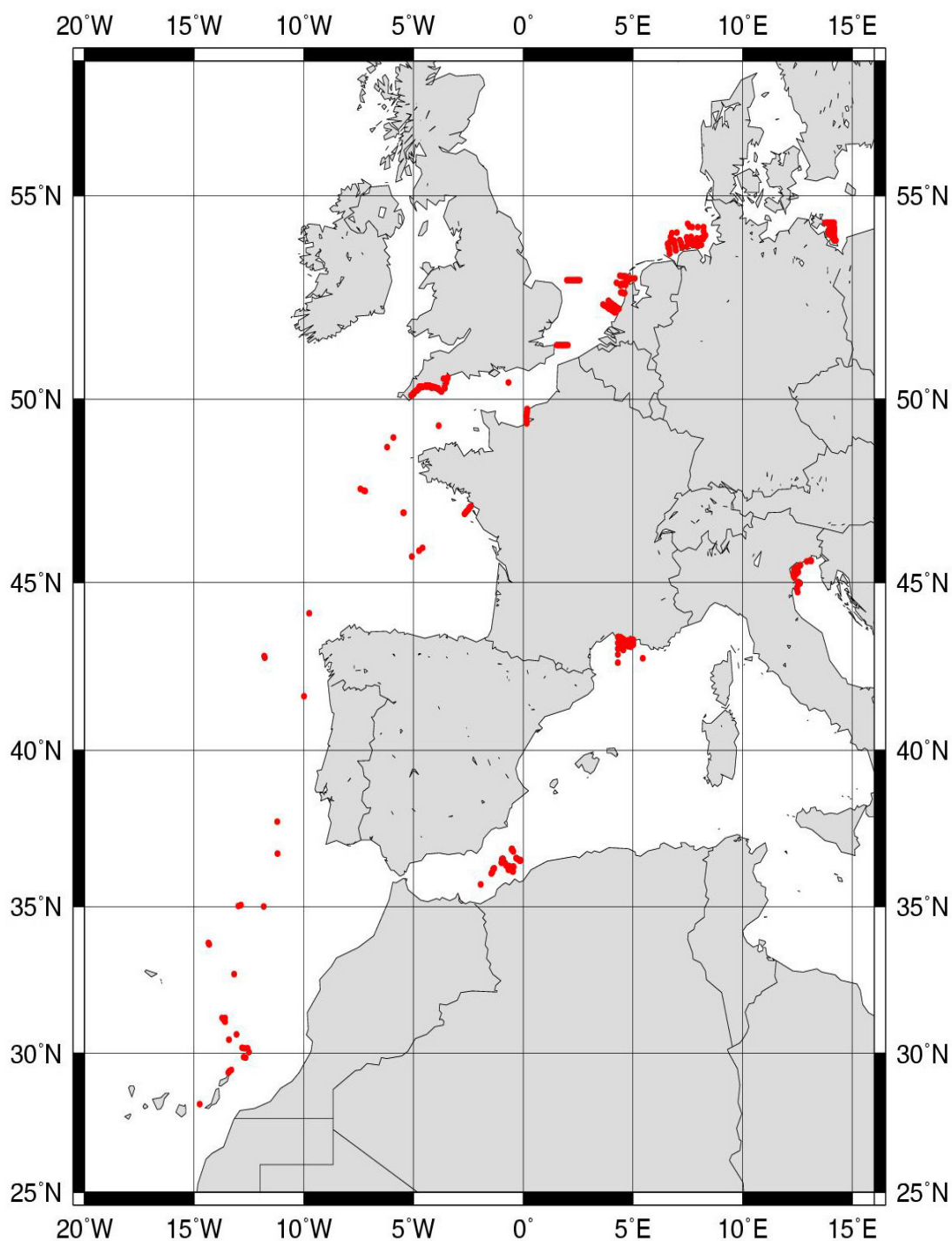
Figure 4.1. The locations of stations visited during COASTLOOC cruises, taken from *Babin* [2000].

Absorption spectra of particles were measured using the modified Filter-Transfer-Freeze (FTF) method, which eliminates the path length amplifications effect occurring with measurements on GF/F filters [*Allali et al.,* 1995]. The water sample was filtered onto 0.4μm polycarbonate membrane filters. The optical density of the particles was measured from 350 to

800 nm by a Perkin-Elmer Lambda 19 double-beam spectrophotometer. Then absorption coefficients of particles were obtained from the optical densities. The distinction of absorption spectra of particles (a_p) into algal (a_{p1}) and non-algal (a_{p2}) components was performed by numerical decomposition [*Bricaud and Stramski*, 1990].

