Agriculture and Agri-Food Canada
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A Comparison of Laboratory and Field-based Measurements of Chlorophyll-a, Turbidity, and Dissolved Organic Carbon for Agricultural Surface Waters in Ontario and British Columbia, Canada

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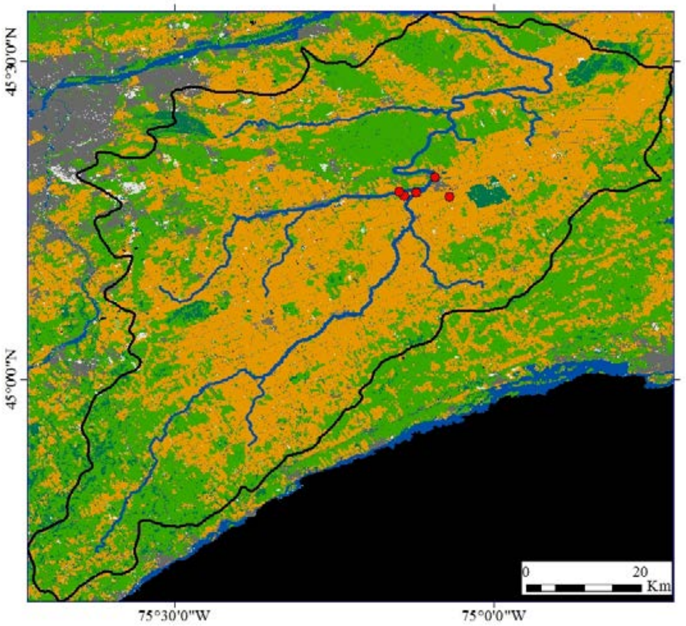
1. Study objective and sites

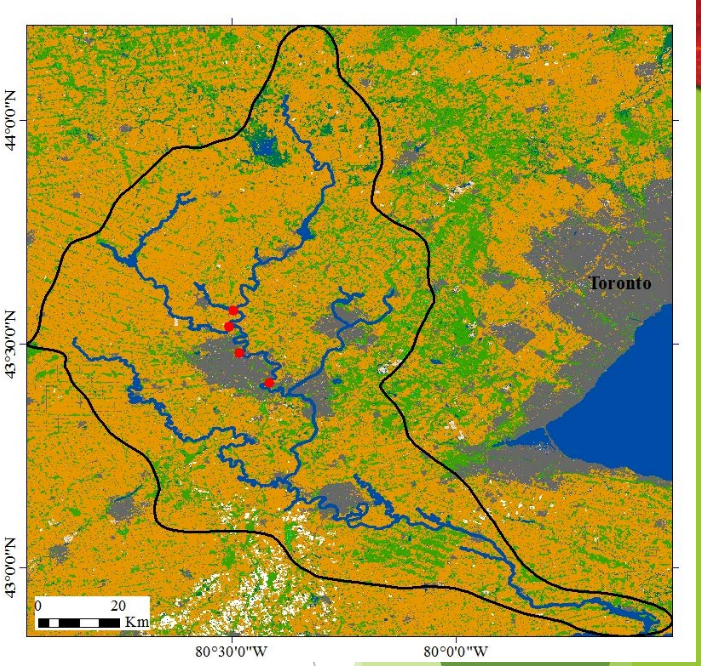
- ✓ There are a variety of optical probe interferences (algal cell character, other water column characteristics, weather, and their seasonal fluctuations) that can confound sensor results, highly inconstant in space and time.

- ✓ The optical sonde measurements of three properties (chl-a; turbidity; and fDOM) are used to determine if indeed site- and time-specific calibration/validation of the optical probe measures would be required.

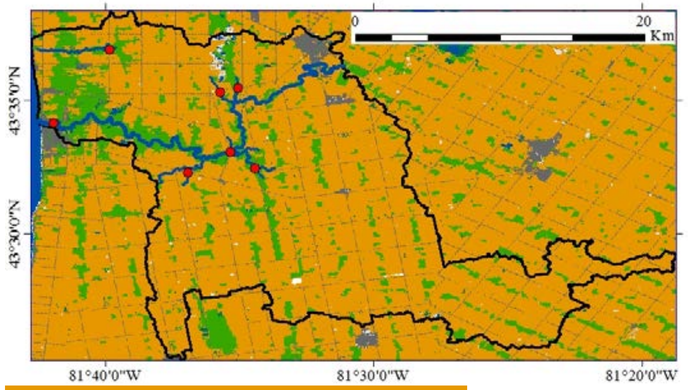
South Nation River (SNR)



