



Global Lakes Sentinel Services

Grant number 313256

Technical report about measurement protocols

TO, SYKE, CNR, WI
2015-02



Global Lakes Sentinel Services

GLaSS is funded by the European Commission (FP7)

Grant number 313256

WP4. Production and validation of test datasets

D.4.2. Nearby lakes: Validation of L2, L3 and GlaSS products by field studies

TO, SYKE, CNR, WI

Change records

Version	Date	Description	Contributors
1	30.01.2014	First draft	TO, SYKE, CNR, WI. Compiled by TO
2	02.03.2015	Additions and comments	WI, SYKE
3	10.03.2015	Additions	CNR

Consortium

No	Name	Short Name
1	WATER INSIGHT BV	WI
2	SUOMEN YMPARISTOKESKUS	SYKE
3	EOMAP GmbH & Co.KG	EOMAP
4	STICHTING VU-VUMC	VU/VUmc
5	BROCKMANN CONSULT GMBH	BC
6	CONSIGLIO NAZIONALE DELLE RICERCHE	CNR
7	TARTU OBSERVATORY	TO
8	BROCKMANN GEOMATICS SWEDEN AB	BG

Task objective (from DoW)

Algorithms developed in Task3 will be validated on the bases of field data both by accordance with MERIS (and other satellite) products and much-ups. Partners will carry out field campaign according to the standardized field protocols and data will be combined to the joint database. Lakes are selected to represent various classes, status, management and importance to the socio-economic development (see Task5). Partners will visit field campaigns in each test lake at least once during the project to exchange experience produce intercalibrations.

Scope of this document

This document focuses on description of measurement methods used both in field and in laboratory by the GLaSS community (CNR-IREA, SYKE, TO, VUWI and Dr. Zhang from advisory board as a data-provider about L. Taihu). It describes used instrumentation and parameters gathered for calibration/validation activities as a background for remote sensing of lakes. It also describes major differences from NASA Ocean Colour protocols, which are generally used as guidelines for *in situ* measurements for remote sensing purposes and gives an overview of the sources of variation of *in situ* data. This document is a start of the development of dedicated protocols for optical measurements and satellite validation for inland waters of different types.

Abstract

In the FP7 project GLaSS, groups from different European countries co-operate on development of algorithms for the new Sentinel satellite series, with a focus on lakes. To be able to compare the results, it is very important to use standard protocols for in situ measurements, which are suitable for lakes. However, there is no standard protocol for optical measurements in lakes. This document is the first step towards such a document. The GLaSS consortium generally follows methods proposed by NASA Ocean Colour protocols, with some exceptions: 1) Chl a is measured not with high performance liquid chromatographic (HPLC) methods, but spectrophotometrically. Used solvents and calculation methods vary widely among GLaSS members. 2) Absorption of particles retained on filter – different solvents for pigment bleaching are used, not just NaClO suggested by NASA. 3) Differences in Rrs measurement in comparison with measurements performed in ocean come from slight difference of measuring angles due to using small boats. In case of lakes more variation is introduced due to bottom reflection and vicinity of the coast. Optical closure tests, where Hydrolight simulations and measured Rrs values were compared, revealed highly matching spectra in size and shape in case of Vesijärvi, matching spectral shape in case of two Finnish lakes and a bit higher mismatch in rest of two Finnish lakes. In case of CNR (L. Garda) and TO (L. Võrtsjärv and Peipsi) larger divergence was observed with Hydrolight-simulated spectra being much lower than *in situ* measured spectra. Also an assessment of the degree of variation of field measurements performed by CNR was included. Field measurements were performed at L. Garda and Maggiore (Italy). The Rrs variation depended the presence/absence of cyanobacterial bloom (formed by *Anabaena lemmermannii*), wind speed, cloud conditions and water depth. The degree of variation of Chl a was about 20% for both lakes, variation can be higher both in cases of very low concentrations (Chl a <1 mgm⁻³) or algal bloom. Patchy cyanobacterial blooms cause increase in variation in TSM concentration as well.

List of abbreviations

Abbreviation	Description
Rsr	Remote sensing reflectance
IOP	Inherent optical properties
SIOP	Specific inherent optical properties
FOV	Field of view

List of related documents

Short	Description	Date
D. 3.1	Initial test dataset	07.10.2013
D. 3.4	Adapted Water Quality Algorithms	31.07.2014

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1 Introduction

In the FP7 project GLaSS, seven groups from different European countries co-operate on the preparation of the uptake of Sentinel data, including use cases to demonstrate the applicability of this new high-resolution data on lakes with a large range of optical properties. Within GLaSS there are work packages on validation, algorithm comparison and atmospheric correction that require comparable and high quality *in situ* measurements of the lakes. Unfortunately, the type of radiometric instruments and lab techniques used by the partners are different with regard specification, performance and sensitivity. Hence, it is very important to use standard protocols to make sure the results are comparable and requirements are fulfilled before validating results. The Ocean Optics Protocols for SeaWiFS Validation, later upgraded to “Ocean Optics Protocols For Satellite Ocean Colour Sensor Validation” (Mueller *et al.* 2003) are set up to allow such harmonization. However, in inland waters many of these standard procedures cannot be applied due to different reasons. Lakes are not deep enough, are much more turbid and much more influenced by nearby land than oceanic waters, requiring changes to the standard protocols. Some instruments or methods just cannot be applied in these environments, or from the smaller ships that are used in lakes. Also, it must be noted that it has been 11 years since these protocols have been updated and instruments have improved significantly over time.

This document is a start of the development of dedicated protocols for optical measurements and satellite validation for inland waters of different types. It focuses on description of methods used within GLaSS community, which has long experience with optical measurements in lakes (CNR-IREA, SYKE, TO, VU/WI and Dr. Zhang from advisory board as a data-provider about L. Taihu). It describes what instruments are used and what kind of data is gathered for calibration/validation activities as a background for remote sensing of lakes, and how the used methods differ from NASA Ocean Colour protocols, which are generally used as guidelines for *in situ* measurements for remote sensing purposes. Field methods and equipment specifications were gathered and described. The methods appeared to differ substantially, due to either available equipment (groups working in lake are generally small and have not so much funding) as well as due to difference in lakes that require different protocols. Protocol harmonisation is therefore not possible, but it was acknowledged that protocols should be comparable. Therefore, a start has now been made to create a precise overview of used methods by lakes optics community, starting here with the GLaSS consortium. Especially, attention goes to clarifications on how and why the protocols by GLaSS members differ from NASA's Ocean Optics Protocols for Satellite Ocean Colour

Sensor Validation.

Additionally, optical closure tests were performed as a quality check to the results obtained with the described methods.

Protocols about field measurements and used methods from following GLaSS partners are included in this document:

- **CNR-IREA** (Italy): CNR-IREA 2014. Cal-val protocol used at CNR-IREA: quantities, instruments and methods, 5 pg.
- **SYKE** (Finland): Kallio, K., S. Koponen, A. Ruiz-Verdú, T. Heege, K. Sørensen, T. Pyhälähti & R. Doerffer 2007. Development of MERIS Lake Water Algorithms Validation Protocol. ESRIN Contract No. 20436/06/I-LG, 14 pg. (Afterwards only a part about Finnish fieldwork is taken into account). Methods related to absorption measurements are described in detail in Ylöstalo et al. (2014).
- **TO** (Estonia): Uudeberg, K., K. Alikas, K. Kangro, E. Asuküll, M. Ligi, I. Ansko and A. Reinart 2013. Water remote sensing protocols for fieldwork methods. Tartu Observatory, Tõravere, Estonia, 22 pg.
- **WI** (Netherlands): 1) Pasterkamp, R., S.W.M. Peters, M. Laanen 2001. Measurement protocol for the determination of specific inherent optical properties of natural surface water. Institute for Environmental Studies, Vrije University Report W01/15, 38 pg.
2) WISP-3 user guide. Version 1.2. Water Insight B.V., the Netherlands, 25 pg.
- **VU/VUmc** (Netherlands): Pasterkamp, R., S.W.M. Peters, M. Laanen 2001. Measurement protocol for the determination of specific inherent optical properties of natural surface water. Report W01/15, updated 2002, 38 pg.
- **Dr. Zhang** (China): general description about methods used for L. Taihu.

From those 6 protocols an overview of the methods has been generated. Extra input was provided by Peter Hunter about methods used in GloboLakes (Global Observatory of Lake Responses to Environmental Changes) project which will end up in LIMNADES database.

Outline of this document:

1. **Differences between methods used by GLaSS community and NASA's protocols** "NASA/TM-2004-. Ocean Optics Protocols For Satellite Ocean Color Sensor Validation, Revision 5"
2. **Differences in methods within a GLaSS community**
3. **GloboLakes protocols for validation of ocean colour satellite data**
4. **Optical closure test - examples by SYKE, CNR and TO**
5. **Variation assessment of *in situ* data (CNR)**
Annex I WISP-3

2 Differences between methods used by GLaSS community and NASA's protocols

2.1 Parameter collection

Table 1 shows a list of parameters that the GLaSS consortium generally collect during field campaigns with respect to the Ocean Colour recommendations (as listed in Table 2.1 of Fargion and Mueller (2000)). There are radiometric quantities, inherent optical properties, biogeochemical and bio-optical quantities together with ancillary data. Four sets of variables exist in NASA protocol: "Required" - "R", "Highly Desired" - "HD", "Specialized" - "S" and "Derived" - "D" - the last one is calculated based on other measured variables.

CNR usually performs two "types" of activities in the field, for which the collected parameters are different:

- cal/val: carried out during the sensor overpass aiming the EO-product. These campaigns need clear sky conditions, are optimized for multiple stations and are mainly focused to collect Rrs spectra, concentrations of water quality components and AOD;
- optical characterization: carried out to study the optical properties of the lake waters in order to mainly calibrate bio-optical models. These campaigns (also can be carried out in cloudy conditions) require more specialized instrumentation and the surveyed stations are generally few as the measurement session is long. These campaigns may in case of right conditions be used in 'cal/val' activities during sensor overpass.

Thus for CNR three types of markings are used in Table 1: "C" to list data, which was collected in "cal/val" campaigns; the column "Specialized Measurement" (S) to list the data, which is collect in "optical characterization" campaigns. "D" shows the derived quantities.

Other partners did not specify different types of activities, but it can be assumed, that similar approach is used in other institutions as well. However, in this document only for CNR activities are specified. For others the marking "X" is used when a certain measurement is performed, and "D" when parameter is derived from other measurements.

In addition to variables listed in Fargion and Mueller (2000) GLaSS community is measuring also following parameters (marked red in Table 1):

- inorganic suspended matter (organic suspended matter can then be derived from TSM and SPIM);
- Lambertian SpectralonTM panel radiance on air for reference measurements;

- phytoplankton wet weight;
- dissolved organic carbon (DOC);
- Chl a concentration and phaeopigments using spectrophotometrical method.

Table 1. List of measured/calculated parameters according to NASA/TM-2004-. Ocean Optics Protocols (NASA OO), GLaSS community (CNR, TO, SYKE, WI/VU), advisory board member Prof. Zhang and GloboLakes. For NASA OO the marking is R (Required), HD (Highly desired), S (Specialized), D (Derived); for CNR C (Calibration study), S (Specialized), D (Derived); for all others X (measured), D (derived). Parameters in red are additionally measured by GLaSS community.