Table 4.1. Information on the COASTLOOC data set

Campaign	Provider / PI	Area	Time	Case II stations
COASTLOOC 1	M. Babin	North Sea	April 1997	12
COASTLOOC 2	M. Babin	Mediterranean Sea	July 1997	15
COASTLOOC 3	M. Babin	Northern Adriatic Sea	July, August 1997	34
COASTLOOC 4	M. Babin	Mediterranean Sea (Golfe du Lion)	October 1997	36
COASTLOOC 5	M. Babin	English Channel, North Sea	May 1998	56
COASTLOOC 6	M. Babin	English Channel, North Sea, Baltic Sea	Sep. 1998	178
Total				331

Regarding the measurement of CDOM absorption, the particulate material was firstly removed from seawater samples by 0.4μm membrane filters. Then the optical density of the filtrate were measured from 350 to 800 nm by a Perkin-Elmer-Lambda-19 double-beam spectrophotometer. Finally, absorption coefficients of particles were derived from optical densities [*Ferrai and Dowell*, 1998].

The spectral absorption, $a(\lambda)$, and beam attenuation, $c(\lambda)$, coefficients were measured using an ac-9 profiler (WET Labs) deployed either from a ship or from a helicopter. The particle scattering coefficient, $b_p(\lambda)$, is then obtained directly from $c(\lambda)-a(\lambda)$.

Suspended particulate matter was measured as the weight of material (dried at 70°C) collected on pre-weighted GF/F filters. Pigment concentrations were measured using high pressure liquid chromatography (HPLC) techniques, using the procedure described by *Vidussi et al.* [1996]. The concentration of particulate organic carbon (POC) was determined using a Carlo-Erba-NCS-2500 elemental analyzer. The concentration of particulate organic matter (POM) was obtained using the following statistical relationship [*van Raaphorst and Melschaert*, 1996]:

$$POM=2.6\times POC \qquad (4.1)$$

Downward and upward irradiance at 13 wavelengths was measured by a SPMR radiometer (Satlantic Inc.). The subsurface hemispherical reflectance was obtained by the division of the extrapolated upward and downward irradiance just below sea surface.

4.3. Inherent Optical Properties of Oceanic Constituents in Case II Waters

Oceanic constituents in Case II waters can be divided into 5 groups [*Babin*, 2000]: pure seawater, phytoplankton and associated particles, endogenous CDOM, exogenous particles, and exogenous CDOM. The corresponding absorption and scattering coefficients are, respectively, a_w and b_w, a_{p1} and b_{p1}, a_{y1}, a_{p2} and b_{p2}, and a_{y2}. The total absorption coefficient in Case II waters is composed of the contributions of all absorbing substances:

$$a = a_w + a_{p1} + a_{p2} + a_{y1} + a_{y2} \qquad (4.2)$$

In practice, the contributions of endogenous CDOM and exogenous CDOM (a_{y1} and a_{y2}) to total CDOM absorption can not be separated from each other. Therefore, a_y is used as the sum of a_{y1} and a_{y2}. So, Eq. (4.2) can be modified as:

$$a = a_w + a_{p1} + a_{p2} + a_y \qquad (4.3)$$

The total scattering coefficient in Case II waters is composed of the contributions of all scattering substances:

$$b = b_w + b_{p1} + b_{p2}, \qquad (4.4)$$

where the subscripts p1 and p2, respectively, indicate endogenous and exogenous particles. The scattering of CDOM is assumed as zero. Actually, the contributions of endogenous and exogenous particles to total particles scattering can not be separated from each other. Therefore, b_p is used as the sum of the b_{p1} and b_{p2}. So, the Eq. (4.4) can be rewritten as:

$$b = b_w + b_p \qquad (4.5)$$

The IOPs models used in this chapter are listed in Table 4.2. More information on these models has been given in Section 2.2. Some of the IOPs models, such as for pure sea water and the absorption coefficient of phytoplankton, are commonly used. Other IOPs models, such as for the absorption coefficient of non-algal particles (exogenous particles) and yellow substance, as well as scattering coefficient of particles, were derived from the COASTLOOC data set.

The atmosphere has been considered in the simulations in order to provide a realistic diffuse light field incident on the sea surface. Since variations of the atmospheric composition have little influence on the oceanic reflectance, an atmosphere with Maritime aerosol and Rayleigh scattering for a constant surface air pressure was deemed sufficient for the execution of the present study.

Table 4.2. Parameterisation of inherent optical properties of pure sea water and constituents of Case II waters.