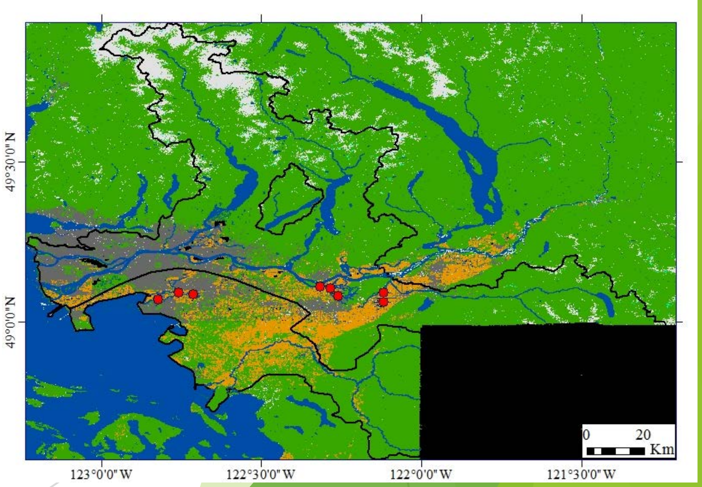
Grand River (GR)



Ausable-Bayfield River (ABR)



lower Fraser River (FR)

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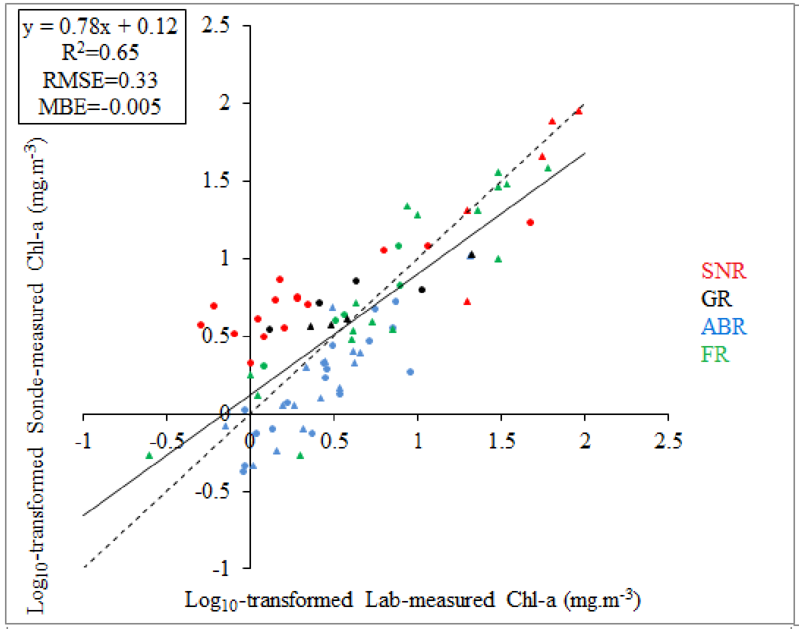
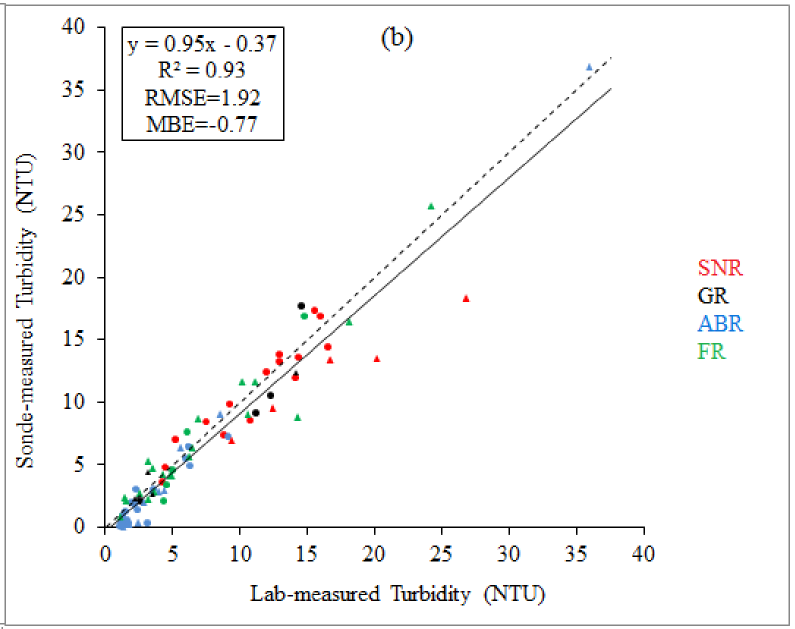
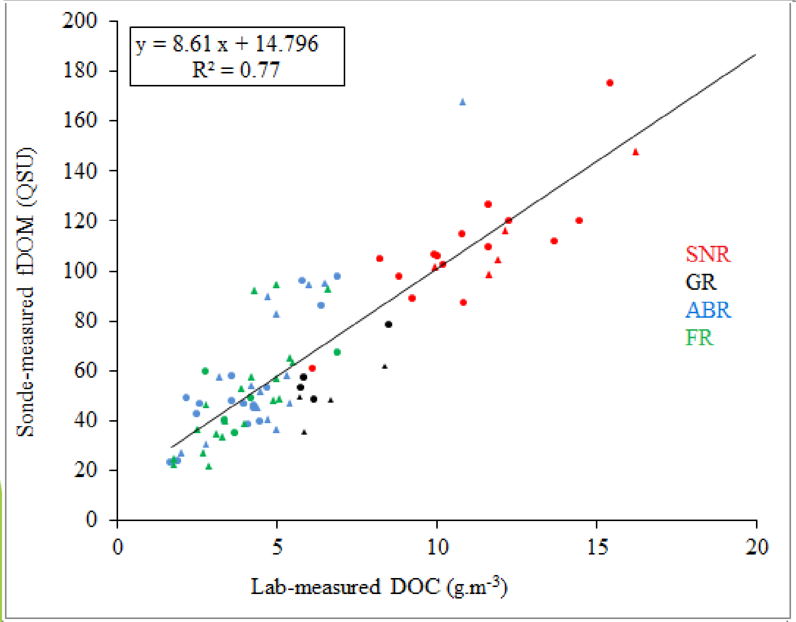
Descriptive statistics of raw laboratory and sonde measurements of chl-a, turbidity, DOC, TSS, fDOM, and water temperature in 2015 for the different study regions.

