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# Airborne Laser-Induced Fluorescence (LIF) Light Detection and Ranging (LiDAR) for the Quantification of Dissolved Organic Matter Concentration in Natural Waters

**Stephanie R. Rogers · Tim Webster ·
William Livingstone · Nelson J. O'Driscoll**

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**Abstract** Analysis of dissolved organic matter (DOM) concentration and composition is essential to quantifying biological and chemical oxygen demand and atmosphere–ocean heat flux exchange in natural waters. However, manual water sampling is costly and time consuming over large areas. The purpose of this research was to analyze the applicability of airborne laser-induced fluorescence light detection and ranging (LiDAR) for the detection of DOM in estuarine ecosystems impacted by agriculture. A fluorescence LiDAR system (Airborne Marine) (FLS-AM) was used to assess the DOM concentration of the Annapolis River and Basin, Nova Scotia, Canada, as well as three rivers and their estuaries in Prince Edward Island, Canada. Two FLS-AM flight missions were conducted in the summers of 2008 and 2009 and the resulting datasets were compared with spectral fluorescence signature (SFS DOM) and dissolved organic carbon (DOC) analysis of in situ water samples. Significant positive correlations were found at five of seven sites between the FLS-AM DOM and SFS DOM relationship which indicates that the FLS-AM sensor is a good surrogate for traditional sample collection of DOM data in estuaries in this region. Positive correlations were also found at all sites between FLS-AM DOM values and DOC. FLS-AM DOM patterns show that DOM values are significantly higher in rivers and estuaries that drain watersheds which are heavily impacted by agricultural practices. The results of this study show that the FLS-AM can be used efficiently as a general indicator for how estuaries are affected by runoff from agricultural watersheds in real time and thus reduce the requirement for traditional water sample collection and laboratory analysis methods.

**Keywords** Water quality · Remote sensing · GIS · Dissolved organic matter · Dissolved organic carbon · Agriculture · LiDAR · Fluorescence

## Introduction

Research in the area of dissolved organic matter (DOM) is of significant environmental importance due to the major role it plays in the global carbon balance (Jiang et al. 2008). Early fluorescence studies have used DOM as a tracer of riverine inputs of dissolved organic carbon (DOC) (Colbe 1996). The concentration and composition of DOM can influence many processes including: microbial and planktonic abundance, trace metal speciation and transport, solar radiation attenuation, and thermal regulation (Lean 1998). DOM is one of the key indicators of water quality as it is closely tied to biological and chemical oxygen demand and therefore the process of eutrophication (Yang et al. 2008). Eutrophication is caused by an increase in limiting nutrients to a water body which results in increased productivity and biomass at the base of the food web and ultimately increased organic carbon in the system (Wetzel and Likens 2001).

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S. R. Rogers · T. Webster · W. Livingstone
Applied Geomatics Research Group, Center of Geographic Sciences (COGS), Nova Scotia Community College,
295 Main St.,
Middleton, NS B0S1M0, Canada

S. R. Rogers · N. J. O'Driscoll
Department of Earth and Environmental Science,
Acadia University,
15 University Avenue,
Wolfville, NS B4P2R6, Canada

S. R. Rogers (✉)
Department of Geography, University of Fribourg,
Chemin du Musée 4,
1700 Fribourg, Switzerland
e-mail: stephrogers5@gmail.com

DOM is a complex and poorly defined mixture of compounds which affect the optical properties of each water body differently, which makes spectral measurements difficult to perform and results difficult to compare (Belzile et al. 2006; Mobley 1994). The abundance and composition of organic matter in freshwaters is affected by the amount of imported detrital organic matter from the surrounding drainage basin or catchment, differences in the sources of the organic material, and the amount of autochthonous autotrophic production occurring within the water body (Wetzel 2001). For example, estuaries whose watersheds are affected by agricultural land use tend to have higher levels of DOM and DOC, thus higher aromaticity levels (Wetzel 2001).

DOM is often measured as DOC concentration as it is made up of 40–60 % carbon (Cumberland and Baker 2007). DOC levels range from about 0.45 mg $L^{-1}$ in the open ocean to 30 mg $L^{-1}$ in some bogs, with lakes and rivers usually averaging between 2 and 10 mg $L^{-1}$ (Thurman 1985; Wetzel 2001). DOC analysis is commonly a result of in situ water samples measured using wet or thermal oxidation of carbon followed by spectroscopic detection of carbon dioxide gas in the infrared. Spectral fluorescence spectroscopy (SFS) is also a common method used to detect DOM in the lab due to the fact that it is a nondestructive analysis technique. The electrons found in fulvic acid, humic acid, and protein fractions that are present in the aromatic rings of DOM become excited by the laser pulse and the resulting emission of light is measured (Saadi et al. 2006). Humic and fulvic acids are responsible for much of the color seen in water due to the presence of chromophoric structures in their molecules (Jiang et al. 2008) and are often referred to as colored dissolved organic matter (CDOM). CDOM absorbs radiation in both the ultraviolet and visible ranges of the electromagnetic spectrum (Rochelle-Newall et al. 1999) and is considered to be an essential but highly variable part of the DOC pool due to the terrestrial, riverine, and autochthonous components that comprise it (Zhao et al. 2009). High concentrations of CDOM, or DOM, are found in marshes, lakes, and rivers where there are high levels of organic matter. Low concentrations of CDOM are found in the open ocean where there is low nutrient availability and low primary productivity unlike estuaries and coastal regions which tend to have moderate nutrient inputs and concentration of DOM (Thurman 1985; Wetzel 2001). The relative florescence intensity of humic substances also depends on the molecular size and the aromaticity of the molecules (Alberts et al. 2004). Vidon et al. (2008) determined that DOM produced in an agricultural watershed is more aromatic than DOM in a mixed land use watershed. As the number of aromatic rings in DOM condense in a straight chain, so do the number of conjugated bonds, thus increasing the fluorescence of DOM (Alberts et al. 2004).

Fluorescence occurs typically in aromatic molecules when an atom is raised to an excited state by some type of electromagnetic radiation at the correct absorbance wavelength, i.e., a radiation source or laser (Babichenko et al. 1993). In laboratory experiments, Colbe (1996) employed the use of excitation/emission matrix spectroscopy (EEMS) (similar to SFS analysis used in this study). EEMS spectroscopy is used to identify fluorescence compounds present in complex mixtures of water, examine the range of environmental variability in the fluorescence of DOM, and determine whether DOM from different sources can be distinguished using fluorescence spectroscopy. The fluorescence range of DOM acts as its spectral signature which makes it easily detectable when excited by electromagnetic radiation, making it a feasible target for remote sensing initiatives. The original remote sensing fluorosensor was invented for the airborne detection of oil spills but has since been developed to undertake a variety of different missions (Measures 1984). Some of the first experiments with airborne laser fluorosensors used a variety of different methods for the detection of chlorophyll *a* found in algae (Browell 1977; Bristow et al. 1981; Hoge and Swift 1981) total suspended solids, the fluorescent pigments in phytoplankton, and DOM (O'Neil et al. 1980; Exton et al. 1983; Hoge et al. 1993). It has been determined that with the optimum excitation wavelength, any of these substances can be defined from the spectral response in the water body (Exton et al. 1983).