Constituents	IOP	Model / Measurement	Reference
Pure sea water	Absorption	Directly measured	*Pope and Fry* [1997]
	Scattering	$b_w(\lambda) = 0.00288(\dfrac{\lambda}{500})^{-4.32}$	*Morel* [1974]
	Phase function	$p_w(\lambda) = 0.06225(1 + 0.835\cos^2\theta)$	*Morel* [1974]
Particulate matter	Absorption	$a_{p1}(\lambda) = A_{ap}(\lambda)[Chl]^{B_{ap}(\lambda)}$	*Bricaud et al.* [1998]
		$a_{p2}(\lambda) = a_{p2}(443)e^{-Sp(\lambda-443)}$, $a_{p2}(443) = A_{p2} < SPM >^{B_{p2}}$, S_p=0.0122, A_{p2}=0.0216, B_{p2}=1.0247	*Babin* [2000]
	Scattering	$b_p(\lambda) = A < SPM >$, A=0.5	*Babin* [2000]
	Back scattering probability	$\widetilde{b}_b = f(r,\lambda)$	To be developed in this thesis
CDOM	Absorption	$a_y(\lambda) = a_y(443)e^{-S_y(\lambda-443)}$, S_y=0.0176	*Babin* [2000]

4.4. Comparing *in-situ* Data and Simulations of the Marine Light Field Using Petzold's Phase Function for Marine Particles

The computer code MOMO [*Fell and Fischer*, 2001] was used to create the radiative transfer simulations. The assumptions and simplifications for the simulations are the same as used in Section 3.2.

Based on the above assumptions and the chosen IOP models in Table 4.2, simulations of the hemispherical reflectance just below the sea surface were made for:

- 196 combinations of constituent concentrations corresponding to those measured at the 196 COASTLOOC stations mentioned above,
- 8 wavelengths: 411, 443, 490, 532, 559, 619, 665, and 705 nm,
- 17 solar zenith angles between 0° and 87°.

The particle phase function most often used for radiative transfer calculations of the marine light field has been derived by *Mobley et al.* [1993] based on measurements on water samples obtained in waters ranging from turbid to oligotrophic [*Petzold*, 1972]. This particle phase function, referred to as Petzold's phase function, is characterised by a back scattering probability

of 1.81 %. As shown below, using one single phase function for marine particles does not allow to accurately simulate the in-water light field over larger wavelengths and constituents concentration ranges. Using absorption and scattering coefficients of pure seawater, particles, and CDOM as defined in Table 4.2, as well as Petzold's phase function as input to the radiative transfer simulations, simulated and measured hemispherical reflectance just below the sea surface compare as follows (Figure 4.2):

(1). There is significant scatter around the 1:1 line of simulations against measurements;

(2). The differences between measurements and simulations decrease with increasing wavelength;

(3). The simulated reflectances in the Baltic Sea are generally overestimated, except for the simulations at 705 nm.

4.5. Modelling the Marine Particle Phase Function in Case II Waters

Assuming that absorption and total scattering coefficients of CDOM and marine particles contained in the COASTLOOC data set are comparably well represented by the corresponding models developed by *Babin* [2000], the observed differences between measured and simulated spectral reflectance must primarily be associated with the phase function employed, largely characterised by the back scattering probability. In order to reconcile simulations and measurements, a new back scattering probability model is proposed for marine particles in Case II waters based on the Fournier-Forand phase function [*Fournier and Forand*, 1994], in the form given by *Haltrin* [1998]. The new backscattering model will be used to select the appropriate phase function for RT simulations. In practice, the back scattering probability model was derived through the following steps:

(1) A set of 40 Fournier-Forand phase functions with back scattering probabilities ranging from 0.2 % to 5.0 % was established;

(2) For each of 196 constituents combinations actually measured, the hemispherical reflectances at 8 wavelengths for the 40 Fournier-Forand phase functions mentioned above have been calculated;

(3) The most appropriate phase function for the specific constituents combination and wavelength in terms of minimum difference between simulated and measured hemispherical reflectance was determined;