		Laboratory				Sonde			
		Chl-a (mg m^{-3})	Turbidity (NTU)	DOC (g m^{-3})	TSS (g m^{-3})	Chl-a mg m^{-3}	Turbidity (NTU)	fDOM (QSU)	Temperature (°C)
SNR	Max.	90.9	26.9	16.2	36.0	89.9	18.3	174.7	27.1
	Min.	0.5	4.3	6.1	3.0	2.1	3.5	60.8	17.0
	Avg.	16.9	12.6	11.3	11.3	16.7	11.8	109.8	22.8
	St. Dev.	26.6	5.5	2.4	7.2	25.0	4.2	32.8	3.0
	N	20	20	20	20	20	20	20.0	20
GR	Max.	21.0	14.7	8.5	18.0	10.5	17.6	78.0	19.8
	Min.	1.3	2.3	5.7	3.0	3.5	2.0	35.2	11.5
	Avg.	6.1	8.1	6.6	8.5	5.5	7.6	53.8	15.7
	St. Dev.	6.7	5.6	1.2	6.4	2.4	5.7	21.4	3.6
	N	8	8	8	8	8	8	8.0	8
ABR	Max.	20.5	36.0	10.8	24.0	10.3	36.9	167.9	25.9
	Min.	0.7	1.2	1.7	1.0	0.4	0.0	22.8	11.6
	Avg.	3.6	4.1	4.4	3.5	2.1	3.2	57.9	18.1
	St. Dev.	3.7	6.2	1.8	4.2	2.0	6.6	31.0	4.5
	N	32	32	32	32	32	32	32.0	32
FR	Max.	60.0	24.3	6.9	17.0	38.6	25.8	94.7	22.3
	Min.	0.3	1.2	1.8	0.5	-0.2	0.9	22.1	12.6
	Avg.	11.5	7.1	4.0	6.9	10.3	6.9	49.9	15.9
	St. Dev.	14.7	5.7	1.3	4.3	12.9	5.8	22.7	2.7
	N	22	25	25	25	22	25	25.0	25
All Regions	Max.	90.9	36.0	16.2	36.0	89.9	36.9	174.7	27.1
	Min.	0.3	1.2	1.7	0.5	-0.2	0.0	22.1	11.5
	Avg.	9.2	7.4	6.1	6.8	8.3	6.6	67.3	18.3
	St. Dev.	15.9	6.6	3.5	6.0	14.8	6.5	34.6	4.4
	N	82	85	85	85	82	85	85.0	85