In previous studies using a fluorescence light detection and ranging (LiDAR) system (FLS), sensors were most commonly mounted on ships and surveys were conducted in open ocean areas where the fluorescence properties changed slowly over great distances (O'Neil et al. 1980; Dudelzak et al. 1991). Hoge et al. (1993) were one of the first to conduct a study to compare fluorescence values collected from an aircraft and ship to compare to traditional laboratory methods. It was found that it was difficult to compare the fluorescence results from a laser-induced fluorescence (LIF) LiDAR system to traditional fluorescence methods due to the fact that there was no commonly used fluorescence standard. Further research conducted with shipborne FLS sensors has shown to be effective in detecting oil, DOM, and phytoplankton in ocean environments from shipborne platforms (Drozdowska 2007; Babichenko et al. 1999; Babichenko et al. 2004). In such environments, georeferencing requirements could be satisfied by matching fluorometer readings with ship logs. Shipborne studies by Barbini et al. (1999) have shown that fluorescence is a good predictor of the humic components in DOM. Spectral signatures were extracted from fluorescence data to determine the types of pollutants present in the Venice Lagoon. The LIF LiDAR they used was able to detect crude oil, polyaromatic hydrocarbons, industrial wastes, and many other substances by analyzing the differences in their spectral signatures. Barbini et al. (1999) collected in situ water samples to analyze in a laboratory to get exact concentrations of DOM and other substances in the water. Similarly, Babichenko et al. (1999) used a shipborne spectrofluorometer along with the LIF LiDAR to calculate concentrations and the composition of DOM. Between the LIF LiDAR and spectrofluorometer data, the researchers found a high correlation ($r^2$=0.91) which indicated that LIF LiDAR can give a good general indication of the amounts of DOM in the water, but it cannot provide exact concentrations. This suggests that fluorescence data need to be compared to absolute data analyzed from in situ water samples in a laboratory (or a spectrofluorometer in situ) to determine specific concentrations (John and Souter 1976).

With the emergence of widely available global positioning system (GPS) receivers, it became possible to integrate FLS sensors with accurate GPS to increase precision of georeferencing and ultimately address applications where changes occur more rapidly and frequently, such as in the coastal environment. The Airborne Marine version of the FLS (FLS-AM) was produced by Laser Diagnostic Instruments International Inc. (LDI$^3$) to survey the open ocean. The FLS-AM consists of a laser source to emit radiation, telescopes for both beam transmitting and receiving, and a highly sensitive optical receiver to evaluate spectral properties (Babichenko et al. 2004). In this study, the sensitivity and accuracy of the FLS-AM was tested for DOM in coastal and estuarine waters. The FLS-AM flights were undertaken in 2008 and 2009 to examine the influence of agricultural land use in watersheds on DOM levels in estuaries in Atlantic Canada (Fig. 1). For the 2008 mission, the FLS-AM used a consumer-grade GPS receiver for georeferencing. The uncorrected FLS-AM dataset consisted of GPS-derived coordinates which led to instances of geographic positioning errors on the order of hundreds of meters due to the lack of an inertial measurement unit (IMU). The meandering nature of survey trajectories led to significant pitch, roll, and yaw of the aircraft, and these issues were not reflected in the GPS coordinates of the receivers, thus, greatly affecting the true direction of the scanning laser beam and the true location of the data acquisition point. These geographic positioning errors were corrected by using a rubber-sheeting method which adjusted the FLS swaths to represent real world coordinates. Prior to the 2009 flight, the FLS-AM was equipped with a position orientation system–airborne vehicle navigation system (combined GPS IMU) to improve the positional accuracy of the laser scan data. The results from the 2009 mission showed accurate geographic positioning and did not require the data to be corrected with the previously stated rubber-sheeting method.

The purpose of this research was to analyze the applicability of FLS-AM for the detection of DOM in estuarine ecosystems impacted by agriculture by comparing LiDAR-derived fluorescence readings to results obtained from water samples collected in situ. Because water runoff during rain events in agricultural areas is unpredictable and can be detrimental to water quality, we have attempted to develop a method using LIF LiDAR to determine, for the first time in Atlantic Canada, how estuaries may be susceptible to disturbances from agricultural land use practices. To determine the correlations between the 2008 and 2009 FLS-AM fluorescence datasets and DOC in this study, comparisons were made between the airborne FLS-DOM values and in situ water samples analyzed for DOM with SFS and DOC with traditional laboratory methods. We have assessed and corrected the geographical positioning errors of the FLS-AM datasets using standard polynomial correction methods, compared the FLS-AM DOM values to SFS DOM samples collected in situ and determined the strength of the relationships between the FLS-AM DOM and DOC values. Based on previous results about fluorescence of DOM in laboratory and open ocean experiments, we hypothesize that the FLS-AM DOM values will be significantly ($p<0.05$) and positively correlated to lab-analyzed SFS DOM measurements from in situ water samples, indicating that remote fluorescence LiDAR can be used as a surrogate for SFS lab analysis. Also, we predict that FLS-AM DOM and DOC data in Atlantic Canadian coastal environments will be significantly correlated and that higher levels of these substances will be found in estuaries that drain watersheds with intensive agricultural practices.

## Methods

### Fluorescence LiDAR

A field crew from LDI$^3$, Ottawa, ON, Canada, conducted airborne surveys with the FLS-AM under contract to the Applied Geomatics Research Group (AGRG), Middleton, NS, Canada in the summers of 2008 and 2009. Missions in 2008 were conducted on August 27 and 28 and included the Annapolis Valley (44 °46′56″ N, 65 °23′42″ W) and Prince Edward Island (PEI) (46 °26′31″ N, 63 °28′6″ W) (Fig. 1), respectively, in a total of 33 flight lines (Fig. 1). In 2009, flights were conducted on September 23 and included the Annapolis Valley which has the highest intensity of agricultural land use in Nova Scotia (Fig. 1).