(4) The back scattering probability corresponding to the selected phase function is related to wavelengths and the ratio of POM to SPM (see below).
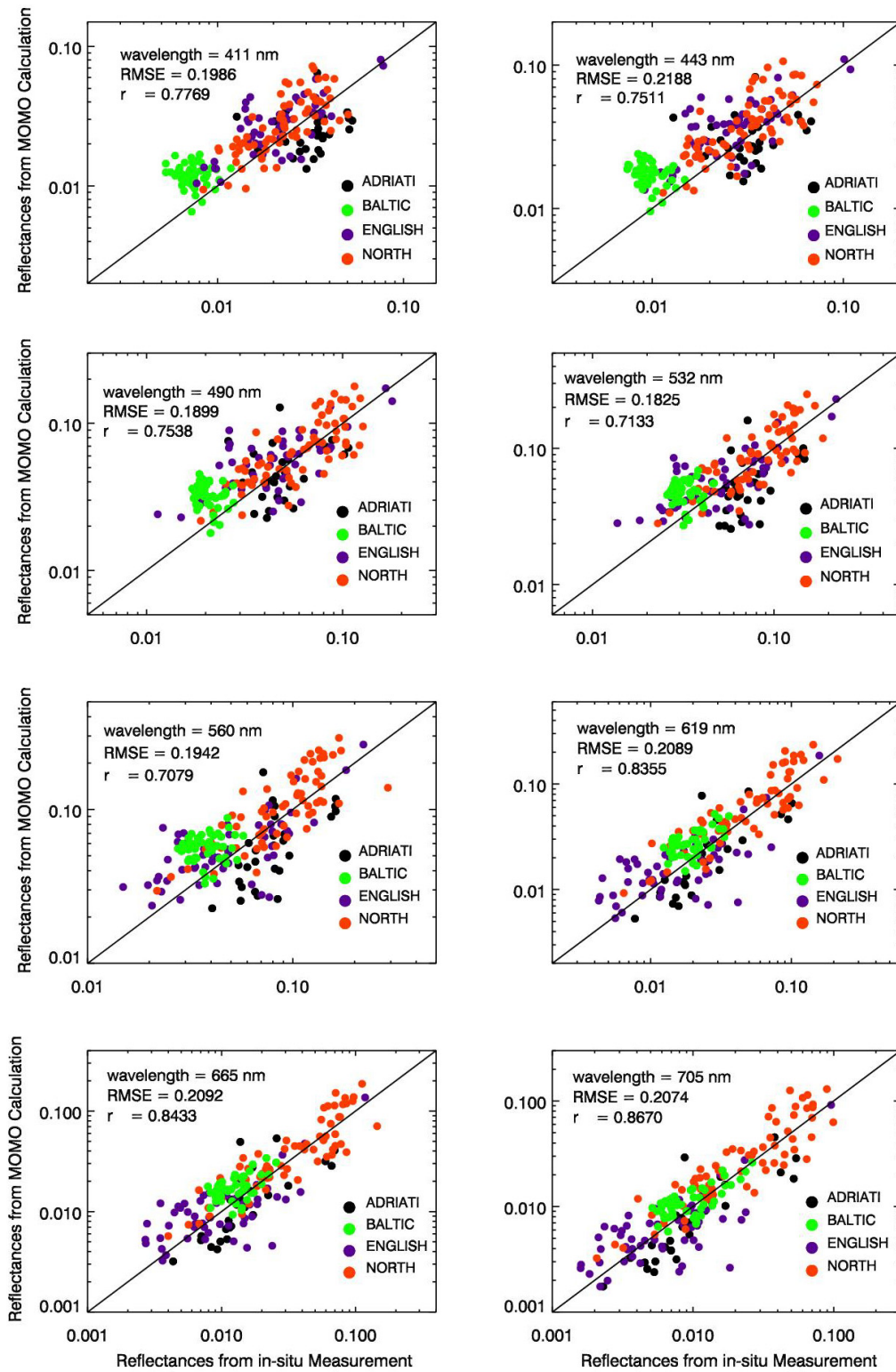
Figure 4.2. Comparison between the simulated hemispherical reflectances just below the sea surface and the corresponding COASTLOOC data. The simulations have been performed using Petzold's phase function (corresponding to a constant back scattering probability of 1.81%).

44

A model for relating the ratio of POM to SPM and wavelength to $\widetilde{b}_b(\lambda)$ was derived from the results of step (4), expressed as:

$$\widetilde{b}_b(r,\lambda) = 0.244 + 1.82 \times 10^{-3} \times \lambda + 0.5[1 - \frac{1}{1 + \exp[-10 \times (r - 0.5)]}], \qquad (4.6)$$