2. Performance of sonde versus lab measurements before calibration





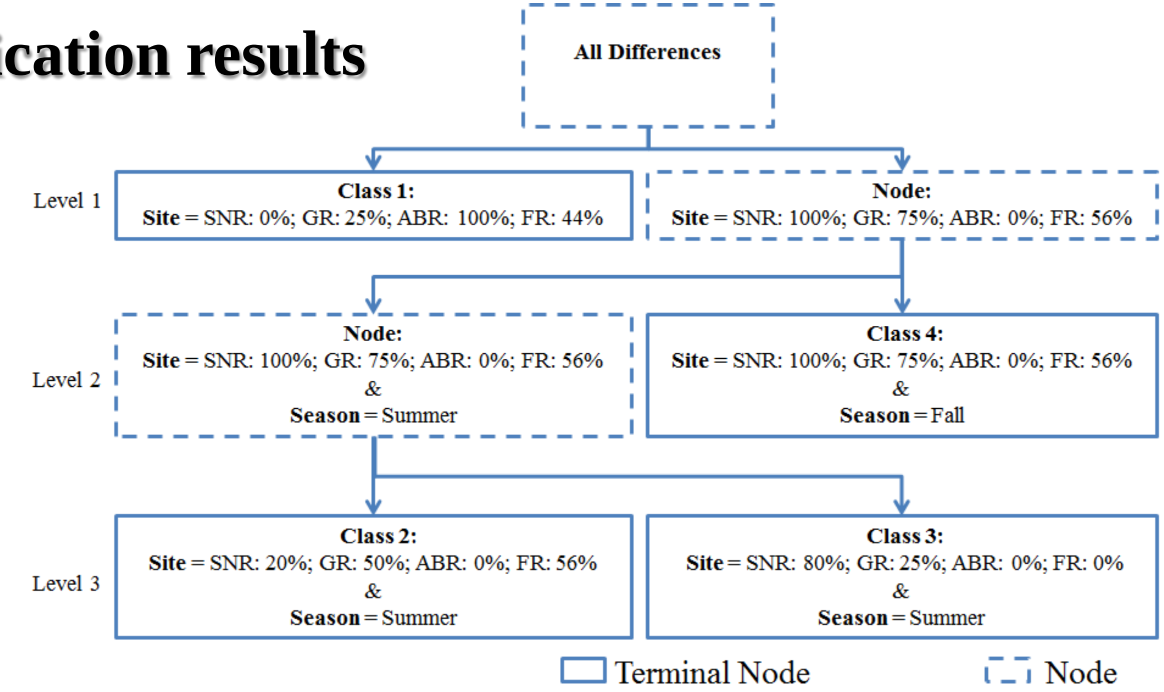


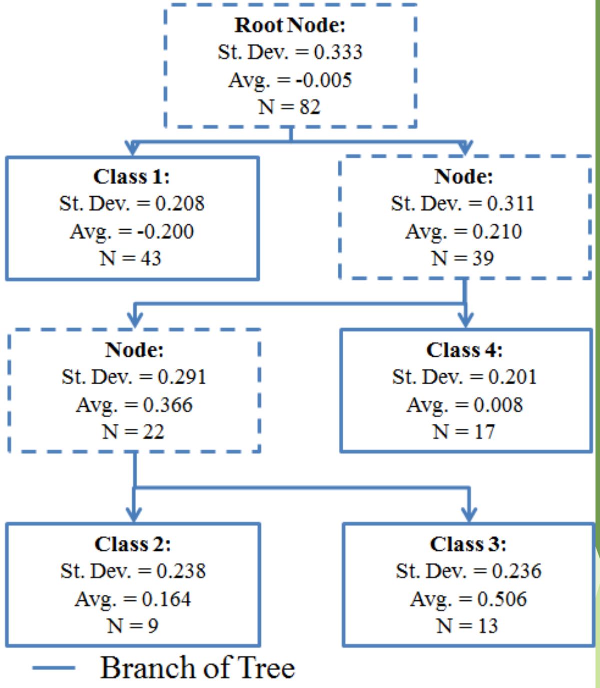
- ✓ The difference between sonde-measured and laboratory-measured properties (sonde minus lab measurements of chl-a and turbidity for all data) are averaged for each study watershed (SNR, GR, ABR, FR) and season (summer and fall). The residuals derived from estimating lab-measured DOC (y; dependant variable) from sonde-measured fDOM (x; independent variable) for all data, is also averaged for each region and season of data collection.
- ✓ The average of residuals derived from the developed OLS linear regression model between sonde-measured fDOM and lab-measured DOC is also summarized for each region and season of data collection.
- ✓ Negative (positive) values are an underestimation (overestimation) with reference to the 1:1 relationship (for chl-a and turbidity) and OLS regression (for DOC prediction from fDOM).