The FLS-AM emits laser pulses at a wavelength of 308 nm, with a pulse energy of 120 mJ and a repetition rate of 99 Hz, using an ultraviolet excimer laser with a non-stable resonator to excite molecules to determine levels of DOM in natural waters. The spectral resolution of the FLS-AM is 1.18 nm and has a 9-m diameter footprint per pulse at a typical flying height of 300 m. The laser pulse is directed across the track using a scanning mirror system that results in a

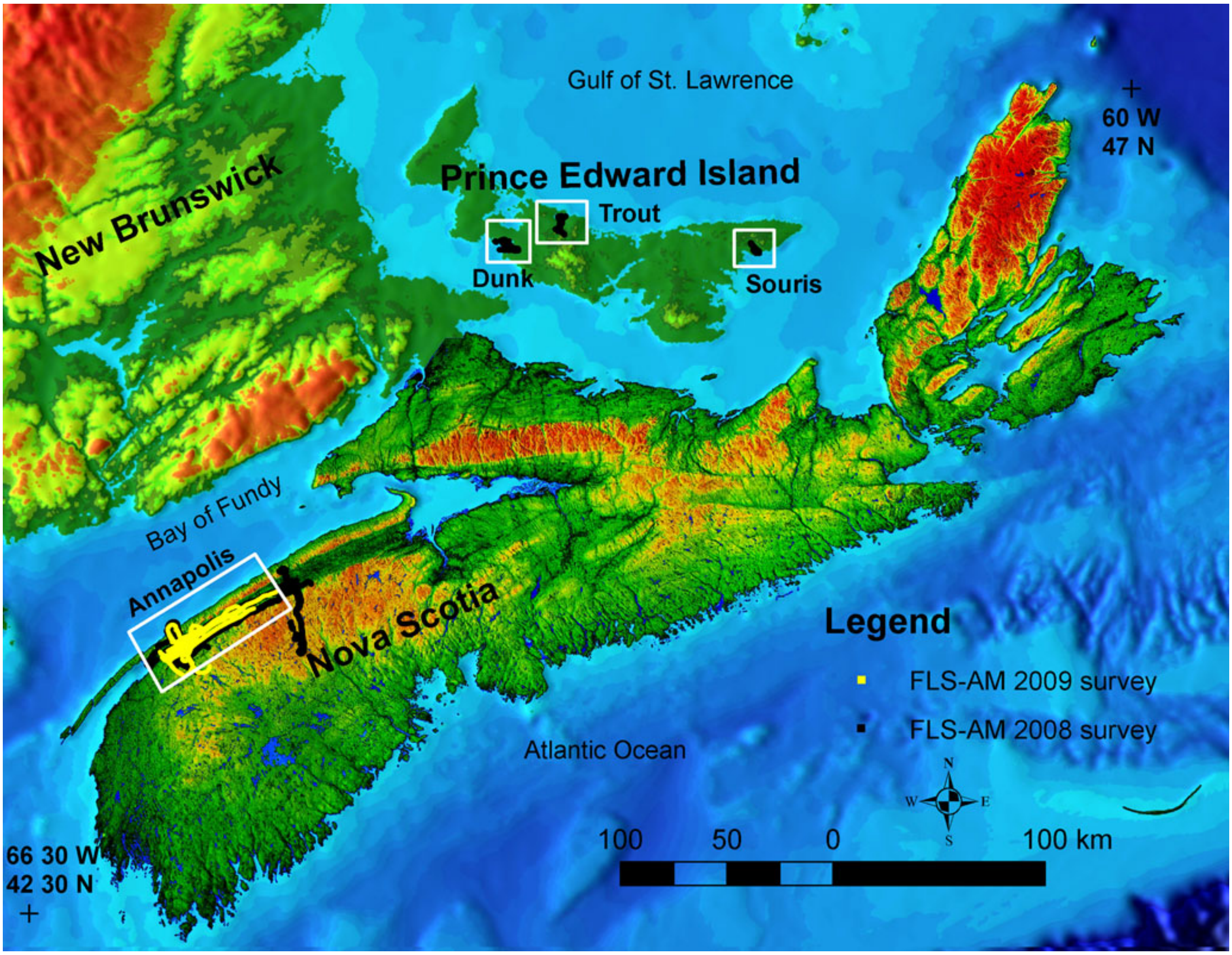

**Fig. 1** Color shaded relief map of the Maritime Provinces showing study areas in *white boxes* and flight lines with *black dots* representing 2008 flights and *yellow dots* representing 2009 FLS-AM surveys over Nova Scotia and Prince Edward Island. The background map shows highest elevations in *red* and lowest elevations in *dark green* for land

swath width of approximately 30 m. The resultant fluorescence is measured in the range from 300–600 nm or 450–740 nm, depending on the desired detection substance, with a 5-nm spectral resolution using a multichannel detector (Babichenko et al. 2004). The FLS-AM technology used Raman scattering (RS) as a preprocessing step to normalize the laser measurements taken by the FLS-AM. RS normalization is employed to determine and calculate fluorescence values when there are changes in temperature or pressure. For example, if the water temperature increases, there should be an even decrease of intensities within the molecules of the water, which allows fluorescence levels to be accurately determined over large areas and time periods (Walrafen 1967). RS data were essential for calculating DOM concentrations because they indicate where the wavelength of scattered energy is shifted as a function of the medium and the wavelength of the incident laser pulse (Mobley 1994). Spectral ranges for RS range from 300 to 600 nm and DOM range from 450 to 740 nm with 500 channels (Babichenko et al. 2004). DOM concentrations from the FLS-AM dataset were derived by calculating the ratio of fluorescence intensity to the RS intensity (Babichenko et al. 2004). LDI$^3$ personnel extracted the DOM concentrations which were represented as unitless values. The DOM values were considered representative of the surface layer of the water body to a depth of approximately 1 m, depending on the clarity of the water and with the assumption of homogeneity in the water column. The estuarine waters in this study are considered well mixed because of the tidal amplitude.

## Geometric Corrections

The August 2008 FLS-AM mission was intended as a trial exercise to test intergroup logistics between the AGRG and

LDI³ and to evaluate the application of these data in estuarine environments influenced by intensive agricultural practices in Atlantic Canada. The FLS-AM LiDAR was configured with a consumer-grade GPS which, by itself, gave a positional accuracy on the order of 5–10 m. Because the FLS-AM dataset was acquired with a limited GPS and no IMU to precisely account for aircraft movement and orientation, the fluorescence return points had limited accuracies in geographic coordinates when the data points were displayed in a geographic information system (GIS) environment. There were disparities between the land/water boundaries, which could be identified in the FLS-AM DOM values obtained over water compared to land, which measured between 150 and 200 m, when compared with the 1:10,000 topographic map shoreline. It was determined that a geometric correction of the FLS-AM DOM data points was required. Geometric corrections were completed using a rubber-sheeting method using ArcGIS and ArcWorkstation. First, all zero values were removed from the FLS-AM datasets in ArcMap, as they indicated that the reading, or measurement, was taken over land. Ground control points (GCPs), or links, were used to relate where FLS-AM points values crossed the land/water boundary to the vector shoreline. Once a sufficient number of GCPs were established (approximately six per swath), the adjust command was then used to establish a triangulated irregular network (TIN), which transformed the FLS-AM swath into the correct location. The linear option was used with the TIN to establish a linear first order polynomial correction.