	NASA OO	CNR	TO	SYKE	VU/WI	Zhang	GloboLakes
	R/HD/S/D	C/S/D	X/D	X/D	X/D	X/D	X/D
Radiometric Quantities							
Downwelled Irradiance $E_d(z, \lambda)$	R	S				X	
Upwelled Radiance $L_u(z, \lambda) = L(z, \lambda, 0, 0)$	R	S				X	
Upwelled Irradiance $E_u(z, \lambda)$	S	S					
Radiance Distribution in water $L(z, \lambda, \theta, \phi)$	HD						
Water Surface Radiance in air $L_{sfc}(\lambda, \theta, \phi)$	R	C, S	X	X		X	
Incident Irradiance in air $E_s(\lambda) = E_d(0^+, \lambda)$	R	C, S	X	X	X		X
Normal Solar Irradiance $E_N(z, \lambda)$	HD						
Lambertian Spectralon Surface Radiance in air		C, S		X		X	
Sky Radiance $L_{sky}(\lambda, \theta, \phi)$	HD	C, S	X	X	X	X	X
Diffuse Sky Irradiance $E_{sky}(\lambda)$	D		D				X
Direct Sun Irradiance $E_{sun}(\lambda) = E_s(\lambda) - E_{sky}(\lambda)$	D						
Water-Leaving Radiance $L_w(\lambda, \theta, \phi, \theta_o, \phi_o)$	D	D	D	D	D	D	
Remote Sensing Reflectance $RRS(\lambda, \theta, \phi, \theta_o, \phi_o)$	D	D	D	D	D	D	D
Attenuation Coefficient $K(z, \lambda)$ for $E_d(z, \lambda)$ and $L_u(z, \lambda)$	D	D	D		D?		
Ocean Bidirectional Reflectance Distribution Function BRDF	D						
Aerosol Optical Depth $\tau_a(\lambda)$	R	C	X				
Aerosol Phase Function $P_a(\lambda, \theta, \phi, \theta', \phi')$	D						
Absorbing Aerosol Height Profiles (LIDAR Profilometer)	S						
Inherent Optical Properties							
Beam Attenuation Coefficient $c(z, \lambda)$	HD	S	X				X
Absorption Coefficient $a(z, \lambda)$	HD	S	X				X

Backscattering Coefficient $bb(z,\lambda)$	HD	S	X				X
Scattering Coefficient $b(z,\lambda) = c(z,\lambda) - a(z,\lambda)$	D						
Volume Scattering Function $\beta(z, \lambda, \theta, \phi, \theta', \phi')$	S						
Particle Absorption Coefficient $ap(z,\lambda)$	HD	S	X	X	X	X	X
Dissolved Material (CDOM) Absorption Coefficient $ag(z,\lambda)$	HD	S	X	X	X	X	X
Non-Pigmented Particle Absorption Coefficient $ad(z,\lambda)$	HD	S	X	X	X	X	X
Phytoplankton Absorption Coefficient $a\phi(z,\lambda)$	HD	D	D	D	D	D	D

Biogeochemical and Bio-Optical Quantities

Phytoplankton Pigment Composition (HPLC method)	R	S					X
Chlorophyll a and Phaeopigments Conc. (Fluorometric method)	R	S					
Spectrophotometrically measured Chl a and phaeopigments		C, S	X	X	X	X	X
Phycobiliprotein Concentrations	S						
Phytoplankton wet weight			X				X
Coccolith Concentrations	S						
Total Suspended Particulate Material (TSM)	S	C, S	X	X	X	X	X
Total Suspended Inorganic Particulate Material (SPIM)		C, S	X	X		X	
Total Suspended Particulate Organic Material (SPOM)		D	D	X		D	
Dissolved organic carbon (DOC)				X			
Fluorescence Intensity, <i>in situ</i> profile $F(z)$	HD	S					

Ancillary Data and Metadata

Latitude and Longitude	R	C, S	X	X	X	X	
Date and Time (UTC)	R	C, S	X	X	X	X	
Wave Height	R		X				
Whitecap Conditions (fractional amount of surface)	HD						
Wind Speed and Direction	R	C, S	X	X			
Surface Barometric Pressure	R						
Cloud Cover (amount, and sun obscuration information)	R	C, S	X	X			
Cloud Type	HD		X				
Secchi Depth	R	C, S	X	X			
Water Depth (only in optically shallow waters)	R	C, S	X				

Conductivity and Temperature over Depth (CTD) T(z), S(z)	HD		X				
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Additionally measured parameters of GloboLakes:

Besides phytoplankton pigment determination with spectrophotometer (according to ISO 10260, 1992, either using ethanol or hot acetone) and HPLC also cell count is determined under microscope. For C-phycoyanin spectrophotometric determination a sonication and freeze-thaw extraction according to Horvath *et al.* (2013) is used. Additionally CDOM fluorescence is measured according to Stedmon & Bro (2008).

2.2 Main differences with NASA OO protocols

Generally, the measurement protocols used by the GLaSS consortium are comparable to the standard protocols for oceanic waters, especially in the context of the IOPs when NASA's protocols are followed most accurately. However, some main exceptions occur in Chlorophyll determination, absorption of particles retained on the filter, absorption of CDOM and above water reflectance measurements. These subjects are discussed below.

1) Chlorophyll a determination

Measurements of Chl a provide the largest difference from NASA protocols, since HPLC or fluorometric measurements are required by NASA but all members of GLaSS are measuring Chl a spectrophotometrically. There are financial reasons causing the lack of instrumentation and also historical reasons – similarly measured previous measurements are more accurately comparable. According to Sørensen *et al.* (2007) an inter-comparison between 20 validation teams analysing water samples from Norwegian coastal waters (Chl a range 1-12 mg m⁻³) the spectrophotometric method yielded 15-20% higher Chl a concentrations (e.g. due to influence of different degradation products) than the HPLC method. Thus it can be assumed that we are overestimating Chl a concentration by performing spectrophotometric measurements.

2) Absorption of particles retained on filter

NASA protocols suggest NaClO for the bleaching solvent to obtain a_{bp} , whereas different solvents are used within GLaSS community (see paragraph 2.2.).

3) Absorption by coloured organic matter (aCDOM)

The ocean optics protocols (Mueller *et al.* 2003) advice to use polycarbonate membrane (0.2

μm) filters, because GF/F filters ($0.7\mu\text{m}$) allow passage for some bacteria, viruses, and colloids, which are not considered dissolved materials and cause rather severe contamination of the filtrate. Membrane filters are difficult to clean and can easily be clogged by particulates. Therefore, the ocean optics protocol (Mueller *et al.* 2003) advice for aCDOM measurement in coastal and turbid inland water bodies to first use GF/F filters to remove larger particulates and filter again through $0.2\mu\text{m}$ membrane filters. However, because absorption of particles are measured over ~ 0.7 GF/F filters, the filtration over $0.2\mu\text{m}$ introduces a gap in determination of the total absorption of a sample. This gap is expected to be low in the open ocean, where the main fraction of suspended matter consists of phytoplankton, and the rest of fraction of suspended matter is very low. In inland waters the contribution may be much higher, e.g. $\sim 13\%$ according to Laanen (2007).

To prevent this gap between the measurements, there are two options. Either the same $0.2\mu\text{m}$ filtration should also be applied to the determination of the IOP of the particulate fraction's phytoplankton and suspended matter; or CDOM absorption should be performed after filtration over $0.7\mu\text{m}$ GF/F filters. Errors due to scattering by e.g. bacteria, viruses, and colloids can be prevented by measuring the absorption for example in a PSICAM device, which is insensitive to scattering (Laanen, 2007). Therefore, for inland waters it is recommended to use GF/F filters and measure the absorption in a PSICAM device.

The Ocean optics protocols recommend pre-soaking of Nucleopore membrane filters in 10% HCl followed by rinsing in MilliQ to remove any colour from the filter. But according to REVAMP protocol (Tilston *et al.*, 2002), this method significantly increase the absorption of the filtrate. GLaSS partners use initially filtration through GF/F and then through MilliQ – rinsed $0.2\mu\text{m}$ polycarbonate filter.

4) Above water remote sensing reflectance

Another difference from NASA's protocols occurs with the calculation of R_{rs} above water. CNR always uses the ocean color approach (geometry of viewing and illumination angles suggested by Mobley (1999), i.e. 40 deg from the nadir and 135 deg from the Sun) but:

- in some cases (after a quality control) they compute R_{rs} without L_{sky} , since it can be affected by adjacent lands (Fig. 1);
- differently from the SeaWiFS protocols (Mueller and Austin, 1995) GLaSS partners do not assume that the water-leaving radiance is zero at 750 nm, because this is not the case in turbid lakes. This means that the value of R_{rs} at 750 nm can be attributed to residual

reflected-sky radiance and therefore no adjustment of the final estimate of R_{rs} by subtracting R_{rs} at 750 nm is made.

For spectrophotometers ASD and PR-650 the E_d is retrieved from radiance measurements from a Lambertian Spectralon™ panel (CNR, Zhang) (with WISP-3 as an exception, since it measures E_d directly). The virtue of this method (Mobley, 1999) to estimate R_{rs} is that all measurements are made with an instrument that does not require an absolute/updated radiometric calibration.

SYKE and TO follow NASA's protocols for above-water measurements of R_{rs} (see 2.3) with occasional slight modifications of measuring angles while using small boats.

It should always be specified, whether π is included into calculation formula or not.

Because several GLaSS partners use the WISP-3 radiometer for reflectance measurements, extra attention is put to check the performances of this instrument. The spectral resolution, wavelength and radiometric accuracy, sampling interval, stray light rejection tests of WISP-3 with reference to radiometric requirements set by NASA for above water spectral reflectance measurements presented in Annex I.

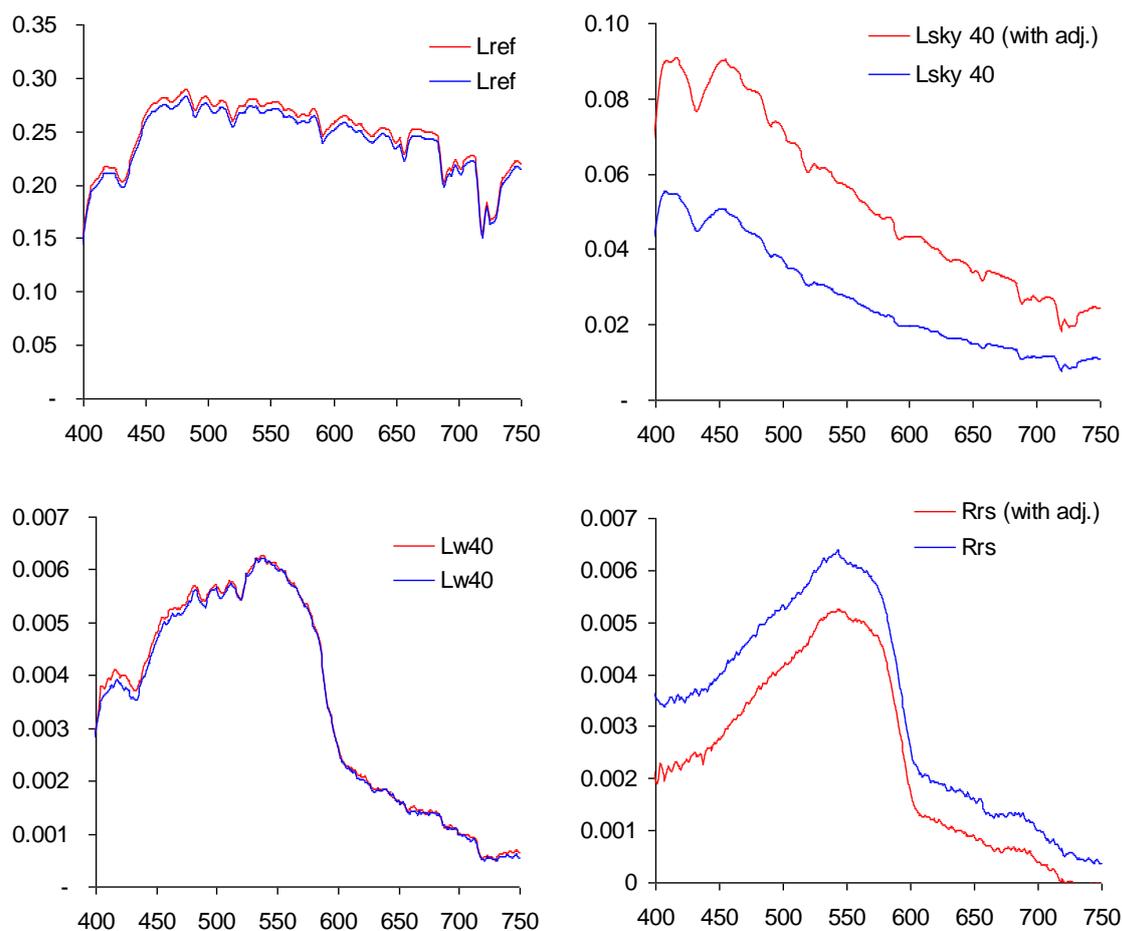


Figure 1. Radiances (in $Wm^2sr^{-1}nm^{-1}$) measured in a coastal station in Lake Maggiore (in less than 2 min.) and the related computation of a $R_{rs}=(L_w-0.028 \cdot L_{sky})/(\pi \cdot L_{ref} / p_{ref})$ (where p_{ref} is the Spectralon panel reflectance). The L_{sky} plot clearly shows the increase of the signal due to the contamination of adjacent lands and its impact on the R_{rs} spectra is not negligible.