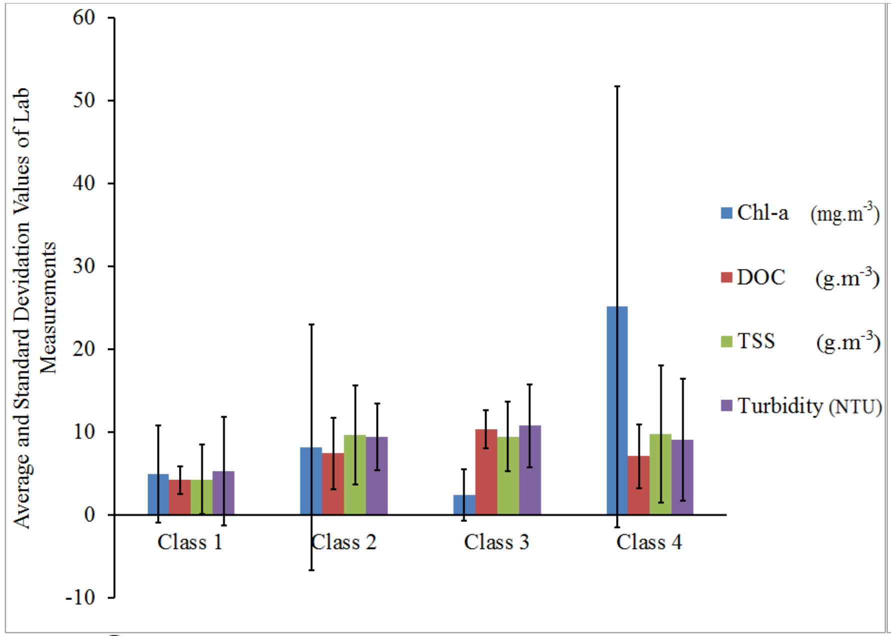
	SNR	GR	ABR	FR	Summer	Fall
Log_{10} Chl-a (mg m^{-3})	0.300	0.096	-0.224	0.003	0.092	-0.102
Turbidity (NTU)	-1.416	-0.454	-0.901	-0.201	-0.681	-0.770
fDOM-DOC (g m^{-3})	0.022	-0.060	-0.043	0.050	0.023	-0.015

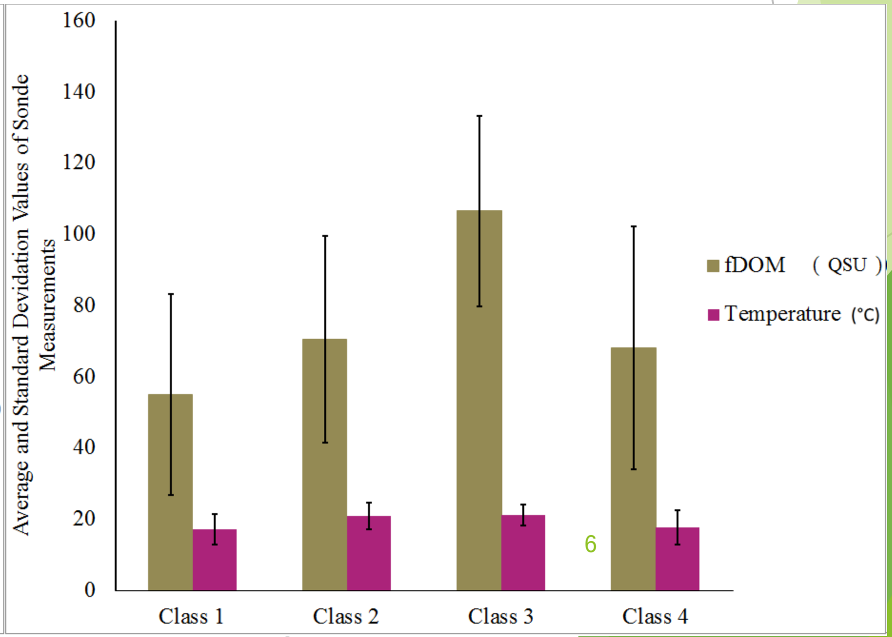
3. Classification results

(A): CART analysis targeting differences between lab-measured and sonde-measured chl-a, on log scale