where r=POM/SPM, and λ is wavelength. Eq. (4.6) may be applied within the ranges $0.1 \leq r \leq 1$ and $411 \leq \lambda \leq 705$ nm. If r≤0.1 then $\widetilde{b}_b(r,\lambda) = \widetilde{b}_b(0.1,\lambda)$; if r≥ 1 then $\widetilde{b}_b(r,\lambda) = \widetilde{b}_b(1,\lambda)$. The resulting model is plotted in Figure 4.3.
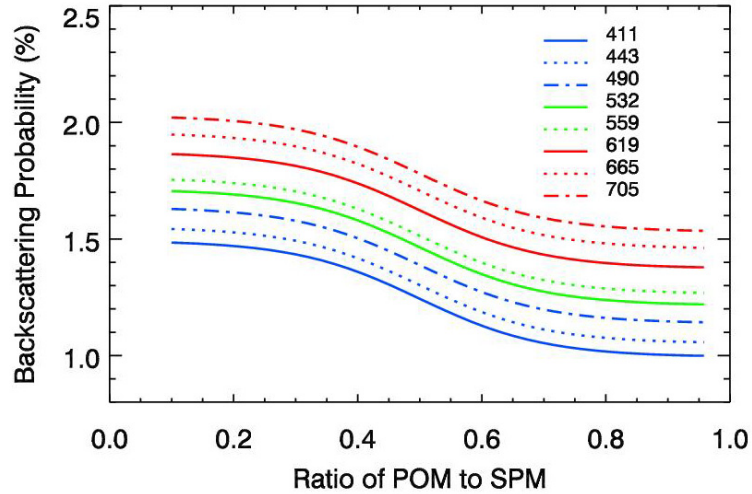

Figure 4.3. The model for the back scattering probability of marine particles in Case II waters as function of the ratio of POM to SPM and wavelength.

Theoretically, the back scattering probability of marine particles mainly depends on the ratio of organic to inorganic particles and wavelengths. Marine particles consist of two types: organic particles and inorganic particles. The scattering properties of these two types are different from each other. Organic particles are characterised by a lower refractive index, which results in smaller back scattering probabilities. Inorganic particles are characterised by higher refractive index, which results in larger back scattering probabilities. This is the reason that the particle back scattering probability is related to the ratio of POM to SPM.

In Eq. (4.6), r is a variable. Therefore, if this model is applied to radiative transfer simulations, there is one more variable besides CHL, SPM and CDOM. However, this will make it more complex to retrieve oceanic constituents. In order not to increase the complexity of oceanic constituents retrieval, a replacement of POM was found in this thesis, which is a combination of CHL and CDOM.

During the COASTLOOC cruises, the concentration of particulate organic matter (POM) was determined. In order to investigate the correlation between POM and other variables, the concentration of POM was related to $a_y(443)$, $a_y(443)+a_{ph}(443)$ (shown in Figure 4.4), and $a_{ph}(443)$, respectively. These relationships are expressed as:

$$\log(POM) = 0.587 + 0.859 \times \log[a_y(443)] \qquad (r^2 = 0.689, N = 283) \quad (4.7)$$

$$\log(POM) = 0.457 + 0.995 \times \log[a_{ph}(443) + a_y(443)] \quad (r^2 = 0.789, N = 258) \quad (4.8)$$

$$\log(POM) = 0.707 + 0.875 \times \log[a_{ph}(443)] \qquad (r^2 = 0.627, N = 269) \quad (4.9)$$

From the above results, it can be seen that there is a statistical significant relationship between POM and $a_y(443)+a_{ph}(443)$. Therefore, $a_y(443)+a_{ph}(443)$ through Eq. (4.8) is used to represent POM in Eq. (4.6). The resulting model of the backscattering probability is plotted in Figure 4.5.
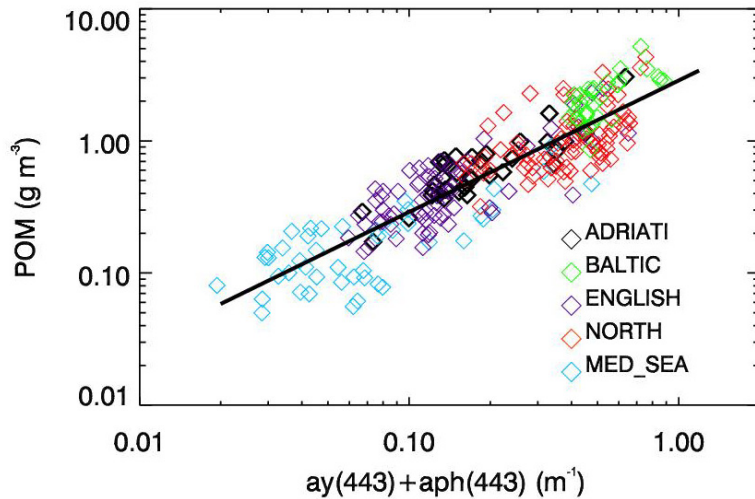