3 Differences in protocols within the GLaSS community

3.1. Determination of in-water constituents

Obtaining Chl *a* concentration is an example of the most variable measurement procedure (Table 2.), where both used solvents and calculations vary among partners. TO uses 96% **ethanol** in room temperature. SYKE, WI, VU and Zhang use hot (WI/VU 75°) ethanol (Zhang and WU/VI - 80%). CNR uses 90% **acetone**. SYKE uses Chl *a* value obtained without acidification and all others use acidification with HCl. For computations CNR uses Lorenzen (1967) and TO Jeffrey-Humphrey (1975) formulas. VU and WI determine concentration photometrically by measuring the extinction coefficient at 665 and 750 nm before and after acidification of the sample, using following formula by Pasterkamp *et al.* (2001).

$$\text{Chl } a = 296[(E_{\text{extract}}(665) - E_{\text{extract}}(750)) - (E_{\text{acid}}(665) - E_{\text{acid}}(750))] \quad (1)$$

Prof. Zhang measures Chl *a* spectrophotometrically at 750 and 665 nm with correction for phaeophytin-*a* according to Simis *et al.* (2005).

Table 2. Overview of the instrumentation and main differences between used methods of GLaSS community.

		CNR	SYKE	TO	VU/WI	Zhang
Radiometric Quantities						
Downwelled Irradiance $E_d(z, \lambda)$	TRiOS RAMSES (0-)	X				
Upwelled Radiance $L_u(z, \lambda) = L(z, \lambda, 0, 0)$						
Upwelled Irradiance $E_u(z, \lambda)$						
Radiance Distribution in water $L(z, \lambda, \theta, \phi)$						
Water Surface Radiance in air $L_{sfc}(\lambda, \theta, \phi)$	ASD field spectrometer	X	X			X
	TRiOS RAMSES(0+)			X		
	WISP-3	X	X	X	X	
	PR-650 Colorimeter	X				
Incident Irradiance in air $E_s(\lambda) = E_d(0+, \lambda)$	WISP-3	X	X	X	X	
	TRiOS RAMSES (0+)			X		
	ASD field spectrometer	X	X			
	PR-650 Colorimeter	X				
Lambertian Spectralon Surface Radiance in air	PR-650 Colorimeter	X				
	ASD field spectrometer	X				X

Sky Radiance $L_{sky}(\lambda, \theta, \phi)$	PR-650 Colorimeter	X				
	ASD field spectrometer	X	X			
	CIMEL CE-318	X		X		
	WISP-3	X	X	X	X	
	TRiOS RAMSES(0+)			X		
Vertical diffuse attenuation K_d	LI-192SA	X				
	TRiOS RAMSES (0-)	X				
Aerosol Optical Depth $\tau_a(\lambda)$	Microtops II Sunphotometer	X		X		
	EKO MS-120	X				
	CIMEL CE-318	X		X		

Inherent Optical Properties

Beam Attenuation Coefficient $c(z, \lambda)$	WET Labs ac-9	X				
	WET Labs ac-s			X		
Absorption Coefficient $a(z, \lambda)$	WET Labs ac-9	X				
	WET Labs ac-s			X		
Scattering Coefficient	$b(z, \lambda) = c(z, \lambda) - a(z, \lambda)$	X		X		
Backscattering Coefficient $b_b(z, \lambda)$	HOBILabs HydroScat-6	X				
	Bb3			X		
	VSF3			X		
Particle Absorption Coefficient $a_p(z, \lambda)$	Dual-beam spectrophotometer, integrating sphere	X	X	X		
	USB4000 single beam				X	
	Shimadzu UV-2401PC UV-Vis					X
Dissolved Material (CDOM) Absorption Coefficient $a_g(z, \lambda)$		X	X	X	X	X
Non-Pigmented Particle Absorption Coefficient $a_d(z, \lambda)$	Dual-beam spectrophotometers, integrating sphere	90% acetone	80% ethanol	NaClO		
	USB4000 single beam				80% ethanol	
	Shimadzu UV-2401PC UV-Vis					100% methanol
Phytoplankton Absorption Coefficient $a_{ph}(z, \lambda)$	$a_{ph} = a_p - a_d$	X	X	X	X	X

Biogeochemical and Bio-Optical Quantities

Spectrophotometrically measured Chl a and phaeopigments	Dual-beam spectrophotometer	90% acetone	hot ethanol	90% ethanol		
	Ocean Optics single beam				80% hot ethanol	
	Shimadzu UV-2401PC UV-Vis					80% hot ethanol

Phytoplankton wet weight	light microscopy			X		
Total Suspended Particulate Material (SPM)	gravimetrically	X	X	X	X	X
Total Suspended Inorganic Particulate Material (SPIM)	heating 450° 4h					X
	heating 550°	X	X	X		
	heating 600°				X	
Total Suspended Particulate Organic Material (SPOM)	SPM-SPIM	X	X	X	X	X
Dissolved organic carbon (DOC)	Shimadzu TOC-VCPH analyzer		X			
Fluorescence Intensity, <i>in situ</i> profile F(z)	Cyclops-7 Turner Design	X				

Ancillary Data and Metadata

Secchi Depth	Secchi disc	X	X	X		
Water Depth (only in optically shallow waters)		X		X		
Conductivity and Temperature over Depth (CTD) T(z), S(z)	CTD			X		
	FATA flow-through-system	X				

For spectrophotometric measurements generally GF/F filters are used. The question what solvent to use for chlorophyll extraction has been up for a long time (Wright *et al.*, 1997). Traditionally 90% acetone is used for marine waters (Aminot & Rey, 2001), and ethanol is suggested for freshwater (ISO10260, 1992). For safety reasons ethanol should be preferred (Wright *et al.*, 1997), since acetone is highly volatile, flammable, causes headaches and skin irritation (gloves are not protecting against it), thus requiring higher precaution when handled (Ritchie, 2006). Methanol is also toxic, but less volatile and flammable, and a good solvent (Porra, 2002, Ritchie, 2006), which is widely used (Zhang *et al.*, 2009 and references therein). Both methanol and acetone blemish plastic cuvettes (Ritchie, 2006), thus causing measurement errors. Methanol may produce additional errors due to incomplete extraction and wavelength shift in the maximum absorption of phaeophytin absorption bands (Tilstone *et al.*, 2002). Other possible errors during every step of chlorophyll measurement procedure are described in Wasmund *et al.* (2006).

An example of Chl *a* calculation with different formulas based on 196 cases from Estonian lakes Võrtsjärv and Peipsi is given at fig. 2. Chl *a* concentration varied between 2.7-77.7 mg/m³ and generally a bit smaller concentration (averagely 16%) was aquired with calculations according to Lorenzen (87% of cases) compared to Jeffrey-Humphrey formula. Concentrations of total suspended matter (measured according to Strömbeck & Pierson

(2001) and NEN 6484 (1982) by WI) and CDOM are measured nearly similarly by all partners. Small difference in measuring TSM may come from different filters: SYKE uses 0.4 μm polycarbonate filter, whereas TO and CNR use \varnothing 47 mm Whatman GF/F filters.

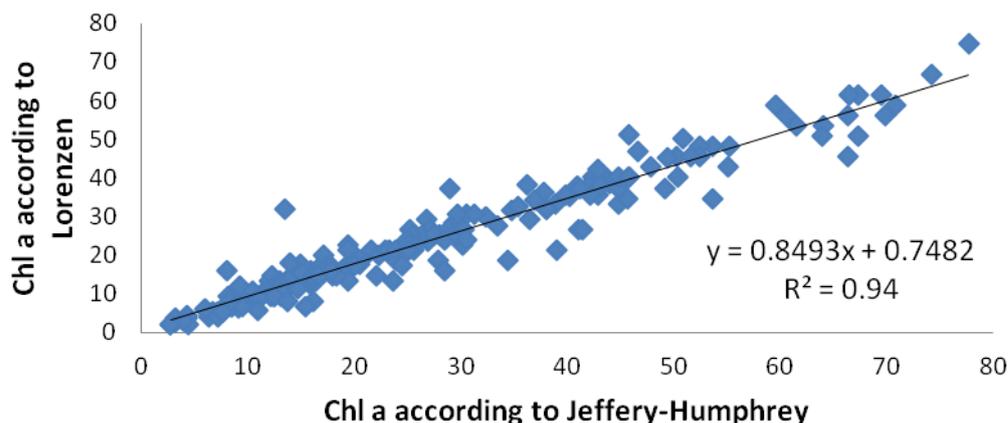


Figure 2. Chlorophyll a calculated according to Jeffrey-Humphrey (1975) and Lorenzen (1967).

3.2. Determination of IOPs.

For measurements of inherent optical properties, the present version of the ocean optics protocols assume the use of a commercial dual beam spectrophotometer, with the sample and reference targets illuminated by the collimated output of a grating monochromator. The protocols also prescribe how, with minimal modifications, measurements using a single-beam monochromator or otherwise similar optical configuration can be carried out.

The single-beam USB4000 used by WI fulfils the SeaWifs requirements for a single beam set-up. However, the Ocean Optics protocol recommends dual-beam instruments, which generally have a more stable (physical) set-up and will avoid errors due to changing light intensities of the lamp between the measurement of the blank and the sample. However, such a dual-beam set-up is more expensive and not affordable for each small group. An advantage of a single-beam set-up with a USB4000 is that it can easily be taken to the fieldwork area or even on a large boat, so that measurements can be done immediately after sampling.

Absorption by particles $a_{\text{tot}}(\lambda)$ and bleached particles $a_{\text{bp}}(\lambda)$ are measured in laboratory with the filter pad method using dual-beam spectrophotometer equipped with integrating sphere (TO, SYKE, CNR). WI uses single beam system USB4000 (see more 3.2.1). Prof. Zhang uses Shimadzu UV-2401PC UV-Vis spectrophotometer and quantitative filter technique (QFT), for details look Zhang *et al.* (2007).

Absorption coefficient of bleached particles $a_{bp}(\lambda)$ is another parameter, which is acquired with **different extraction solvents** by all partners: WI, VU use 80% ethanol, TO uses NaClO with 0.1% of active chlorine, CNR uses 90% acetone, Zhang uses 100% methanol. a_{ph} is calculated as a difference between a_{tot} and a_{bp} .

Generally Tassan and Ferrari (1995) T-R method is used and they recommended NaClO as a bleaching agent, especially for cyanobacteria and chlorophyte-rich waters. Binding *et al.* (2008) argued that bleaching with NaClO leads to bleaching of tripton and DOM and from TO experience this is a problem in dark-water lakes. Canuti and van der Linde (2006) suggested additional photooxydation procedure and constant monitoring of the depigmentation process with spectroradiometer to prevent overbleaching.

Total absorption and scattering coefficients are obtained similarly by using the WET Labs' absorption-attenuation meters: either ac-9 (SYKE, CNR; 9 bands in the 412-715 nm range) or ac-s (TO, continuous spectra in 400-730 nm range).

3.3. Remote sensing reflectance (Rrs)

Calculation depends on equipment, whether it is calculated from **above-water or in-water measurements**.

- Rrs from above-water measurements can be calculated:

$$a) \quad Rrs = \frac{Lt - \rho Lsky}{Ed}, \quad (2)$$

Generally light emerging from water (L_t) is measured about 42 degree elevation angle from nadir and about 135 degree azimuth angle from the Sun. Light from sky is measured (L_{sky}) about 42 degree angle from zenith and about 135 degree azimuth angle from the Sun. These are in accordance with NASA's protocols.