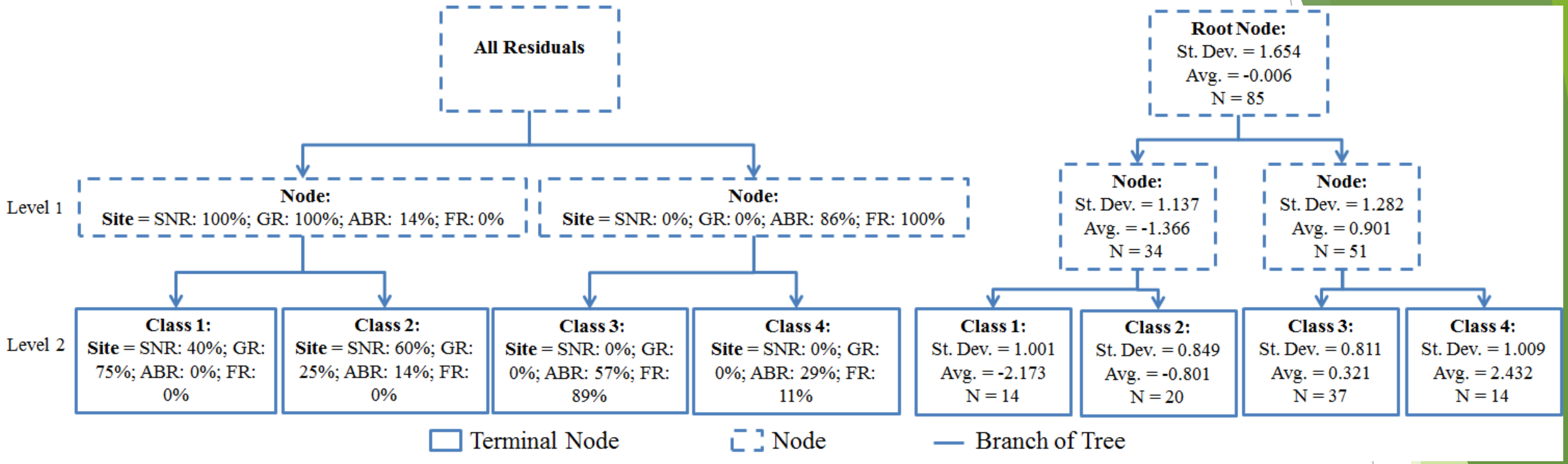


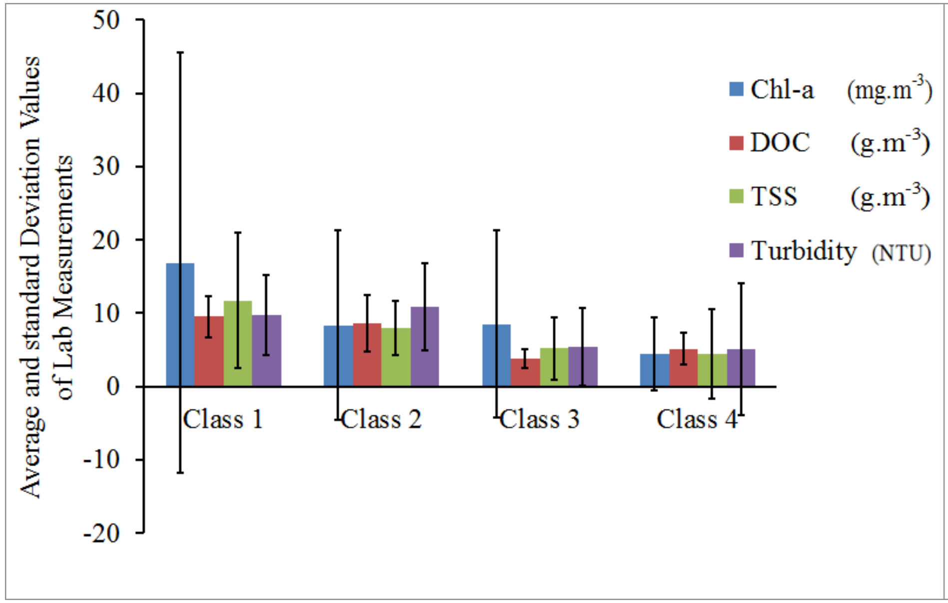
Results from the CART classification show that

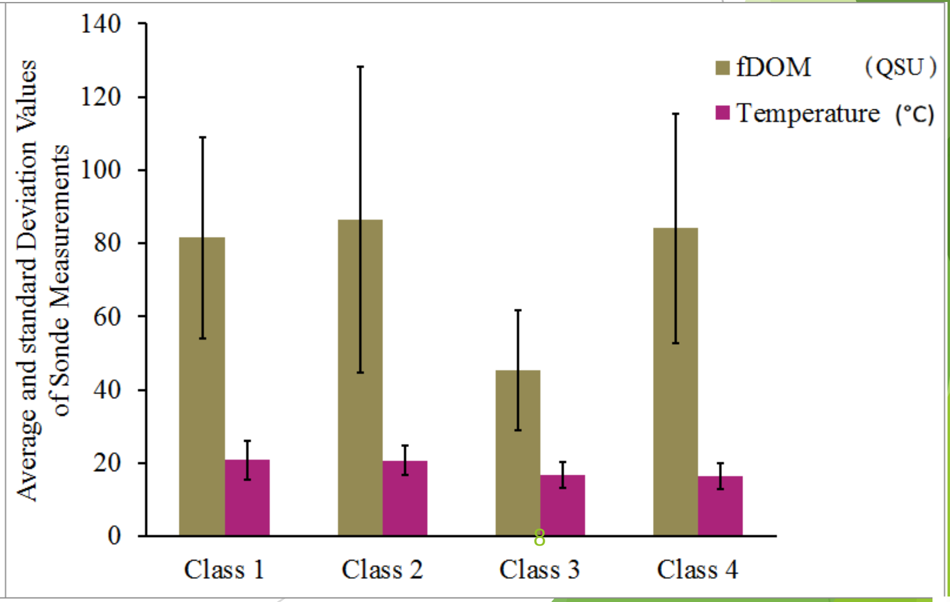
- ✓ In waters with lower relative NTU and low chl-a concentrations, the sonde optical probe underestimated laboratory measurements
- ✓ The sonde overestimated chl-a in the relatively turbid classes and overestimation increased as turbidity increased.
- ✓ The degree of overestimation of chl-a fluorometric sonde-measurements increased as fDOM concentrations increased.
- ✓ The most accurate measurements of chl-a were for less turbid classes at relatively higher chl-a concentrations.