To determine the relationship between the FLS-AM DOM values and the in situ water samples, spatial analysis was used to compare the in situ measurements with the proximal FLS-AM DOM values. As a result of the uncertainty in our correction method and no compensation for aircraft orientation (i.e., IMU), a 400-m buffer was constructed around each in situ water sample point to provide a sufficient number of FLS-AM DOM data points for statistical analysis. FLS-AM swath data that intersected with the buffer were extracted for each water sample site and the DOM values were compared to the DOC and DOM water samples. Means of FLS-AM swath data within the 400-m buffer and standard deviations of the FLS-AM DOM data were calculated in ArcMap and recorded in Table 1. The effect of varying buffer size was tested by creating a 200- and 400-m buffer for the PEI sites. It was determined that the differences in results were insignificant with a 200- or 400-m buffer. For example, in Dunk River and estuary, FLS-AM mean values were 0.2 units (7.1 %) higher with larger standard deviations (2.5 %) when using a 200-m buffer compared to a 400-m buffer. There were fewer sample sites in the range of 200 m from the FLS-AM data, therefore the buffer size of 400 m was considered sufficient for analysis. The number of soundings within the 400-m buffers varied from site to site from 60 (08-ANN18) to 2,481 (08-SOURIS10). The unitless DOM swath samples were then statistically compared to the water sample DOC and SFS DOM values.

Similar methods were used to evaluate the positional accuracy of the 2009 FLS-AM data. By analyzing the land/water boundary, it was found that the FLS-AM data were consistent with those of the vector shoreline; thus, geometric corrections were not required for the 2009 survey. The improved geometric accuracy was a result of the implementation of the IMU and survey-grade GPS upgrade to the navigation system of the FLS-AM. As a result of the improved georeferencing of the FLS-AM data in 2009, a 200-m buffer was used for the spatial analysis to compare FLS-AM DOM values with in situ water samples. This buffer resulted in the similar number of FLS-AM DOM sample returns as the 400-m buffer for the 2008 analysis (Table 1).

### In Situ Water Samples

Surface water samples for DOC and SFS DOM analysis were collected on August 27 and 28, 2008 from the Annapolis Valley and PEI and September 23, 2009 from the Annapolis Valley and were positioned with handheld WAAS-enabled GPS with an accuracy of 3–5 m (Table 1). Two types of water samples were collected to calculate (1) the correlation between in situ (SFS DOM) measurements and FLS-AM DOM data; (2) the correlation between in situ (DOC) measurements and FLS-AM DOM data; and (3) the correlation between in situ (DOC) and SFS DOM data. DOC samples were collected by hand using powder-free latex gloves into two 50 ml polypropylene containers and syringe filtered to 0.45 μm using a 25-mm nylon membrane then frozen with minimal headspace until analysis. Samples were taken at approximately 25 cm below the surface of the water and as close to the same time as the FLS-AM readings as possible, within 1 to 2 h of each other. In 2008, the Annapolis Valley sampling consisted of six samples taken from the Annapolis Basin and 12 taken from the Annapolis River ranging from Annapolis Royal to Middleton. In PEI, six samples were taken from Dunk River and estuary, nine from Souris River and estuary, and eight from Trout River and estuary. In 2009, there were eight samples collected for the Annapolis Basin and six collected for the Annapolis River. DOC samples were thawed and analyzed using thermal combustion non-dispersive infrared detection technique on a Shimadzu, TOC-V Total Organic Carbon Analyzer with an ASI-V autosampler which used internal calibration standards of 1,000 ppm stock solutions of both inorganic carbon and total carbon.

A 200-mL water sample was collected using an amber colored glass bottle from approximately 25 cm below the