Difference may come from ρ , whether it is taken as a **constant** (Zhang, $\rho = 0.0245$; SYKE, $\rho = 0.028$) **or changing** during every measurement due to changes in wind speed:

$$\rho = 0.0256 + 0.00039W + 0.000034W^2 \quad (3)$$

where $\rho(W)$ is the sea surface reflectance as a function of wind speed W (m/s)

The $R_{rs}(\lambda)$ is calculated for every L_t , L_{sky} , E_d triplet. Difference may come in certain wavelengths whether any NIR corrections are applied or not.

Another difference may come from **outlier selection**: for example in TO the quality checks rely on per-station statistics of $R_{rs}(555)$. Data deviating by more than 10% from the median value are rejected and the results passing filtering are then averaged.

- b) The WISP-3 instrument calculates $R(0^-)$ from L_t , L_{sky} , E_d triplet, and further processing to R_{rs} is done by WI via WISPweb.

The spectral resolution, wavelength and radiometric accuracy, sampling interval, stray light rejection tests of WISP-3 with reference to radiometric requirements set by NASA for above water spectral reflectance measurements are given in Annex 1.

- c) CNR and Prof. Zhang use Lambertian reference panel:

- $R_{rs}(\lambda)$ is calculated as the ratio of water-leaving upwelling radiance $L_w(\lambda)$ to incident downwelling irradiance $E_d(\lambda)$:

$$R_{rs}(0^+) = [L_t(0^+) - \rho L_{sky}(0^+)] / [\pi L_{ref}(0^+) / \rho_{ref}(\lambda)], \quad (4)$$

with CNR using Fresnel reflectance coefficient $\rho = 0.028$

$L_t(\lambda)$ is the upwelling radiance from water, and $L_{sky}(\lambda)$ is the sky radiance measured at the same azimuth angle and at 40° zenith angle.

$L_{ref}(\lambda)$ refers to measurement of the radiance of the Lambertian reference panel and $\rho_{ref}(\lambda)$ is the reflectance of the reference panel, which in case of Prof. Zhang was accurately calibrated to 30%.

- R_{rs} from underwater measurements

The preferred method for estimating R_{rs} is to first measure the upwelling radiance below surface towards nadir ($L(z, \lambda)$), extrapolate it to just below surface ($L(0^-, \lambda)$) and convert that to water leaving radiance ($L_w(\lambda)$):

$$L_w(\lambda) = L(0^-, \lambda) t n^{-2}, \quad (5)$$

where t is the upward Fresnel transmittance of the air-sea interface (~ 0.975) and n is the refractive index of (sea)water. The term $t n^{-2}$ has a value of 0.543 for seawater and is not sensitive to wind speed (NASA 2003). The value for freshwater is only slightly different ($t n^{-2} = 0.55$ instead of 0.543 according to Palmer & Williams, 1974).

$R_{rs}(\lambda)$ can then be derived from $L_w(\lambda)$ divided by the downwelling irradiance just above water surface towards zenith.

Shelf-shading corrections of the measuring device are also necessary. These depend on the radius of the instrument, absorption, empirical factor equal to 2 and refracted solar zenith angle.

A degree of variation is introduced due to patchy algal/cyanobacterial bloom (Fig. 9, table 6).

3.4. Additional measurements

All parameters from AERONET (or AERONET-OC) stations are measured similarly with similar instrument (CIMEL CE-318) with identical calibration using the same methodology.

From AERONET following parameters are retrieved:

- direct sun irradiance
- sky radiance
- aerosol properties e.g. aerosol optical thickness
- columnar ozone amount
- precipitable water vapour content

The atmospheric data have three quality levels: level 1.0 (unscreened), level 1.5 (cloud screened), and level 2.0 (cloud-screened and quality-assured). The level 2.0 of atmospheric properties are used for atmospheric correction, and also the level 1.5 have been largely used for remote sensing applications.

AERONET-OC towers are located further offshore and give additionally the above-water total radiance measurements to atmospheric parameters (average of 11 measurements is taken into account and a deviation within) and normalized water-leaving radiance as a final outcome. Information about Chl a concentration can also be achieved.

CNR can use data from AERONET station in ISPRA for L. Maggiore and triangulated data from ISPRA & Venice tower for L. Garda with an upcoming new measuring site on Sirmione Peninsula. TO has an AERONET station.

4 GloboLakes protocols for validation of ocean colour satellite data

Within the project GloboLakes, protocols for inland lakes were harmonised. Their methods

are summarised in this chapter. Their methods are similar to those used by GlaSS community, but with additional addition of the time period: e.g. measuring inherent optical properties median of 5-min cast with outlier removal is performed (for backscattering, dissolved matter absorption and particulate matter optical properties). For in-water constituents often the mean of 3 replicate samples is calculated (e.g. spectrophotometric measurement of Chl a), which is usually not performed within GlaSS community.

4.1. Inherent optical properties

For Inherent Optical Properties, generally a median value is calculated from measurements of five minutes (Table 3.)

Table 3. *Inherent optical properties measuring instruments and processing methods by GloboLakes.*

Parameter	Procedure / Instrument	Measurement and processing method
Particulate absorption	Wetlabs AC-S	Median of 5-min cast with outlier removal. Scattering correction after Zaneveld
Particulate attenuation		
Particulate scattering		
Dissolved absorption	Wetlabs AC-S + 0.2 µm filter	Median of 5-min cast with outlier removal
Particulate absorption	TriOS OSCAR PSICAM	Median of 3-min measurement on single sample
Backscattering	Wetlabs BB3	Median of 5-min cast with outlier removal.
Particulate absorption	Dual-beam Cary-100 spectrophotometer with integrating sphere	Single determination; duplicate sample analysed only if problem with first measurement
Phytoplankton absorption		
Non-algal particle absorption		

4.2. Apparent optical properties

For Rrs calculations from TriOS Ramses and Satlantic HyperSAS measurements the Simis fingerprint method (Simis & Olsson, 2013) and Ruddick NIR similarity spectrum are used (Ruddick *et al.*, 2006).

4.3 In-water constituents

In-water constituents are obtained either from single measurement (pigments via HPLC, CDOM concentration and fluorescence) or as a mean of three replicate measurements (Table 4.).

Table 4. Instrumentation and processing methods used for in-water constituents by GloboLakes.

Parameter	Procedure / Instrument	Measurement and processing method	References
Chlorophyll-a	Spectrophotometric. ISO 10260 (Hot ethanol)	Mean of 3 replicate samples	ISO 10260, 1992.
Phycocyanin	Spectrophotometric with sonication and freeze-thaw extraction	Mean of 3 replicate samples	Horváth et al., 2013.
Phytoplankton pigments	HPLC	Single determination; duplicate sample analysed only if problem with first measurement	
Total suspended matter (and organic /inorganic fractions)	Gravimetric	Mean of 3 replicate samples	Strickland and Parsons, 1972.
Coloured dissolved organic mater (CDOM)	Dual-beam spectrophotometry	Single sample	Mitchell et al., 2000.
Dissolved organic carbon (DOC)	Shimadzu TOC analyser	Mean of 3 replicate samples	
Particulate organic carbon (POC)	Carlo-Erba CNO 1108 elemental analyzer	Mean of 3 replicate samples	http://www.epa.gov/glnpo/monitoring/sop/chapter_2/LG207.pdf

Coloured dissolved organic mater (CDOM) fluorescence	EEM fluorometer	Single sample	Stedmon & Bro, 2008.
Phytoplankton cell counts	Microscopy	Single sample	

5 Optical closure test

For quality control of the total set of measurements, optical closure checks (model-measurement) were performed. Average SIOP data about lakes and actual concentrations of Chl a, TSM and CDOM absorption were given to SYKE, where simulations with the radiative transfer model Hydrolight were performed. Later a comparison of Hydrolight spectra with corresponding *in situ* R_{rs} measurements (cf. GLaSS tasks 3.1 and 3.4) was made.

5.1. Optical closure for Finnish lakes

Five lakes (Vesijärvi, Päijänne, Säkylän Pyhäjärvi, Lammin Pääjärvi and Keravanjärvi) in Finland were taken as test sites and their spectra were measured with ASD FR during fieldwork 2007-2013. Additionally turbidity, SD, Chl a, TSM, particulate absorption and CDOM absorption were recorded. Transparency was highest in Päijänne (5 m), and lowest in Keravanjärvi (1.3 m) where there were also highest Chl a values (8.2 $\mu\text{g/l}$) and CDOM absorption (20.4 m^{-1} at 400 nm). The remote sensing reflectance (R_{rs} , 1/sr) simulations were made in SYKE using the HydroLight radiative transfer model version 5.2.0 (Mobley & Sundman, 2013a, b). Vesijärvi was measured seven times with highest concurrence between measured and simulated R_{rs} (Fig. 3). In Pyhäjärvi differences between measured and simulated R_{rs} were high over the whole spectral range, with simulation underestimating R_{rs} , but spectral shape was fitting well. In Päijänne differences were between 500-700 nm, but the spectral shape was also simulated well with higher magnitude. In Pääjärvi and Kerajjärvi the spectral shape was not captured by simulation (underestimated CDOM absorption and higher peaks via simulation in region 500-700 in Pääjärvi and 600-700 in Keravanjärvi). The results of these optical closure tests for Finnish lakes confirms the consistency of the sets of *in situ* measurements of GLaSS partner SYKE.

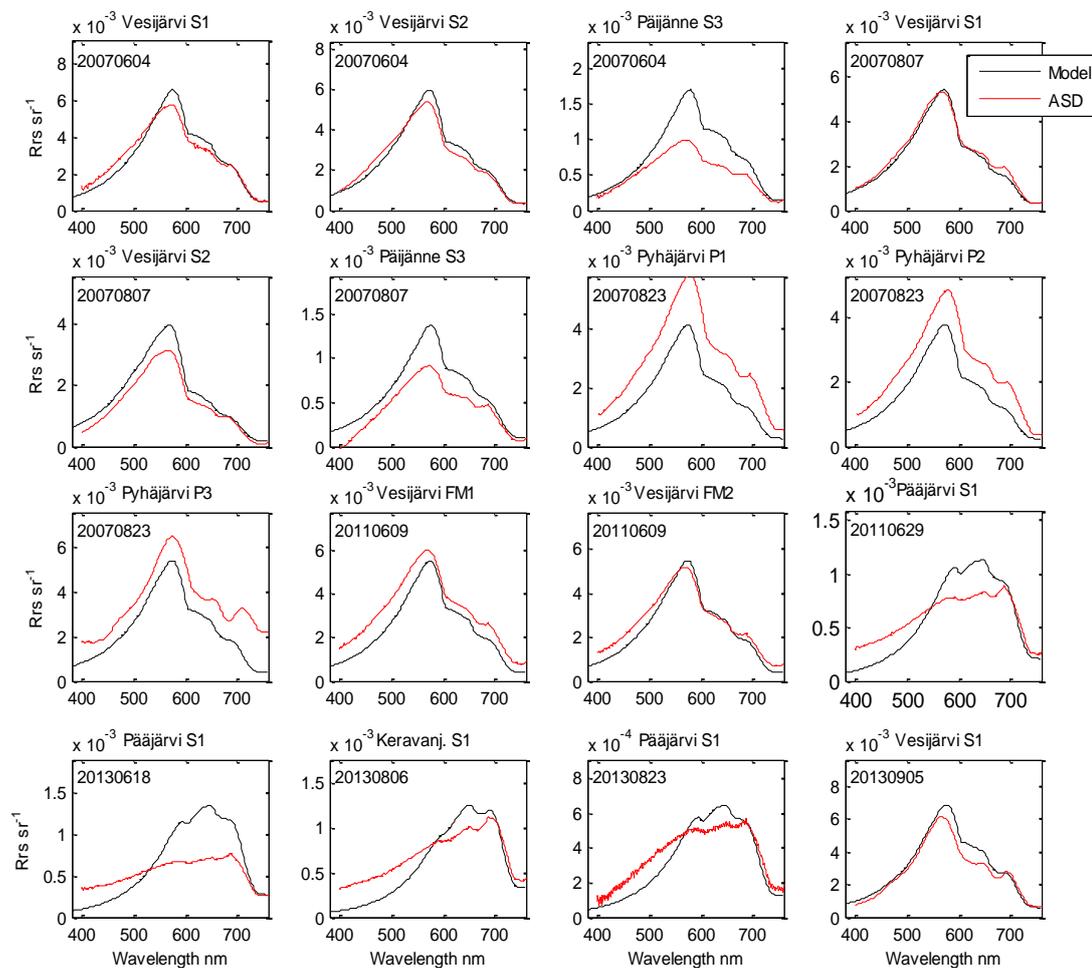


Figure 3. Rrs measured with ASD FR instrument and simulated with Hydrolight in Finnish lakes. Measurement dates (yyyymmdd) are also presented. Note different values on y-axis.