3. Classification results

(B): CART analysis targeting the residuals estimated from prediction of DOC from fDOM







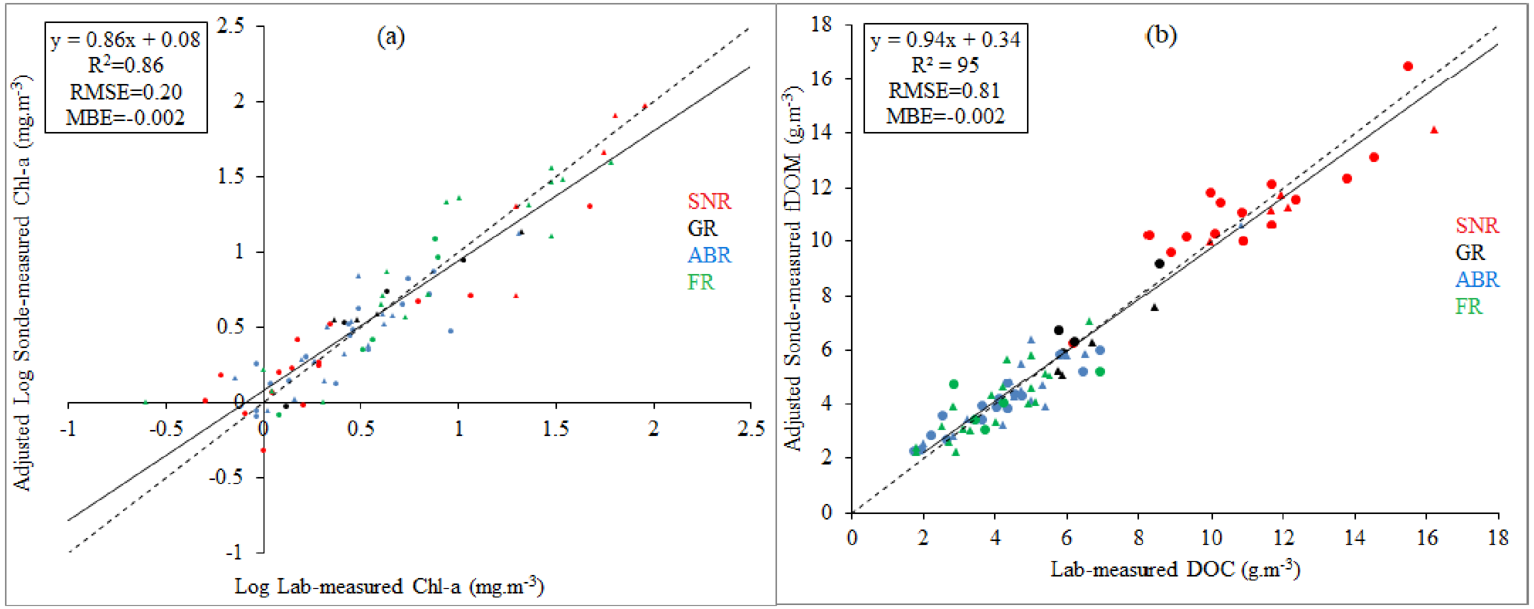
Results from the CART classification show that

- ✓ Results from our study suggest that the fDOM concentrations underestimated DOC concentrations for warmer water conditions for these riverine systems.

- ✓ The fluorescence measurement of fDOM is known to be influenced inversely by water temperature.

- ✓ Also, water turbidity resulting from organic and inorganic suspended matter can interfere with the transmission of the excitation wavelengths of the optical probe to measure specific wavelengths designed for fDOM.

4. Calibration of sonde measurements, based on CART grouping



Improved OLS regressions between adjusted sonde-measured and laboratory-measured chl-a (a); and the adjusted fDOM against the laboratory-measured DOC (b), after CART class inclusion/application of OLS CART hybrid modeling.