**Table 1** Site coordinates, DOC, FLS-AM DOM and SFS DOM results for all sites

| Water body | Site ID | Latitude | Longitude | DOC (mg/L) | FLS-AM DOM (au's) | Standard deviation | SFS DOM (mg/L) | Number of Returns |
|---|---|---|---|---|---|---|---|---|
| Annapolis Basin | 08-ANN1 | 44.7442 | −65.5222 | 1.28 | 1.46 | 0.17 | 0 | 898 |
| Annapolis Basin | 08-ANN2 | 44.7330 | −65.5368 | 1.70 | 1.23 | 0.17 | 0.65 | 1466 |
| Annapolis Basin | 08-ANN3 | 44.7116 | −65.5721 | 1.37 | 0.91 | 0.08 | 0.29 | 1184 |
| Annapolis Basin | 08-ANN4 | 44.6831 | −65.6162 | 1.54 | 0.57 | 0.07 | 0.05 | 834 |
| Annapolis Basin | 08-ANN6 | 44.6574 | −65.6842 | 0 | 0.44 | 0.06 | 0 | 673 |
| Annapolis Basin | 08-ANN8 | 44.6273 | −65.7480 | 1.05 | 0.53 | 1.50 | 0 | 1525 |
| Annapolis Basin | 09-ANN1 | 44.7393 | −65.5257 | 0.65 | 2.30 | 0.29 | 2.26 | 516 |
| Annapolis Basin | 09-ANN2 | 44.7273 | −65.5442 | 0 | 1.90 | 0.36 | 3.41 | 780 |
| Annapolis Basin | 09-ANN3 | 44.6900 | −65.6067 | 0 | 0.92 | 0.17 | 0.80 | 609 |
| Annapolis Basin | 09-ANN4 | 44.6591 | −65.6350 | 0 | 0.57 | 0.29 | 0 | 128 |
| Annapolis Basin | 09-ANN5 | 44.6458 | −65.6561 | 0.66 | 0.56 | 0.06 | 0 | 537 |
| Annapolis Basin | 09-ANN6 | 44.6245 | −65.6895 | 0 | 0.43 | 0.06 | 0 | 537 |
| Annapolis Basin | 09-ANN7 | 44.6407 | −65.7037 | 0 | 0.31 | 0.05 | 0 | 878 |
| Annapolis Basin | 09-ANN9 | 44.6207 | −65.7491 | 0 | 0.36 | 0.05 | 0.21 | 818 |
| Annapolis River | 08-ANN10 | 44.8389 | −65.2915 | 5.88 | 14.97 | 3.41 | 8.07 | 138 |
| Annapolis River | 08-ANN11 | 44.8295 | −65.3148 | 6.10 | 19.65 | 8.94 | 7.35 | 891 |
| Annapolis River | 08-ANN12 | 44.8203 | −65.3340 | 4.89 | 15.74 | 6.43 | 6.74 | 858 |
| Annapolis River | 08-ANN13 | 44.8127 | −65.3609 | 3.92 | 18.66 | 9.25 | 6.27 | 982 |
| Annapolis River | 08-ANN14 | 44.8085 | −65.3820 | 3.92 | 14.81 | 7.74 | 5.92 | 508 |
| Annapolis River | 08-ANN15 | 44.7825 | −65.3938 | 3.50 | 9.45 | 4.26 | 0.87 | 796 |
| Annapolis River | 08-ANN16 | 44.7898 | −65.4243 | 3.10 | 11.12 | 5.10 | 4.43 | 507 |
| Annapolis River | 08-ANN17 | 44.7663 | −65.4611 | 2.68 | 4.52 | 1.37 | 3.16 | 629 |
| Annapolis River | 08-ANN18 | 44.9533 | −65.0016 | 6.65 | 12.69 | 3.16 | 8.31 | 60 |
| Annapolis River | 08-ANN19 | 44.9369 | −65.0661 | 6.85 | 22.35 | 6.09 | 7.43 | 436 |
| Annapolis River | 08-ANN20 | 44.8808 | −65.1579 | 6.50 | 31.92 | 13.86 | 7.65 | 707 |
| Annapolis River | 08-ANN21 | 44.8674 | −65.2064 | 6.08 | 24.49 | 8.94 | 7.44 | 1124 |
| Annapolis River | 09-ANN11 | 44.7663 | −65.4611 | 5.37 | 3.59 | 1.81 | 4.24 | 537 |
| Annapolis River | 09-ANN15 | 44.8127 | −65.3614 | 14.18 | 21.02 | 6.21 | 7.20 | 149 |
| Annapolis River | 09-ANN16 | 44.8203 | −65.3340 | 13.82 | 14.45 | 6.29 | 8.06 | 261 |
| Annapolis River | 09-ANN17 | 44.8295 | −65.3148 | 10.74 | 15.84 | 5.69 | 8.12 | 315 |
| Annapolis River | 09-ANN23 | 44.8808 | −65.1579 | 11.13 | 10.96 | 1.99 | 7.42 | 74 |
| Annapolis River | 09-ANN24 | 44.9369 | −65.0661 | 10.93 | 10.93 | 2.27 | 6.43 | 163 |
| Dunk River/Estuary | 08-DUNK1 | 46.3551 | −63.7349 | 1.79 | 2.96 | 1.39 | 2.37 | 984 |
| Dunk River/Estuary | 08-DUNK2 | 46.3579 | −63.7415 | 1.07 | 2.55 | 0.68 | 1.67 | 851 |
| Dunk River/Estuary | 08-DUNK3 | 46.3578 | −63.7578 | 0.04 | 1.51 | 0.27 | 1.58 | 870 |
| Dunk River/Estuary | 08-DUNK4 | 46.3679 | −63.7726 | 1.24 | 1.27 | 0.18 | 1.22 | 1819 |
| Dunk River/Estuary | 08-DUNK5 | 46.3842 | −63.7879 | 0.97 | 1.29 | 0.16 | 0.56 | 1871 |
| Dunk River/Estuary | 08-DUNK6 | 46.3866 | −63.8213 | 0.29 | 0.98 | 0.13 | 0.84 | 1535 |
| Souris River/Estuary | 08-SOURIS7 | 46.3522 | −62.2771 | 2.51 | 0.99 | 0.19 | 0.70 | 1255 |
| Souris River/Estuary | 08-SOURIS8 | 46.3809 | −62.2944 | 5.05 | 4.10 | 2.15 | 4.08 | 1444 |
| Souris River/Estuary | 08-SOURIS9 | 46.3755 | −62.2892 | 3.91 | 3.17 | 1.48 | 1.60 | 1996 |
| Souris River/Estuary | 08-SOURIS10 | 46.3710 | −62.2841 | 5.28 | 1.31 | 0.43 | 1.21 | 2481 |
| Souris River/Estuary | 08-SOURIS11 | 46.3652 | −62.2761 | 4.28 | 1.02 | 0.19 | 0.99 | 2382 |
| Souris River/Estuary | 08-SOURIS12 | 46.3604 | −62.2710 | 4.13 | 0.96 | 0.13 | 0.95 | 1544 |
| Souris River/Estuary | 08-SOURIS13 | 46.3621 | −62.2768 | 2.92 | 0.99 | 0.18 | 0.60 | 1215 |
| Souris River/Estuary | 08-SOURIS14 | 46.3602 | −62.2663 | 4.57 | 0.95 | 0.14 | 1.34 | 1413 |
| Souris River/Estuary | 08-SOURIS15 | 46.3536 | −62.2664 | 2.28 | 0.67 | 0.07 | 0.67 | 855 |
| Trout River/Estuary | 08-TROUT16 | 46.4211 | −63.4415 | 2.95 | 1.87 | 0.34 | 1.85 | 424 |

**Table 1** (continued)

| Water body | Site ID | Latitude | Longitude | DOC (mg/L) | FLS-AM DOM (au's) | Standard deviation | SFS DOM (mg/L) | Number of Returns |
|---|---|---|---|---|---|---|---|---|
| Trout River/Estuary | 08-TROUT17 | 46.4742 | −63.4588 | 0.94 | 1.11 | 0.15 | 0.67 | 1123 |
| Trout River/Estuary | 08-TROUT18 | 46.4591 | −63.4675 | 1.76 | 1.04 | 0.18 | 0.94 | 1544 |
| Trout River/Estuary | 08-TROUT19 | 46.4440 | −63.4740 | 1.40 | 1.24 | 0.94 | 1.10 | 2045 |
| Trout River/Estuary | 08-TROUT20 | 46.4295 | −63.4573 | 4.20 | 1.89 | 0.31 | 1.89 | 2040 |
| Trout River/Estuary | 08-TROUT21 | 46.4412 | −63.4714 | 1.32 | 1.27 | 0.71 | 1.02 | 625 |
| Trout River/Estuary | 08-TROUT22 | 46.4430 | −63.4886 | 1.41 | 1.34 | 1.05 | 1.34 | 356 |
| Trout River/Estuary | 08-TROUT23 | 46.4370 | −63.4777 | 2.05 | 1.52 | 0.63 | 1.33 | 883 |