5.2. Optical closure for Italian lakes

First, the Hydrolight spectra (forward modeling) with corresponding *in situ* Rrs measurements were compared (cf. tasks 3.1 and 3.4). Then a comparison with the concentrations used by Hydrolight to simulate Rrs spectra with the concentrations estimated by BOMBER (inverse modeling) was made, starting from the corresponding Hydrolight-simulated spectra. Both BOMBER and Hydrolight are parameterised with the same SIOPs.

5.2.1. Forward modeling

The simulation with Hydrolight was based on concentrations of water quality parameters (i.e., chl-a, TSM and CDOM) and SIOPs data gathered in Lake Garda. In particular, 101 samples of triplets' concentrations of Chl a, TSM and CDOM were available. These triplets were used by SYKE to run Hydrolight according to the SIOPs values of Lake Garda. Finally, 101 Rrs spectra at the spectral setting of S3, S2, MERIS and Landsat-8 were simulated.

To perform the exercise on the optical closure we used a subset of 30 spectra because only for 30 triplets of chl-a, TSM and CDOM there were the corresponding *in situ* measured Rrs spectra.

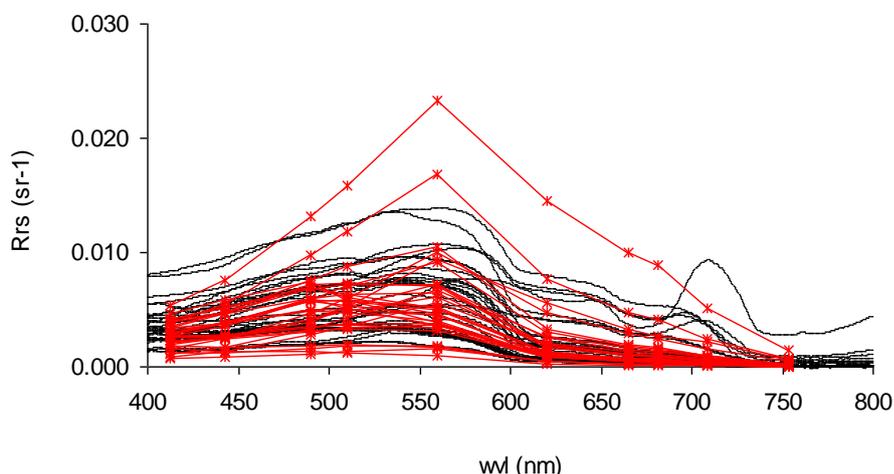


Figure 4. Comparison between Hydrolight-simulated (in red for the S3 band setting) and *in situ* measured (continuous lines in black) Rrs spectra (ASD and WISP-3 data).

Figure 4 shows the 30 spectra generated with Hydrolight plus the 30 spectra measured in the field. Some divergencies are observed with Hydrolight-simulated spectra and *in situ* data.

Such discrepancy can be mainly due to following reasons:

- uncertainty in Chl a, TSM and CDOM concentrations (due to lab analysis. These errors that might generate Hydrolight spectra different from those measured *in situ*);
- inappropriate setting of SIOPs (during time, and also within the lake' sub-basins, the SIOPs can change so that the Hydrolight spectra might result different from those measured *in situ*);
- *in situ* Rrs spectra affected by environmental noise (e.g. bottom effects; water surface roughness, presence of clouds which was not taken into account by the Hydrolight simulations).

Unfortunately, it is unfeasible to identify the main cause of mismatching in the above list but some discussion is given to find out the most likely cause of it.

First, 11 of the 30 *in situ* Rrs spectra whose location and shape made reasonable to assume that they were affected by residual bottom effects were removed. Except for two spectra the optical closure between field and Hydrolight was better than in the previous case (cf. Figure 5 vs. Figure 4).

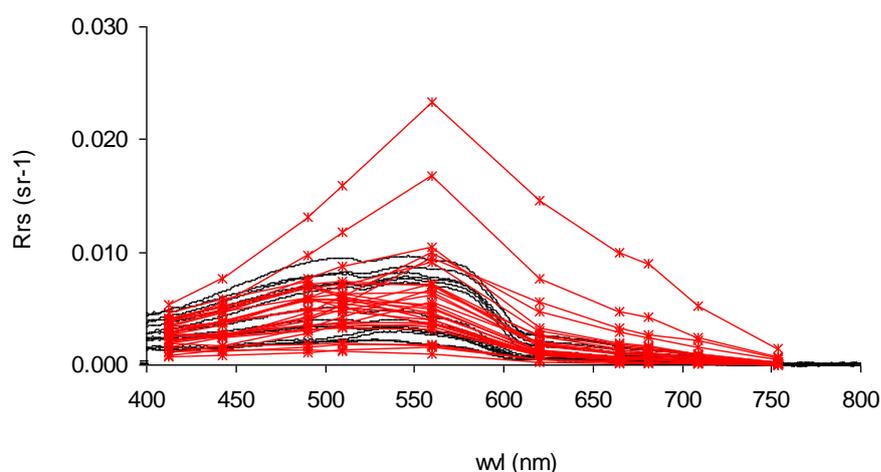


Figure 5. Comparison between Hydrolight-simulated (in red for the S3 band setting) and *in situ* measured (continuous lines in black) Rrs spectra (ASD and WISP-3 data). With respect to Fig.1, 11 spectra with a suspect degree of bottom-effect contamination were removed.

To improve the analysis and for evaluating if the optical closure was generally reached in terms of spectrum shape, both the Hydrolight simulated spectra and field data were normalized at a reference wavelength (560 nm). To the aim, *in situ* ASD and WISP-3 spectra were resampled according to the S3 band setting. The normalization indicated a satisfactory optical closure between *in situ* and Hydrolight spectra was reached.

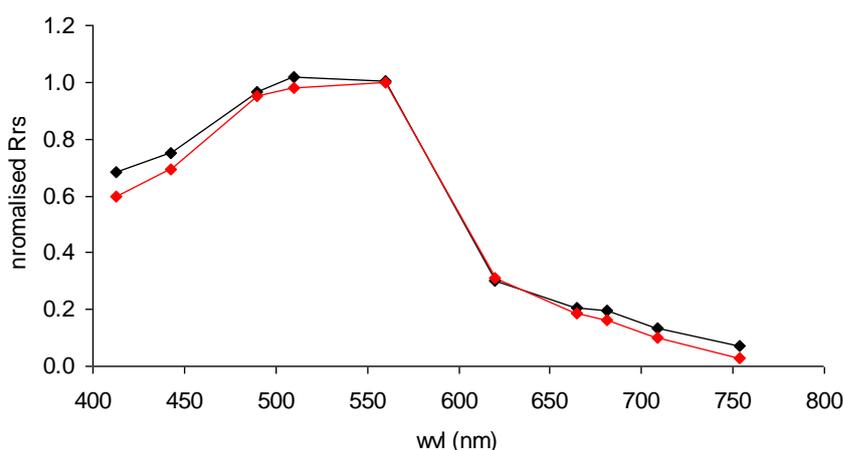


Figure 6. Comparison between Hydrolight-simulated (red) and in situ measured (black) Rrs spectra. Each spectrum is the average values of 19 Rrs spectra normalized at 560 nm. The corresponding average values of water quality parameters are Secchi disk 6.08 m, chl-a 1.12 mgm^{-3} , TSM 0.94 gm^{-3} and CDOM 0.09 m^{-1} .

Because the normalization of Rrs spectra finally provided the best match between Hydrolight and *in situ* spectra we assumed that there is a scale factor responsible for the slight mismatch shown in Figure 5. We can also assume that the magnitude of the scale factor mainly depends on TSM concentrations and/or on the specific back-scattering coefficient of TSM bb^*_{TSM} . By assuming that the measurements of TSM concentrations are realistic (even if for such low concentrations –average 0.94 gm^{-3} – the uncertainty are higher) we might conclude that the bb^*_{SPM} given as in input in Hydrolight was not so appropriate for the water quality conditions at the time of *in situ* measurements of Rrs data. Indeed, it was the first time we modelled the backscattering in Lake Garda based on bb^*_{TSM} only. In previous works (Bresciani *et al.*, 2012; Giardino *et al.*, 2007) the backscattering coefficient was depending both on Chl a and tripton.

We might conclude that further research efforts on assessing the impact of bb^*_{TSM} (with variation in time and space) on Rrs are necessary to improve the optical closure analysis.

5.2.2 Inverse modeling

The 101 Rrs spectra simulated with Hydrolight (from the triplets of chl-a, TSM and CDOM and from the Lake Garda SIOPs, see above) were given as input in BOMBER to estimate chl-a, TSM and CDOM concentrations. The bio-optical model implemented in BOMBER was parametrized by using the SIOPs data (of Lake Garda) provided to SYKE for the forward Hydrolight runs (see above). The spectral inversion with BOMBER was performed with the Hydrolight spectra aggregated according to S3, S2, MERIS and Landsat-8 bands. The

concentrations estimated by BOMBER from each Rrs spectrum were then compared to Chl a, TSM and CDOM values used to run Hydrolight.

Generally, the concentrations retrieved with BOMBER agreed the triplets of Chl a, TSM and CDOM used to generate the corresponding Hydrolight spectrum. Better results were achieved for Chl a and TSM. Lower agreement was found for CDOM were BOMBER-outputs are always underestimated. Moreover, for Lake Garda it seems that there are no big differences by using Rrs spectra aggregated with different band settings for estimating water quality parameters. Nevertheless, we cannot conclude that the investigated sensor performs equally as other differences (e.g., radiometric sensitivity) are not considered in this analysis.

Table 5. Summary of the statistics used to evaluate the BOMBER results. MAE (mean absolute error), rRMSE (relative root mean square error) and the coefficient of determination (R^2) of the regression line (with slope and intercept) are computed for chl-a, TSM and CDOM and for different band settings. All the results are statistically significant.

		MAE	rRMSE	R^2	Slope	Intercept
Sentinel-3	chl-a	0.316	20.726	0.956	0.841	0.146
	TSM	0.075	7.780	0.996	0.941	0.051
	CDOM	0.081	79.117	0.919	1.856	-0.017
Sentinel-2	chl-a	0.294	17.915	0.974	1.204	-0.200
	TSM	0.108	11.702	0.982	1.032	0.017
	CDOM	0.068	63.293	0.904	1.496	-0.016
MERIS	chl-a	0.358	22.474	0.960	0.798	0.266
	TSM	0.074	7.631	0.996	0.939	0.059
	CDOM	0.083	78.610	0.934	1.824	-0.010
Landsat-8	chl-a	0.308	18.839	0.942	0.854	0.342
	TSM	0.091	7.531	0.993	1.007	0.047
	CDOM	0.091	89.921	0.931	2.098	-0.014

The optical closure check is good in terms of spectrum shape but poor in terms of magnitude. It seems that the bb_{SPM}^* given as in input in Hydrolight was inappropriate for the water quality conditions at the time of *in situ* measurements.