		Regression Model	R^2	RMSE	MBE	N	α
Chlorophyll-a	Standard model	y=0.78x+0.12	0.65	0.33	-0.005	82	<0.05
	After using OLS CART hybrid model(s)	y^*=0.86x+0.08	0.86	0.20	-0.002	82	<0.05
Turbidity	Standard model	y=0.95x-0.37	0.93	1.92	-0.77	85	<0.05
	After using OLS CART hybrid model(s)	-	-	-	-	85	<0.05
fDOM-DOC	Standard model	y=8.61x+14.80	0.77	-	-	85	<0.05
	After using OLS CART hybrid model(s)	y^*=0.94x+0.34	0.95	0.81	-0.002	85	<0.05

Conclusion

This study suggests that the relationship developed between sonde- and lab-measured analytes can be improved when these relationships are developed in consideration of water optical properties, changing in space and time.

Laboratory methods for water quality properties.

Region; Laboratory	Chlorophyll-a (Chl-a)	Turbidity	Dissolved organic carbon (DOC)	Total suspended solids (TSS)
SNR and GR; ROPEC laboratory[1]	APHA 10200-H (Spectrophotometry)	APHA 2130-B (Nephelometry)	APHA Method 5310-C (Persulfate-Ultraviolet)	APHA Method 2540-D (dried at 103-105ºC)
ABR; ALS laboratory[2]	APHA 10200-H (Fluoremetry)	APHA 2130-B (Nephelometry)	APHA Method 5310-B (High-temperature combustion)	APHA Method 2540-D (dried at 103-105ºC)
FR; Exova laboratory[3]	APHA 10200-H (Spectrophotometry)	APHA 2130-B (Nephelometry)	APHA Method 5310-B (High-temperature combustion)	APHA Method 2540-D (dried at 103-105ºC)

Table 1. Accuracy and resolution of the optical sensors on the multi-parameter sondes used within this study. QS: Quinine sulfate, QSU: Quinine sulfate unit, QSE: Quinine sulfate equivalent, WT: water tracing. QSU is the unit of fDOM, where 1 QSU = 1 ppb quinine sulfate.

Parameter	Range	Resolution	Accuracy
Chl-a	0 to 400 mg m^{-3}	0.01 mg m^{-3}	Linearity: R^2 >0.999 for serial dilution of Rhodamine WT solution from 0 to 400 mg m^{-3} Chl-a equivalentes
Turbidity	0 to 4000 NTU	0.01 to 0.1 NTU (range dependent)	0 to 999 NTU: ±2% of reading; 1000 to 4000 NTU: ±5% of reading
fDOM	0 to 300 ppm QSU	0.01 ppb QSU	Linearity: R^2 >0.999 for serial dilution of 300 ppb QS solution, Detection Limit: 0.07 ppb QSE
Temperature	-5 to 50°C	0.001°C	-5 to 35°C: ±0.01°C 35 to 50°C: ±0.05°C

The OLS regression models applied to CART terminal nodes

laboratory chl-a (y; dependant variable) and sonde chl-a (x; dependent variable)

	Slope	Intercept	MBE	RMSE	R^2	N	α
Class 1	0.88	0.24	0.001	0.213	0.77	43	<0.05
Class 2	1.50	-0.54	-0.036	0.278	0.85	9	<0.05
Class 3	1.38	-0.78	-0.030	0.279	0.60	13	<0.05
Class 4	1.03	-0.04	0.003	0.215	0.87	17	<0.05

laboratory DOC (y; dependant variable) and sonde fDOM (x; dependent variable)

	Slope	Intercept	R^2	RMSE	MBE	N	α
Class 1	0.096	1.72	0.87	1.162	-0.024	14	<0.05
Class 2	0.090	0.82	0.95	0.942	-0.018	20	<0.05
Class 3	0.068	0.72	0.70	0.78	0.018	37	<0.05
Class 4	0.065	-0.31	0.82	0.83	-0.031	14	<0.05

- ✓ The levels of chl-a, turbidity, DOC, TSS, fDOM concentrations, and water temperature differ by location and season.

- ✓ This spatial and temporal variation impacts the performance of sonde.

To explore the influence of laboratory method on deviations between laboratory and sonde measurement:

We used laboratory as an additional predictor in CART analysis in an exploratory data analysis manner;

The results showed that this factor is a secondary surrogate of site (not a primary splitter) with an association factor of 0.72, and 0.82 in chl-a and fDOM_DOC CART analysis, respectively.

This means that using only site and season as the predictor will result in the best classification model and laboratory method was a rescinded predictor.

Also noteworthy, due to practical circumstances associated with the geography of water sampling sites, that different instruments (same model) were used to characterize optical sensing.

The CART classification results are based on the combined impact of all these factors affecting the relationship between laboratory and sonde measurements.

Yet, as Zamyadi et al. (2016) note, there are a variety of optical probe interferences (algal cell character, other water column characteristics, weather, and their seasonal fluctuations) that can confound sensor results.