Figure 4.4. The relationship between $a_y(443)+a_{ph}(443)$ and the concentration of particulate organic matter. The black line was plotted based on Eq. (4.8).
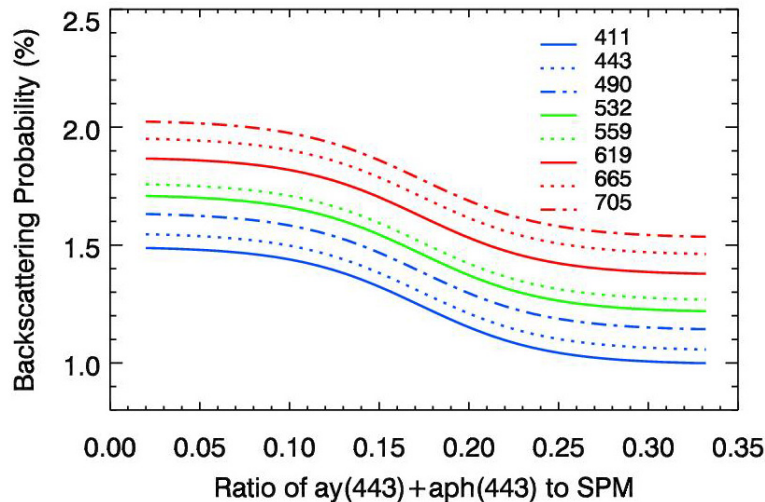

Figure 4.5. The model for the back scattering probability of marine particles in Case II waters as function of the ratio of $a_y(443)+a_{ph}(443)$ to SPM and wavelength.