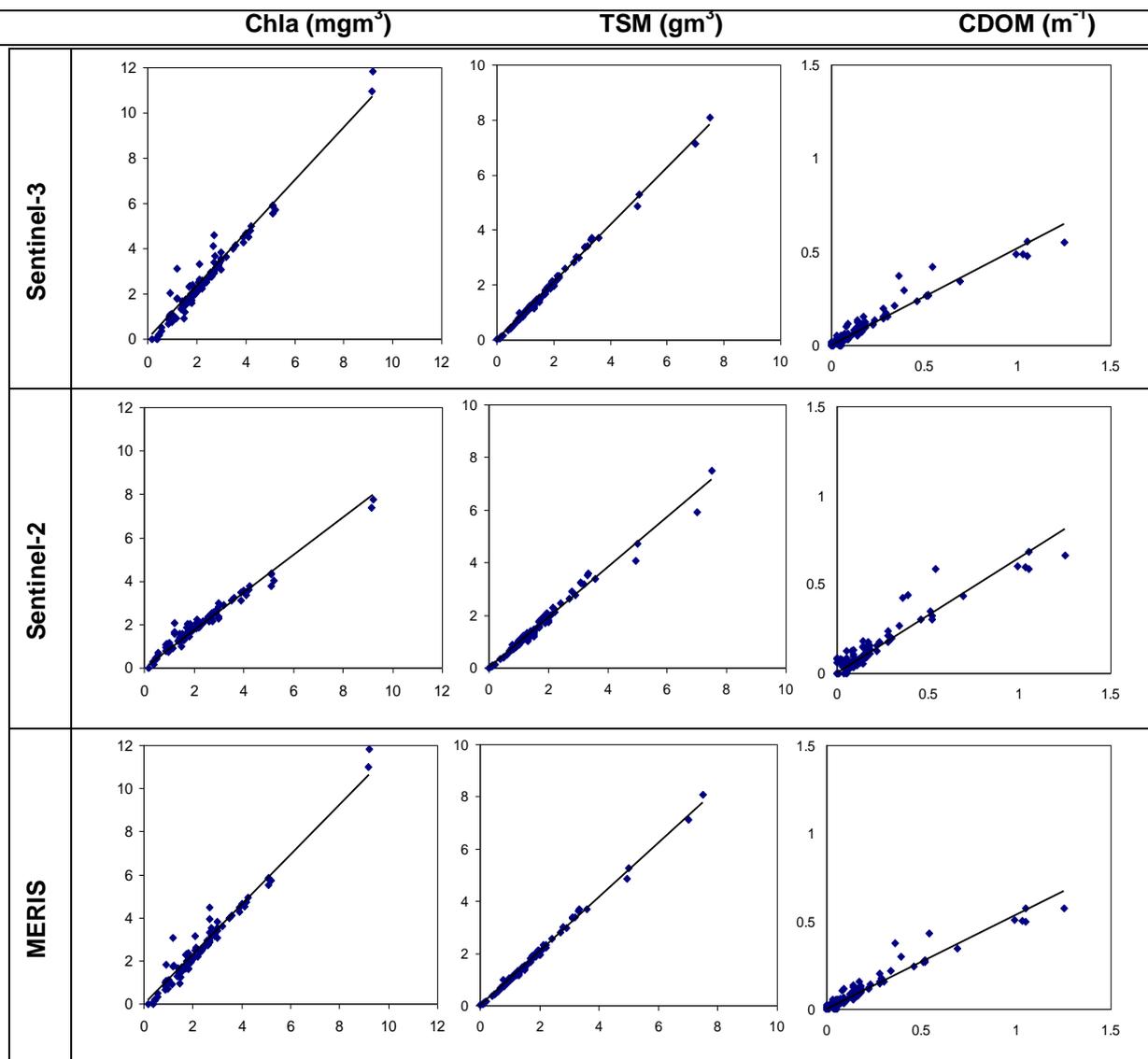
With respect to the inverse modeling, overall the concentrations estimated with BOMBER agree the corresponding Hydrolight inputs. Better results are achieved: 1) by inverting Rrs spectra aggregated with the S3 band setting and 2) for Chl a and TSM (lower agreement is found for CDOM with underestimated BOMBER-outputs).

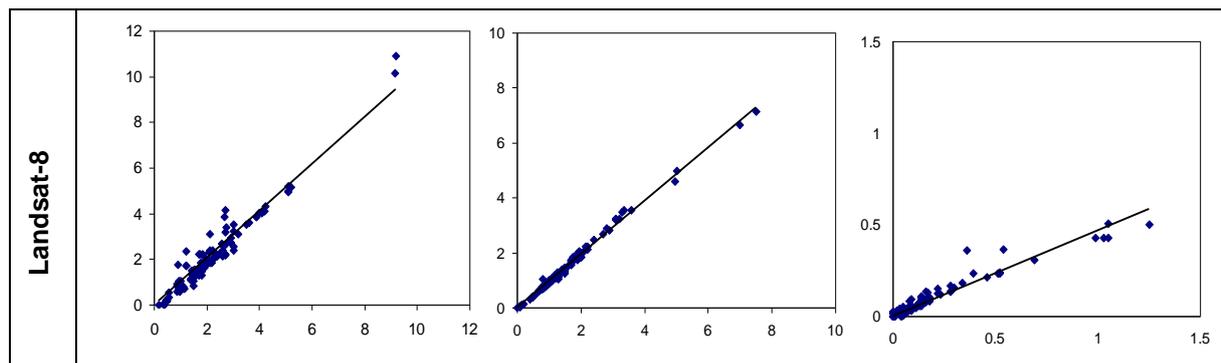
The analysis is limited to Lake Garda as both the SIOPs and the concentrations of Chl a, TSM and CDOM used to run Hydrolight are related to this lake only.

The results of these optical closure tests for Italian lakes confirms the consistency of the sets

of in situ measurements of GLaSS partner CNR.

Figure 7. Comparison between the concentrations used by Hydrolight to simulate R_{rs} spectra (x-axis) and those estimated by BOMBER (y-axis), starting from the corresponding R_{rs} spectra. From left to right Chl-a, TSM and CDOM. The rows show the results by running BOMBER according to R_{rs} spectra resampled by using S3, S2, MERIS and Landsat-8 band settings.





5.3. Optical closure for Estonian lakes

Water quality parameters about L. Peipsi and L. Võrtsjärv were given to SYKE for simulations with Hydrolight. Altogether 357 simultaneous measurements (87 about Võrtsjärv and 270 about L. Peipsi) of Chl a, total suspended matter (TSM) and CDOM absorption were provided for the period of 4 years. Rrs was measured with TriOS Ramses (above-water measurements) during 26 times from L. Peipsi and 11 times from L. Võrtsjärv. Additional information was provided about SIOPs (Chl a-specific phytoplankton absorption, spectral slope coefficients of CDOM and NAP absorption, specific absorption of NAP at 400 nm, specific scattering coefficient of TSM at 555 nm, scattering exponent of TSM and backscattering ratio).

For optical closure test 26 spectra from L. Peipsi and 11 from L. Võrtsjärv were used, since for those both measured and simulated Rrs were available. Spectral setting of S3, S2, MERIS and Landsat-8 were simulated, but only S3 is used in figure.

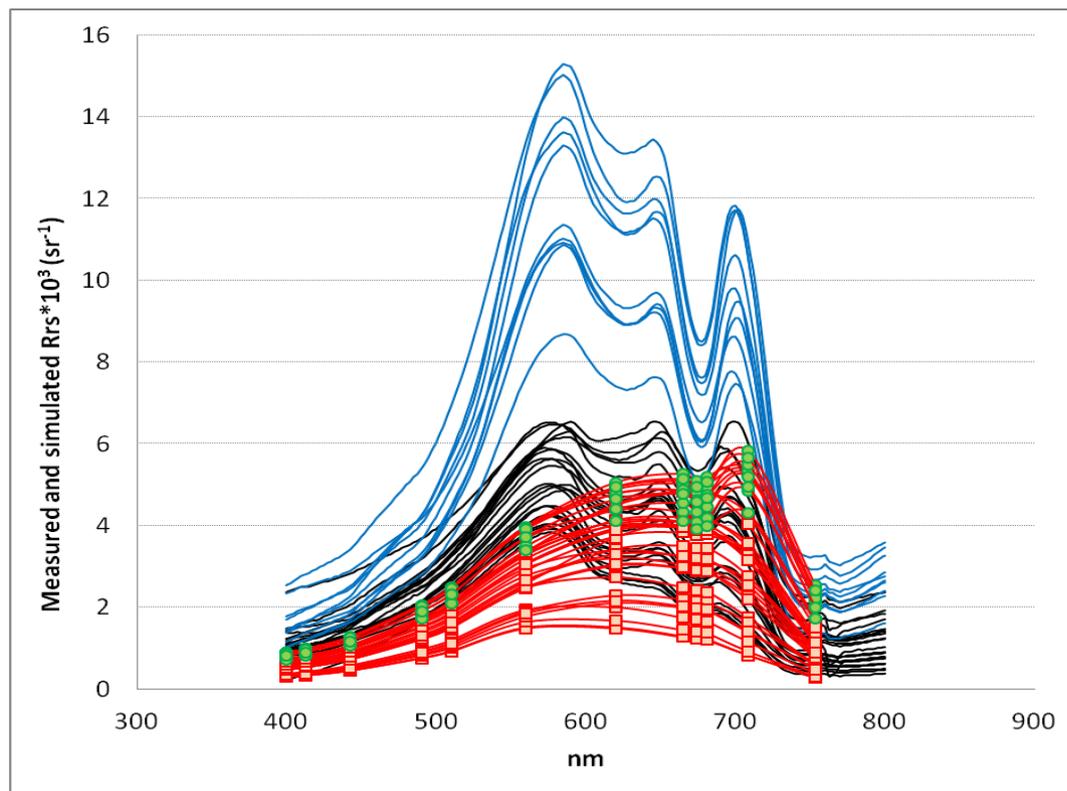


Figure 8. Measured Rrs from L. Vörtsjärv (blue line) and L. Peipsi (black line) together with simulated Rrs (red line): S3 channels are represented with green dots (L. Vörtsjärv) and red squares (L. Peipsi).

Measured Rrs were generally higher in L. Vörtsjärv (Fig. 8). Hydrolight simulations did not correspond well with measured values, underestimating especially the peak around 580 nm in both lakes. Probably given averaged numbers were too low for those selected cases and a case-by-case modelling with specific results would increase the match.

6 Variation assessment of *in situ* data from L. Garda and Maggiore (CNR)

Based entirely on the document by CNR: final contribution about methods to Work Package 4 - Production and validation of test datasets, november 2014.

6.1. Variability of *in situ* observations within a station

6.1.1 Remote sensing reflectance

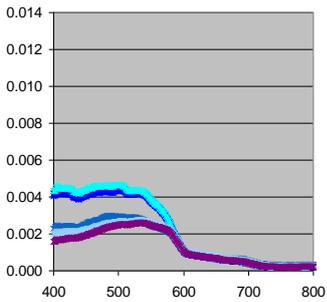
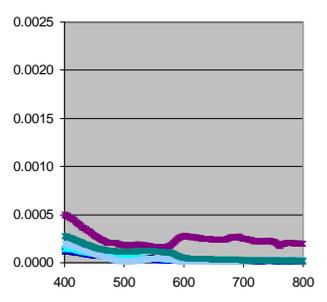
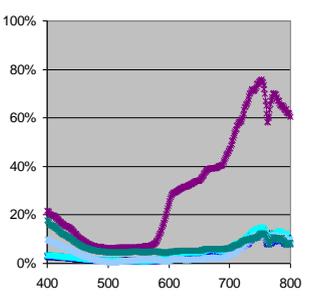
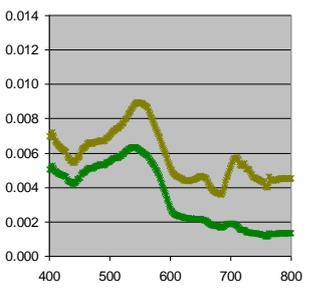
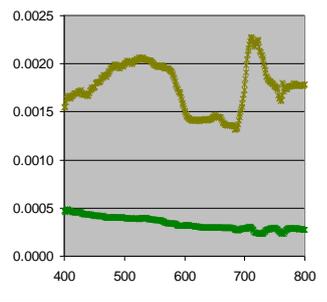
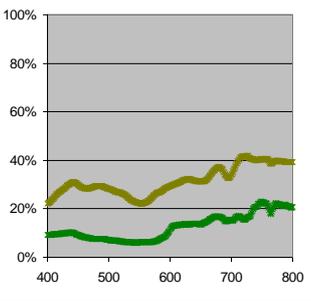
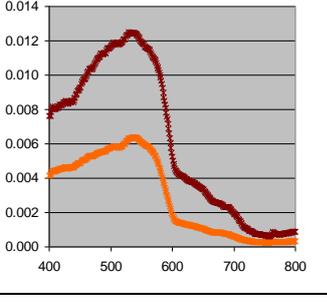
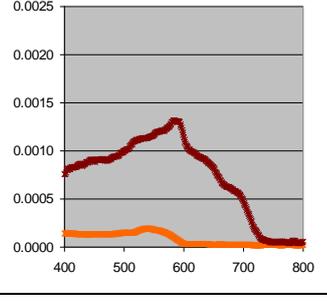
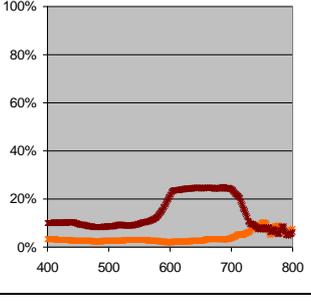
To assess the degree of variation that can be associated to field measurements, the spectra measured in our nearby lakes (Garda and Maggiore) were analysed depending on environmental conditions. In particular, for 9 stations we computed the average, the standard deviation and the coefficient of variation from a series of 5 (i.e. the number of replicates we make in each station). WISP-3 spectra were measured in each station.