Locations of each water sample are indicated by latitude and longitude coordinates. DOC and SFS analysis results from water samples analyzed in the laboratory are included, as well as results from fluorescence LiDAR (averaged to obtain one reading from within the 400 m (2008) and 200 m (2009) buffers used for spatial and statistical analyses)

surface for SFS DOM analysis. Samples were stored in the dark at 4°C and SFS analysis was completed within 12 h of sampling. Subsamples (2 mL) were placed into quartz cuvettes and analyzed for SFS using an Instant Screener IS55 from LDI³. The samples were excited in the 240 to 360 nm range at 5 nm intervals and fluorescence emission was measured in the range of 250 nm to 580 nm, with the peak emission occurring between 400 and 450 nm. The primary absorbance band for SFS DOM has been found to be in the 240 to 260 nm range (Babichenko et al. 1999). SFS analysis data were recorded as coordinate pairs in a matrix based on the levels of fluorescence intensity from various excitation and emission wavelengths (Dudelzak et al. 1991). The SFS is the total sum of the emission spectra of an object at different excitations which allows different substances to be recognized in the matrix (Babichenko et al. 2000b. The analysis plot of intensities was broken down into components corresponding to the expected analytes (i.e., DOM, Raman) based on the spectral properties determined in past studies and collected in a spectral fluorescence library. The analysis by SFS allows for the recognition of major groups of organic substances such as DOM (Babichenko et al. 1998). For example, DOM can be defined by its fluorescent portion of humic substance in the UV range (Babichenko et al. 2000a). The maximum intensity of each analyte was converted to a concentration using the following equation:

$$C = a0 + a1 \cdot \mathrm{Int}$$

where $a0$ (0.201) and $a1$ (0.0071) were calculated during the construction of the analysis library from multiple experiments with known concentration ($C$) and Int is the highest intensity of the excitation/emission matrix. Fluorescence values obtained by the SFS system were converted to DOM concentration in milligrams per liter for each sample based on the spectral signature library provided by LDI³ (Babichenko et al. 1998) and then compared to in situ DOC data as well as FLS-AM data to obtain statistical correlation values.

### Statistical Analysis

Statistical analysis was conducted to calculate linear regression ($r^2$) values to determine the strength and significance of the relationships between water samples for DOC and SFS DOM values obtained from the ground sampling and the FLS-AM DOM values obtained during the flight. Linear regressions indicate how well the linear model fits the dataset, thus, representing how accurately FLS-AM fluorescence can be used to predict DOC from water samples and DOM for SFS values. Relationships were considered to be significant if the $p$ value was less than 0.05 ($\alpha$=0.05). Analysis was run on all sites within the Annapolis and PEI, as well as on each individual site to compare the differences in the findings.

## Results

### Fluorescence LiDAR

The 2008 FLS-AM survey, with a swath width of 30 m, collected 33 flight lines of fluorescence DOM data which ranged from 0 to 115 in unitless DOM values calculated from laser measurements which were dependent on the system hardware and interpreted based on the correlation with RS. In the 2009 survey, a total of nine flight flights were collected with FLS-AM DOM values ranging from 0 to 106 units. When visualized in a GIS, the 2008 FLS-AM swath data displayed a distinct bias across the swath. Higher fluorescence values were continuously found on the left side of the swath to a magnitude of almost 1.5 times greater than the right side of the swath. Before the flight mission in 2009, a spectral correction was implemented to the FLS-AM to improve the scanning system to negate the swath bias for the 2009 flight mission.

### Geometric Corrections

In the 2008 data, the geometric errors were not evenly distributed and did not have any consistent pattern throughout the flight lines due to the lack of an IMU and adverse weather conditions which caused irregular aircraft trajectories. Although not a direct objective of the 2008 mission, geometric adjustments were required to complete evaluation of the proposed correlation within the scope of this study.

To adjust the FLS-AM swaths into a format suitable for this study, each flight line was spatially adjusted according to the specific local swath errors. Some of the adjustments included translating or scaling the swaths. For areas such as the Annapolis Basin and the PEI Rivers, corrections were completed effectively by matching the links to their respective land/water boundary on a 1:10,000 topographic map and applying the geometric adjustments required to properly line up the swath data to the water body boundary. However, the small width and the meandering pattern in the upstream portion of the Annapolis River made it difficult to adjust the swath with confidence for that area. As stated in the "Introduction" section, geometric corrections were not required for the 2009 data.

### In Situ Water Samples

#### *Annapolis*

DOC and SFS DOM concentrations in Annapolis Basin and estuary showed a wide range of variation. As seen in Table 1, the water sample values for DOC in the Annapolis River in 2008 (08-ANN10–08-ANN21) ranged from 2.68 to 6.85 mg $L^{-1}$ and from 5.37 to 14.18 mg $L^{-1}$ in 2009 (09-ANN11–09-ANN24). The values for SFS DOM in the Annapolis River in 2008 ranged from 0.87 to 8.31 mg $L^{-1}$ and 4.24 to 8.12 mg $L^{-1}$ in 2009. The values for the Basin in 2008 (08-ANN1–08-ANN4, 08-ANN6, and 08-ANN8) had much lower values that ranged from 0 to 1.70 mg $L^{-1}$ for DOC and 0–0.65 mg $L^{-1}$ for SFS DOM. In 2009, the values for the Basin (09-ANN1–09-ANN9) ranged from 0 to 0.66 mg $L^{-1}$ for DOC and 0–3.41 mg $L^{-1}$ for SFS DOM.

#### *PEI*

Samples values for Dunk River and estuary were only collected in 2008 and ranged from 0.04 to 1.79 mg $L^{-1}$ for DOC and 0.56–2.37 mg $L^{-1}$ for SFS DOM. Souris River and estuary values were 2.51–5.28 mg $L^{-1}$ and 0.70–4.08 mg $L^{-1}$ (Fig. 2) while Trout River and estuary values ranged from 0.94 to 4.20 mg $L^{-1}$ and 0.71–2.98 mg $L^{-1}$ for DOC and SFS DOM, respectively.

### Spatial Analysis

The spatial analysis consisted of extracting the unitless FLS-AM DOM point sample data in a radius of 400 m around each water sample site in 2008 and 200 m radius in 2009 due to the higher accuracy of the FLS-AM in 2009. The means (±one standard deviation) and standard deviations calculated in ArcMap are listed in Table 1. Means of the FLS-AM DOM (±one standard deviation) for the Annapolis Basin in 2008 range from $0.44 \pm 0.06$ to $1.46 \pm 0.17$ and $0.31 \pm 0.05$ to $1.9 \pm 0.36$ in 2009. Values from the estuary were comparatively much higher, ranging from $4.52 \pm 1.37$ to $31.92 \pm 13.86$ in 2008 and $3.59 \pm 1.81$ to $21.02 \pm 6.21$ in 2009, due to the dilution effect once the organic matter reached the basin (Fig. 3). Mean FLS-AM DOM values for PEI were relatively consistent ranging from $0.67 \pm 0.07$ to $4.10 \pm 2.15$ with the majority of values less than 2. The highest and lowest values were both found in the Souris River (Fig. 2).

### Statistical Analysis

#### *Annapolis*

Linear regression analysis for all Annapolis sites (river and basin) showed significant ($p<0.05$) relationships for all three variable pairs in both 2008 and 2009. High correlations were determined for FLS-AM DOM–DOC in 2008 ($p<0.001$, $r^2=0.80$, $n=18$) (Fig. 4a) and 2009 ($p<0.001$, $r^2=0.91$, $n=14$) (Fig. 4d), FLS-AM DOM–SFS DOM in 2008 ($p<0.001$, $r^2=0.77$, $n=18$) (Fig. 4b) and 2009 ($p<0.001$, $r^2=0.84$, $n=14$) (Fig. 4e), and SFS DOM–DOC in 2008 ($p<0.001$, $r^2=0.89$, $n=18$) (Fig. 4c) and 2009 ($p<0.001$, $r^2=0.89$, $n=14$) (Fig. 4f) (all values in Table 2).