When applying this new model to the RT simulations (Figure 4.6), the differences between the simulations and the measurements are significantly reduced as compared to RT simulations based on Petzold's phase function (Figure 4.7).
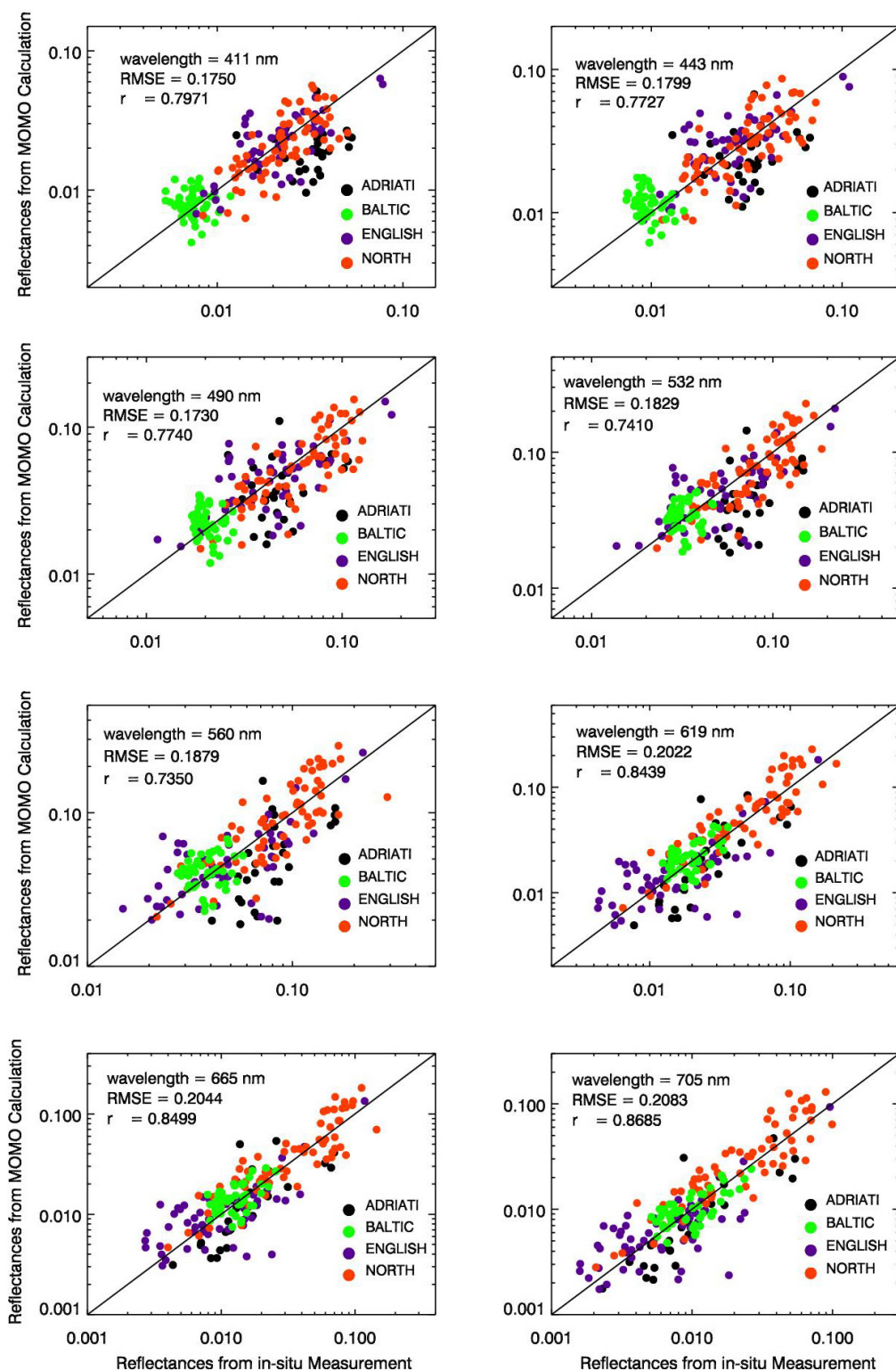
Figure 4.6. Comparisons between the simulated hemispherical reflectances and the corresponding COASTLOOC data. The simulations have been performed with the new model for the back scattering probability of marine particles proposed in this study.
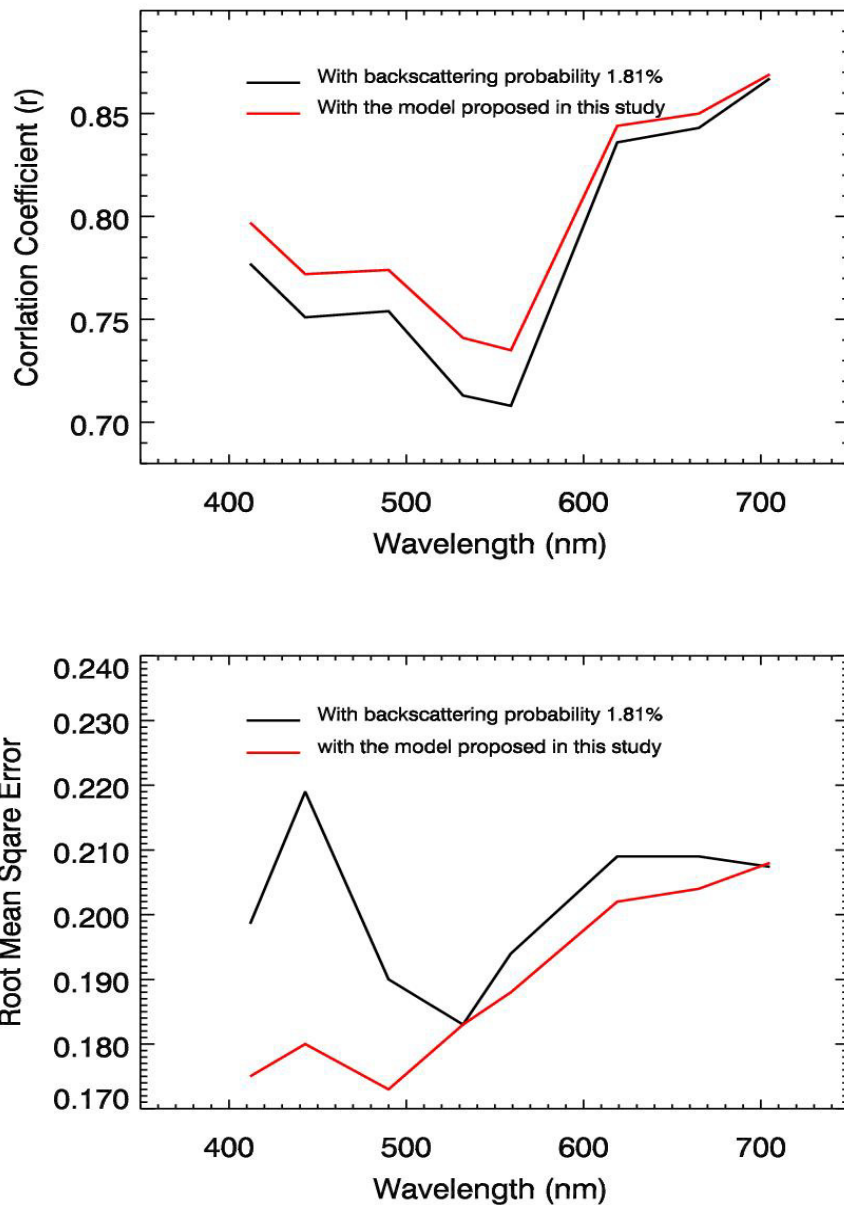
Figure 4.7. Comparison of statistical parameters between the simulations with the new model and 1.81% back scattering probability.