The results are shown in Table 6 and are grouped depending on water and environmental conditions. Overall, the standard deviation of WISP-3 measurements in the whole spectrum in optically deep waters is on average lower than 0.0003 sr^{-1} for data acquired during strong wind (~ 12 knots). In that case both the operator (who is working on a rolling boat, Fig. 9) and water roughness, introduce a high degree of variability. Then, the R_{rs} variation is highest (standard deviation up to 0.002 sr^{-1}) during the presence of bloom (that was measured under scattered clouds and a turbid atmosphere conditions). In case of blooming, the water radiance measurement is strongly depending on the FOV footprint size/position due to the patchy structure of cyanobacterial bloom of *Anabaena lemmermannii* (Fig. 9). Similarly, in case of optically shallow waters, the measured water radiance (and hence the R_{rs}) is changing with the FOV footprint size/ position due to the high heterogeneity of substrates. The variation coefficient (CV) is higher in shallower waters (orange lines, standard deviation $\sim 0.001 \text{ sr}^{-1}$, bottom depth 3 m) than in deeper waters (brown lines, standard deviation $\sim 0.0003 \text{ sr}^{-1}$, comparable to those observed in optically deep waters).



Figure 9. Lake Garda field campaigns. On left there is a fieldwork on the windy days of March 2014. In the right picture there is the *Anabaena lemmermannii* bloom observed on 30 September 2014.

Table 6. Average standard deviation and coefficient of variation computed from 5 replicates of WISP-3 data collected in 9 sites (two of those from Lake Maggiore on 14th of May 2014, the others from Lake Garda on 6-7th of March, 10th of June and 30th of September 2014).

Notes	Rrs (sr^{-1})	Standard deviation (sr^{-1})	Variation coefficient (%)
Clear sky, deep waters, chl-a < 1mgm^{-3} , SPM < 1gm^{-3} , CDOM < 0.05m^{-1} . Calm conditions, data in purple (wind speed $\sim 8\text{ms}^{-1}$). Data acquired on 6-7 th of March, 14 May and 10 June			
Haze with scattered clouds, optically deep waters, cyanobacterial blooms (Fig.9); data acquired on 30 September			
Clear sky, optically shallow waters (orange $\sim 7\text{m}$, brown $\sim 3\text{m}$). Data acquired on 10 June and 30 September			

5.1.2 Concentrations of water constituents

The evaluation of the degree of variation that can be found in laboratory measurements for assessing the concentrations of water quality parameters is a major concern. From the moment when the water is sampled until the results from lab analyses are achieved, a series of factors introduce variability.

For instance, in case of Chl a concentration the result might vary depending on, e.g.: 1) the side of the boat where the water sampler is immersed (especially when due to horizontal/vertical heterogeneities occur); 2) the measurement methodology such as different solutions to extract the pigments (acetone vs. ethanol); 3) the amount of phytoplankton collected in the sampling (lower and higher concentrations are more complicated). Due to those effects the uncertainty for *in situ* measurements of Chl a can reach the 50%.

Based on our experience (Pinardi and Oggioni, personal communication) we can reasonably assume a degree of variation of about 20% for both Lake Garda and Lake Maggiore, which can be higher both in case of very low concentrations ($\text{Chl-a} < 1 \text{ mgm}^{-3}$) or in case of algal bloom.

The uncertainty of *in situ* data was more quantitatively assessed with data gathered on 30th of September 2014 in southern Lake Garda. For three pelagic stations water, a sufficient amount of water was collected to make three replicates of measurement for each station. The campaign was coincident with a quite important bloom (at least for Lake Garda) of *Anabaena lemmermannii* (Fig. 9). Figure 10 shows the means with standard deviations from three replicates of laboratory measurements for Chl a, SPM and CDOM (absorption coefficient of CDOM at 440 nm); the exercise was performed in three stations in optically deep waters. The degree of variability of these measurements is quite high. On average, for the three stations, the VCs were 30%, 27% and 9% for Chl a, SPM and CDOM, respectively. We can assume that such variations were mainly due to the patchy distribution of *Anabaena lemmermannii* at the time of sampling.

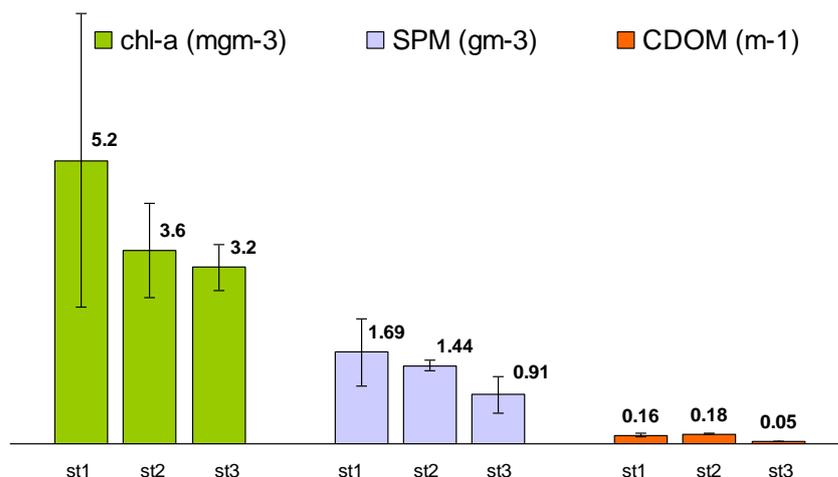


Figure 10. Chl a, SPM and CDOM concentrations in three stations measured on 30th of September 2014 in Lake Garda. Each bar shows the average value (with standard deviation) computed from three replicates (for each parameter and site).

5.1.3 Optical properties

The exercise described in the previous paragraph with data gathered on 30th of September 2014 was also performed with the spectral absorption coefficients of particles and CDOM. Figure 6 (left panel) shows the degree of variation of a_{CDOM} , described in terms of CDOM (absorption at 440 nm) and related slope, computed with the three replicates for each station according to Babin *et al.* (2003). In station 3 the CV was lower (4% for CDOM and 2% for slope) than in stations 1 (CVs of 16% and 15% for CDOM and slope, respectively) and 2 (CVs of 6% and 24% for CDOM and slope, respectively). Figure 11 (right panel) shows the degree of variation of the spectrophotometric determinations of absorption coefficients of particle retained on GF/F filters. The average value from 400 to 750 nm of the CVs of a_p were 51%, 31% and 25% for stations 1, 2 and 3, respectively.

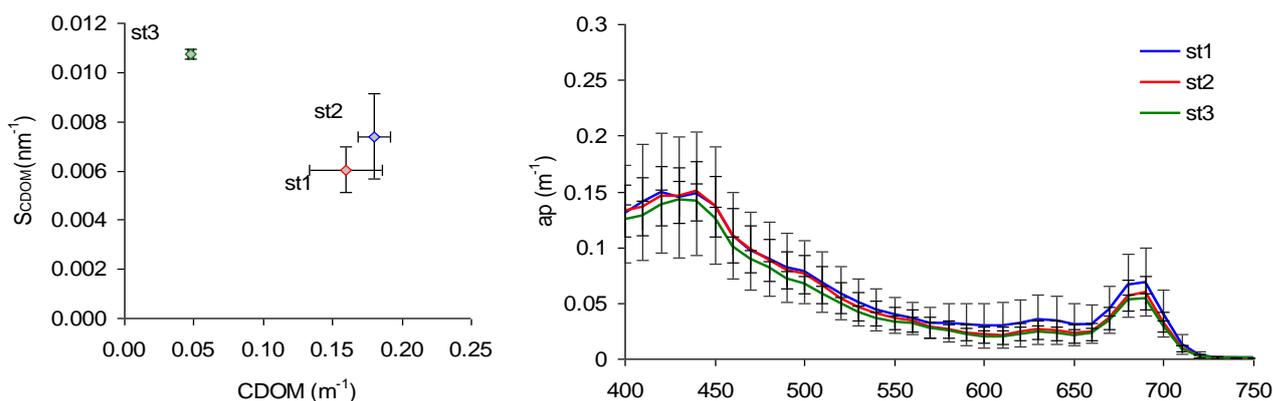


Figure 11. Mean values with standard deviations of laboratory-measured data, collected on 30 September 2014, and computed using the three replicates (for three stations). On the left graph, the variability of CDOM (i.e., the absorption coefficient of CDOM at 440 nm and slope). On the right graph there is the variability of the absorption coefficients of particles retained on GF/F filters.

With data collected on 10th of June 2014 we finally computed the variability found in IOP data gathered during clear water conditions. In particular, the vertical profiles of ac9 and HS-6 were measured and the mean and standard deviation of data gathered at the Secchi disk depth of 8 m were computed. Processing of backscattering data was based on the latest correction version (described in the manual as HydroSoft 2.8) where the correction for attenuation within the optical path of the HS-6 was made using data from the instrument itself together with ac-9 (data are processed according to drift from water calibrations). Figure 12 shows the spectra of the backscattering (bb) and absorption (a) coefficients acquired by keeping the probes there for 10 minutes. Overall, the data are not spread and the CVs of both a and bb are small (~3%). In case of clear water conditions the variation accompanying *in situ* measurements seems confirmed to be lower than in case of heterogeneous condition due to algal bloom.

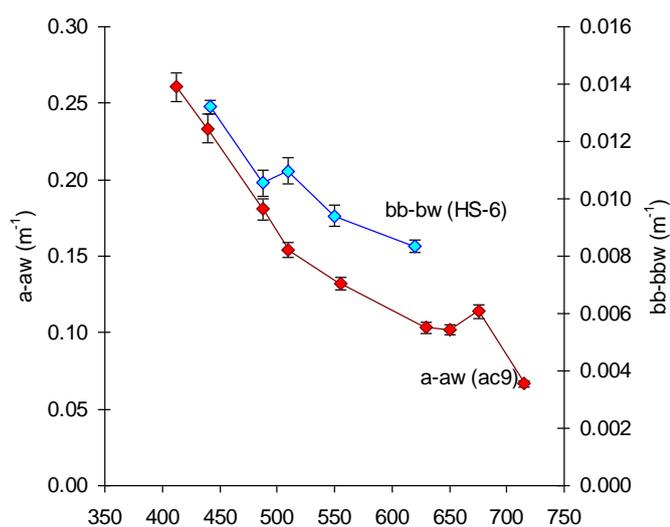


Figure 12. In situ absorption and backscattering spectra (all except pure water) acquired on 10th of June 2014. The plot shows average values with standard deviations for data acquired at 8 m depth for 10 minutes.