In both years, statistical analysis results from the individual groups within the Annapolis River and Basin indicated that the relationships weakened (Fig. 5a–c (2008), d–f (2009)). In the Annapolis Basin in 2008, no significant relationships were found between FLS-AM DOM–DOC ($p=0.263$, $r^2=0.30$, $n=6$), FLS-AM DOM–SFS DOM ($p=0.379$, $r^2=0.20$, $n=6$), or SFS DOM–DOC ($p=0.266$, $r^2=0.29$, $n=6$). In 2009, there was a significant relationship between FLS-AM DOM and SFS DOM in the basin ($p=0.001$, $r^2=0.84$, $n=8$) but not for FLS-AM DOM–DOC ($p=0.313$, $r^2=0.18$, $n=8$) or SFS DOM–DOC ($p=0.748$, $r^2=0.02$, $n=8$). The Annapolis River estuary, however, had significant relationships for all three groups in 2008; FLS-AM DOM–DOC ($p=0.010$, $r^2=0.50$, $n=12$), FLS-AM DOM–SFS DOM ($p=0.025$, $r^2=0.41$, $n=12$), and SFS DOM–DOC ($p=<0.001$, $r^2=0.70$, $n=12$) and for all but

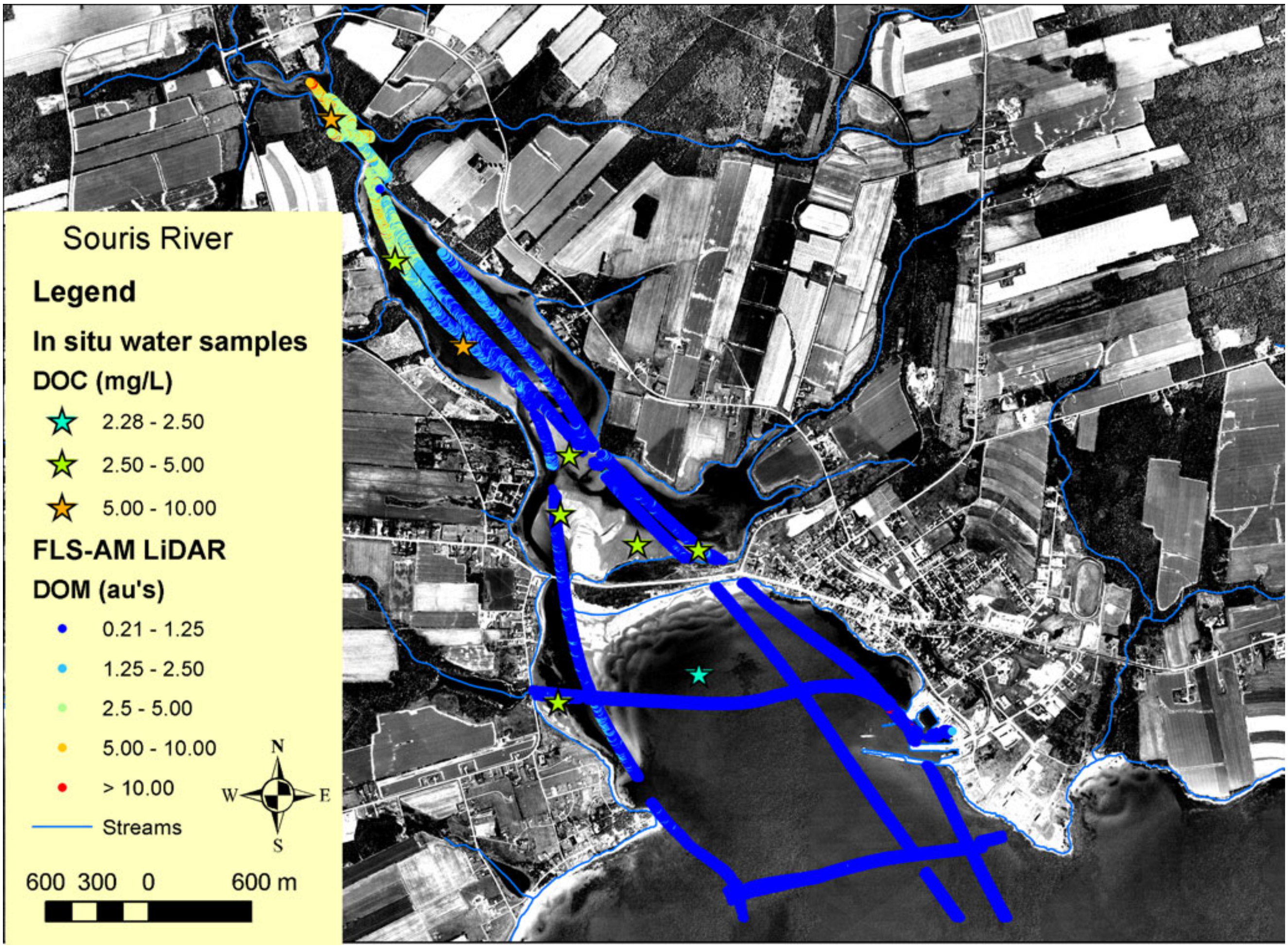

**Fig. 2** Souris River and estuary with FLS-AM DOM swath values and DOC water sample locations overlaid. Background layer is aerial imagery showing intensive agricultural land use. There is a distinct dilution pattern present in all sites with higher DOM values upstream in the river and DOM decreasing as water enters the estuary

one group in 2009; FLS-AM DOM–DOC ($p$=0.019, $r^2$=0.78, $n$=6), FLS-AM DOM–SFS DOM ($p$=0.075, $r^2$=0.59, $n$=6), and SFS DOM–DOC ($p$=0.041, $r^2$=0.69, $n$=6). The relationships weakened when broken down into each respective group due to the fact that the DOC and DOM values in the basin were low while the values in the river were relatively high so when the two groups were compared using the linear model, they produced a linear plot (Fig. 4a–f) which caused a misleading significant relationship due to the data being skewed. Because of this, we focused only on individual sites rather than entire groups of data (i.e., all Annapolis and all PEI).

### *PEI*

Results from the PEI analysis showed that only the FLS-AM DOM–SFS DOM relationship was significant and had high correlation ($p$<0.001, $r^2$=0.78, $n$=23). The other groups of variables, FLS-AM DOM–DOC ($p$=0.250, $r^2$=0.06, $n$=23) and SFS DOM–DOC ($p$=0.094, $r^2$=0.13, $n$=23), were not significant and had very low correlation (Fig. 6a–c and Table 2).