4.6. Discussion

The new model for the back scattering probability of marine particles may be qualitatively interpreted by Mie theory. The higher the ratio of $a_y(443)+a_{ph}(443)$ to SPM, the higher is the proportion of POM to SPM, which results in smaller back scattering probability. In the Baltic Sea, the proportion of POM to SPM is very high [*Babin et al.,* 2003], marine particles should therefore have lower back scattering probability.

However, due to the lack of information on size distribution and complex refractive index, it is impossible to quantitatively validate the presented back scattering probability model. Here, it

was examined if this model is representative of the conditions in natural marine environments using known information on size distribution and complex refractive index by Mie theory.

It was assumed that particles in natural marine environments consist of two types: organic and inorganic particles. The particle size distribution in marine environments is commonly described using a Junge size distribution (a power law model), with slope parameters typically ranging between 3 and 5 [*Bader*, 1970; *Sheldon et al.*, 1972; *Jonasz*, 1983]. Here, minimal and maximal size of marine particles are set equal to 0.02 and 200 μm, respectively. The contribution from particles beyond this range to the total scattering can be ignored [*Morel and Ahn*, 1991; *Stramski and Kiefer*, 1991; *Ulloa et al.*, 1994; *Babin et al.*, 2003]. For the real part of the relative refractive index of mineral particles, a typical value of 1.17 has been chosen [*Lide*, 2001]. The real part of the relative refractive index of organic particles is set to 1.115. It is higher than that of the living algae (1.05) [*Brown & Gordon*, 1974; *Morel & Ahn, ibid*; *Stramski & Kiefer*, 1991]. *Aas* [1996] found that the most important factor for the variation of the refractive index is the algal water content. For the algal dry mass, the average relative refractive index is about 1.15. Organic particles consist of living algal particles and detrital organic particles. Detrital organic particles are characterised by lower water content. Therefore, the real refractive index of organic particles is higher than that of living algal particles (1.05), but lower than that of the algal dry mass (1.15). The imaginary refractive indexes for organic particles and inorganic particles are taken from *Babin et al.* [2003]. The back scattering probabilities calculated by the new model and estimated by Mie theory are depicted in Figure 4.8 for three wavelengths. The inputs for Mie calculations are listed in Table 4.3. As shown in Figure 4.8, a good agreement between the model proposed in this study and Mie calculations was obtained. The model for the back scattering probabilities of marine particles in Case II waters proposed in this study is therefore deemed to be representative of the conditions in natural marine environments.

Table 4.3. Inputs for Mie calculations.

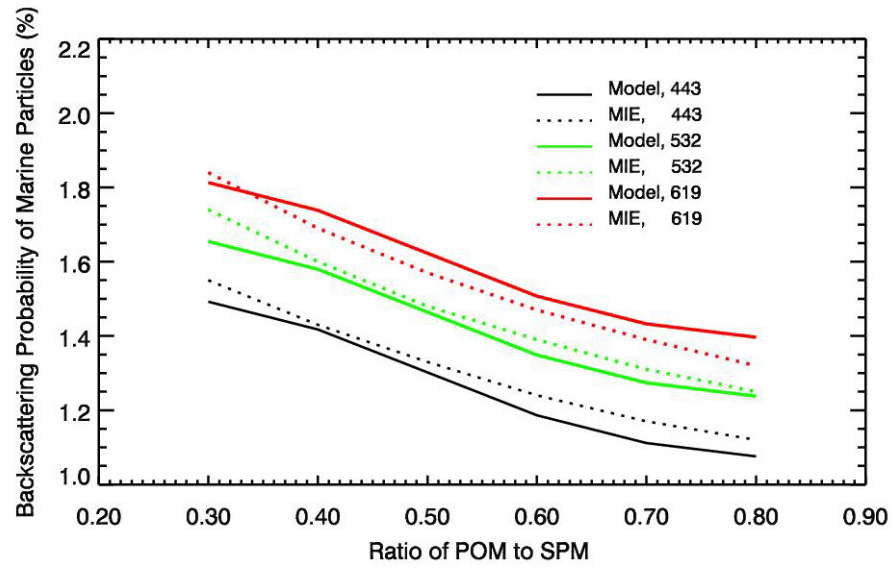| Particle Compound	Size distribution	slope	Size range	Refractive index
Organic particles	Power-law	3.6	0.02~200 μm	$1.115 - 0.0025 * a^*_{ph}(\lambda)$
Inorganic particles	Power-law	3.9	0.02~200 μm	$1.170 - 0.0045 * a^*_{nap}(\lambda)$

Figure 4.8. Comparison between the model of the back scattering probability proposed in this study (Equation 4.6) and the Mie calculations. The inputs of the Mie calculations are listed Table 4.3.