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Annex 1. WISP-3 Instrument specification with reference to radiometric requirements set by NASA for above water spectral reflectance measurements

1.1 WISP-3 for above water radiometric measurements

WISP-3 is an easy to operate handheld hyperspectral radiometer for above water assessing surface water reflectance and water quality. It contains three Ocean Optics JAZ radiometers, to measure the downwelling irradiance (E_d), the downwelling (L_d) and upwelling radiance (L_u). From these, it derives the reflectance.

The irradiance is measured with an CC3 cosine corrector that has 180° FOV with response close to Lambert's cosine law, which states that the irradiance or illuminance measured will vary with respect to the cosine of the angle between the optical axis of the source and the normal to the detector. The other two radiometers point at angles of 42° relative to the zenith and the nadir, to measure both radiance from the sky and the water. These spectrometers are fitted with optical fibers (diameter 400 μ m) connecting to Ocean Optics Gershun tubes with 3° FOV apertures, respectively the CC3. The WISP-3 applies standard band ratios to derive water quality parameters such as water transparency (k_d), concentration of Chlorophyll-a, Phycocyanin and TSM from the reflectance.

The optical range of the WISP-3 is ~380 to 800nm, with a band width Full Width Half Mean (FWHM) of ~4.9 nm, which is narrower than required for the SeaWiFS protocols (~10 FWHM). The WISP-3 maintains a 250:1 signal to noise ratio with a digital resolution of 0.3 nm and dynamic range of 1300:1. It automatically corrects for dynamic dark, which is measured on a number of separate pixels that are not irradiated by external light during the measurements. Errors attributed to linearity are less than 0.3%. Its sampling frequency is 2MHz and all wavelength are sampled within 10⁻³ s.

One of the features of the WISP-3 is the collimating and focusing mirror. It has SAG+ mirror installed that absorb nearly all UV light. Unlike typical silver-coated mirrors, the SAG+ mirrors do not oxidise. They have excellent reflectivity (>95% across VIS-NIR). SAG+ mirror is included to increase the signal in the visible range. As a side effect, the UV light is blocked. Therefore, the optical range of the WISP-3 starts at ~380 nm, which is higher than for some other spectro-radiometers. On the other hand, blocking the UV light also decreased the amount of stray light.

Annex 1, Table 1. Radiometric requirements set by NASA for above water spectral reflectance measurements

	SeaWiFS specification	WISP-3 specification
Spectral Range	380-750/900 nm	~380-800 nm
Spectral Resolution	10 nm(FWHM)	4.9 nm (FWHM)
Wavelength accuracy	0.5 nm	~0.1 nm
Wavelength stability	0.25 nm	~ 0.2 nm
Signal to Noise ratio	1000:1 (at minimum)	(1000:1 for radiance and 250:1 for irradiance)
Stray light rejection	10 ⁻⁶	<0.05% at 600nm; <0.1%at 435nm
Radiometric accuracy	3%	1-2%
Radiometric stability	1%	tbd
FOV maximum	10°	3°
Temperature stability	0 to 35°C	-5°C to 45°C
Linearity	Correctable to 0.1%	Correctable to <0.3%
Sampling interval (sec)	10 ⁻²	10 ⁻³
Sampling frequency(Hz)	1	2000000

From the table above it can be concluded that the WISP-3 fulfils the criteria of the SeaWiFS protocols for above water spectral reflectance measurements. Because of its construction, containing three radiometers which are already set up under the required angles, is it easy to use. It does not need to be connected to a laptop computer or electrical power during measurements. These properties make it easy to use from a small boat in a lake.

2 CALIBRATION OF WISP-3

Water Insight's Gold standard or reference WISP-3 is calibrated against a NIST traceable 1000W quartz Iodine standard spectral irradiance lamp in a dark room at the Royal Netherlands Institute for Sea Research (*NIOZ*). For calibration of the radiance sensors a 99.9% reflection target was used (Spectralon) in combination with the lamp. The standard spectral irradiance lamp is purchased from, and calibrated by, Optronic laboratorie, Inc. An 83-DS power supply with a 0.02 Ω shunt (*a device which allows electric current to pass around another point in the circuit by creating a low resistance path*) provides power for the lamp. A 4.5 digit voltmeter is used to monitor the current and voltage during calibrations. The lamp is allowed to warm up for 10min before each calibration. The current is maintained at 8A (± 1 mA). The lamp transfer

uncertainty relative to the NIST Scale of $\pm 0.5\%$. The other batches of WISP-3 are vicariously calibrated against this NIST calibrated reference WISP-3.

2.1 WISP-3 calibration

To calibrate the reference WISP-3 against the NIST calibrated lamp, the reflective target was placed at 50cm away from the lamp. For the radiance calibrations, the instrument was placed with one spectrometer at the time looking under an angle of 35° looking at the target. Additional correction is used to compensate for non-uniformity in the panel irradiance field. The non uniformity correction term is determined by integrating the computed panel radiance across the field-of-view of the sensor as projected onto the panel (= 0.00126). The spectral radiance, $L(\lambda)$ is calculated as follows;

$$L(\lambda) = I_{\text{Lamp}} * (L_{\text{measured}} * 0.00126) * 1/\pi \quad (1)$$

I_{Lamp} is the irradiance of the lamp, these values are included in the lamp documentation. L_{measured} is the measurements taken after correcting for dark currents. This value is divided by pi since the two sensors measure per steradians. For the irradiance calibration, the WISP-3 is positioned so that its cosine collector is centred on the alignment beam and normal to it.

$$E(\lambda) = I_{\text{lamp}} * (E_{\text{measured}}) \quad (2)$$

I_{Lamp} is the irradiance of the lamp, these values are included in the lamp documentation. E_{measured} is the measurement taken after correcting for dark taken.

After all three channels of the reference WISP-3 were calibrated, the Lu radiometer was calibrated vicariously against and Ld channel, to minimise spectral differences. The original Lu calibration and the vicarious Lu calibration were very similar, indicating a proper calibration. The calibration of the Ld, Lu and Ed sensor (Annex 1, Table 2, 3 & 4) shows error within 1%. The Ocean Optics protocols recommends the error to be <2% hence the calibration of the radiances of the WISP-3 are within the requirements.

Annex 1, Table 2. Spectral response of Lu to the lamp after calibration in $W/m^2/nm/sr$

	412	443	490	510	555	665	780	875
WISP-3 Ld sensor (dark corrected)	3.253	4.988	8.176	9.673	13.075	20.675	25.479	26.731
NIST calibrated lamp	3.254	4.890	7.996	9.429	12.800	20.250	24.900	26.350
Error (WISP/Lamp)	1.000	1.020	1.022	1.026	1.021	1.021	1.023	1.014

Table 3: Spectral response of Lu to the lamp after calibration in $W/m^2/nm/sr$

	412	443	490	510	555	665	780	875
WISP-3 Lu sensor (dark corrected)	3.182	4.892	7.992	9.437	12.821	20.317	25.087	26.481
NIST calibrated lamp	3.254	4.890	7.996	9.429	12.800	20.250	24.900	26.350
Error(WISP/Lamp)	0.9779	1.0004	0.99952	1.00083	1.0016	1.0033	1.0075	1.0049

 Table 4: Spectral response of Lu to the lamp after calibration in $W/m^2/nm$

	412	443	490	510	555	665	780	875
WISP-3 Irradiance (dark corrected)	3.253	4.903	8.059	9.517	12.893	20.482	25.304	26.792
NIST calibrated lamp	3.254	4.890	7.996	9.429	12.800	20.250	24.900	26.350
Error(WISP/Lamp)	1.000	1.003	1.008	1.009	1.007	1.011	1.016	1.01

Other WISP-3 instruments are vicariously calibrated against the reference WISP-3. The method for this is as follows. First, the absolute spectral response of the reference WISP-3 is measured using an Ocean Optics Inc. tungsten halogen light (LS-1-CAL). The spectral intensity of these lamp is calibrated by standards that provide traceability to the National Institute of Standards and Technology (NIST).

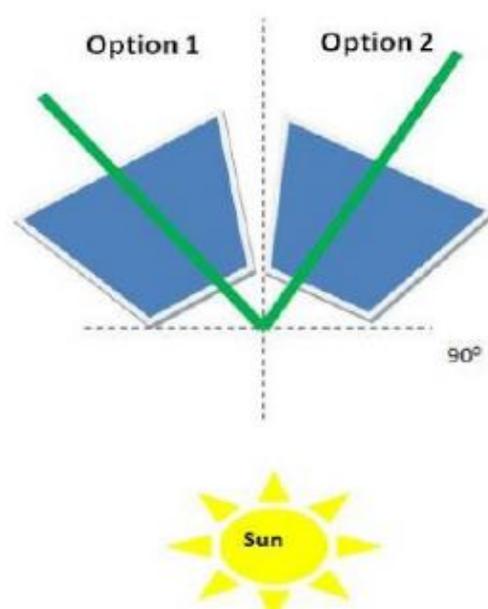
The absolute spectral response for each channel is saved as lamp spectrum and directly after this measurement, the WISP-3 that needs calibration is calibrated versus this lamp using the saved lamp spectrum. After calibration of the WISP-3 radiometers, a measurement of the lamp light field was done, to check the accuracy.

3 REFLECTANCE MEASUREMENTS WITH WISP-3

As mentioned in section 1.1, the WISP-3 is made up of three separate miniature, fiber optic spectroradiometers fixed at a required angles according to protocol. The integration time is varied to provide the necessary dynamic range. For each channel a separate dark reading is obtained when ever the integration time is changed. The WISP-3 internally averages 5 measurements, which can be adjusted.

Ocean optics (Mueller *et al.* 2003) protocols strictly recommend flagging data if sensors are tilted > 5 degree. The WISP-3, nor most of the other available hand-held spectroradiometers register the tilt angle while measuring. The WISP-3 has a bubble to assist the user to keep the instrument level. Equally, important is the angle towards the sun and possible shadows. The WISP-3 follows the ocean optics protocols when deploying measurements. The users are instructed be positioned 135° away from the sun, or in other words at 45° away from

where shadows cast by the sun reach. There are thus two suitable angles, measured either clockwise or anticlockwise from the sun, as illustrated in Figure 1. Reflections of the sun and the sky on the water surface are kept to a minimum when measuring at these angles. According to literature (Mobley, 1999), the angle from the sun should at least be 90° , although closer to 135° is optimal. Angles $< 90^\circ$ (towards the sun) and $\sim 180^\circ$ (opposite to the sun) should absolutely be avoided. If the sky is fully overcast and shadows are not visible, the angle is less critical but measuring towards the position of the sun is still not advised. The FOV of the radiance sensors is fixed to 3 degree in-order to reduce the variability of skylight reflection.



Annex 1, Figure 1 . Correct positioning of the WISP-3 during the measurement

The results are promising and present the WISP-3 as a possible instrument for Sentinel-2 and -3 validation.

4 Specification of a single-beam spectrophotometer USB4000

At Water Insight, a single-beam USB4000 spectrometer is used to derive inherent optical properties. The USB4000 miniature fiber optic spectrometer is purchased from Ocean Optics with wavelength range from 350-1000 nm and a band width (full width half Max) of ~ 1.5 nm. It features a 3648-element Toshiba linear CCD array for increased signal to noise ratio (300:1). The USB4000 maintains at full signal with digital resolution of 0.3nm and dynamic range of 1300:1. Errors attributed due to linearity are less than 0.3%. The set up includes

UV/VIS optical fiber (diameter 200µm) and ocean optics LS-1 light source.

Annex 1, Table 6. *Spectrophotometer requirements set by NASA for IOP measurements*

	Protocols (dissolved materials)	USB4000
Wavelength range	250-850nm	350-1000nm
Spectral resolution (FWHM)	<= 4nm	1.42nm
Baseline noise (OD)	<0.001	<0.001
Noise (OD)	<0.0005	300:1 (SNR) from ocean optics
Adjustable slit width	optional	Yes
Automatic baseline correction	optional	Yes
Automatic spectral calibration	optional	No

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