The PEI group was broken into its respective sites and analysis was conducted on each of Dunk, Souris, and Trout Rivers (Fig. 6d–f). In the Dunk River, a significant relationship was found between FLS-AM DOM and SFS DOM ($p$=0.024, $r^2$=0.76, $n$=6). The other two relationships were not significant and had low $r^2$ values (FLS-AM DOM–DOC: $p$=0.154, $r^2$=0.44, $n$=6; SFS DOM–DOC: $p$=0.346, $r^2$=0.22, $n$=6). In the Souris River, a significant relationship with high correlation was found only in the FLS-AM DOM–SFS DOM pairing ($p$=0.001, $r^2$=0.79, $n$=9). For the other two relationships, Souris River did not have significant relationships, and correlation values were relatively low (FLS-AM DOM–DOC: $p$=0.230, $r^2$=0.20, $n$=9 and SFS DOM–DOC: $p$=0.098, $r^2$=0.34, $n$=9).

The Trout River relationships were all significant and showed the highest positive correlation values for any of

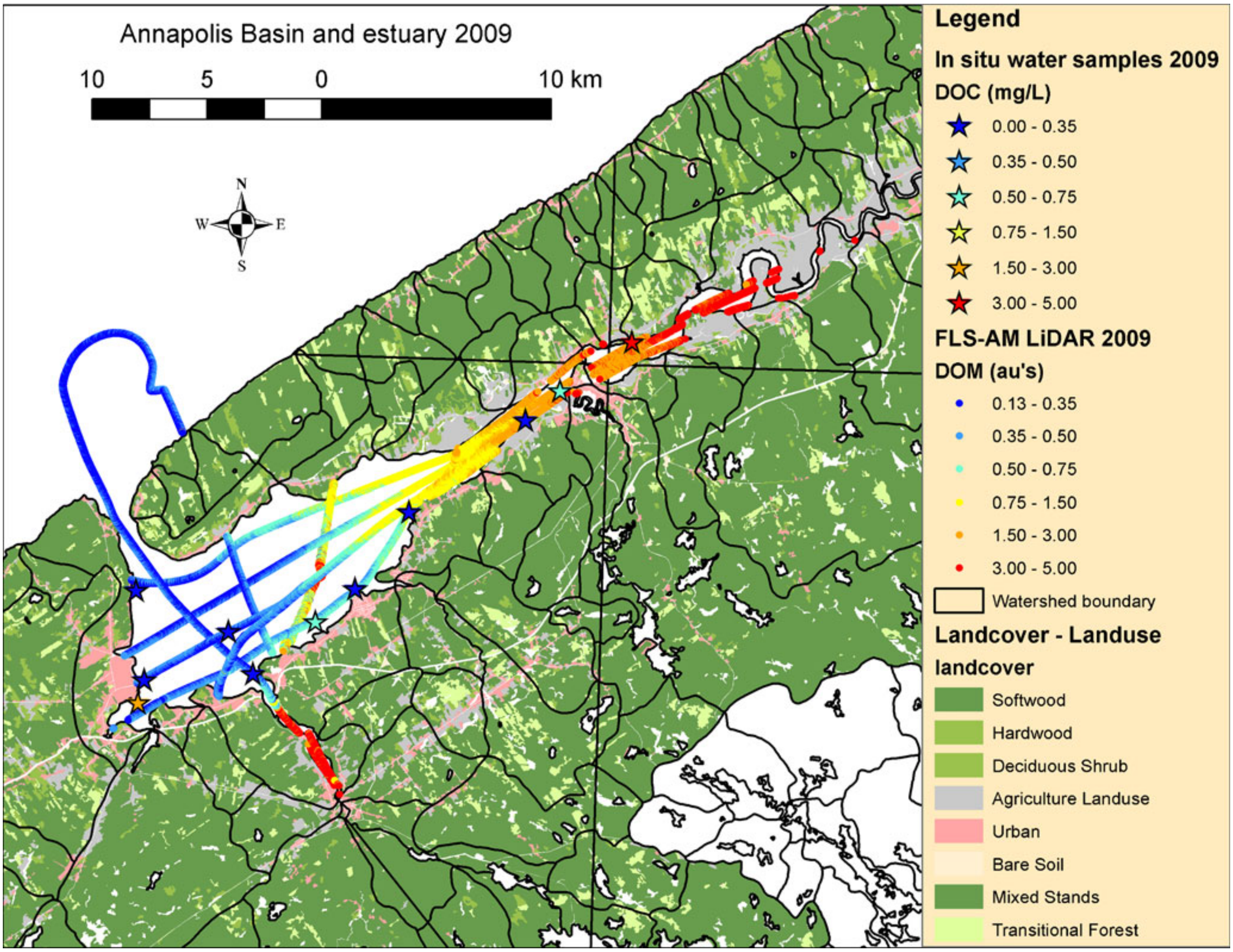

**Fig. 3** The Annapolis River and Basin with FLS-AM 2009 values indicating high DOM values in the narrow upstream part of the river and dilution occurring as the water enters into the estuary and basin. Background is a land use map showing agriculture in *gray* and with watershed delineations depicting the drainage basins for the region

the PEI sites. The strongest relationship existed between FLS-AM DOM and SFS DOM ($p$=<0.001, $r^2$=0.92, $n$=8) while both the FLS-AM DOM–DOC ($p$=0.004, $r^2$=0.78, $n$=8) and the SFS DOM–DOC ($p$=0.003, $r^2$=0.79, $n$=8) relationships were strong and significant as well.

## Discussion

Differences in values and correlations from analyses were found between sample sites for each of the three variables tested (FLS-AM DOM, SFS DOM, and DOC). This was to be expected as all sites had different water quality characteristics. In the Annapolis Valley, the highest concentrations of FLS-AM DOM (2008, 4.52–31.92 units; 2009, 3.59–21.02 units), SFS DOM (2008, 0.87–8.31 mg $L^{-1}$ and 2009, 4.24–8.12 mg $L^{-1}$), and DOC (2008, 5.88–6.85 mg $L^{-1}$; 2009, 5.32–10.93 mg $L^{-1}$) were found in the upstream section of the river due to intensive agricultural practices in that area. A dilution process was detected as water flowed down the Annapolis River and into the Annapolis Basin, where the lowest DOC, FLS-AM DOM, and SFS DOM concentrations were found (Fig. 3). High upstream concentrations of DOM and DOC could be attributed to increased runoff from the surrounding agricultural watersheds that are dominated by agricultural land where farming practices are most common in the Annapolis Valley (Fig. 3). These findings for DOM and DOC are consistent with those of Thurman (1985) and Wetzel (2001). The composition of DOM and DOC in water differs depending on the characteristics of the surrounding watershed. DOM and DOC have higher aromaticities in agricultural watersheds than in mixed or forested watersheds, having effects on the fluorescence properties of the water (Vidon et al. 2008). The results of the FLS-AM DOM statistical analysis with in situ water samples are consistent with the findings of Vidon et al. (2008). The

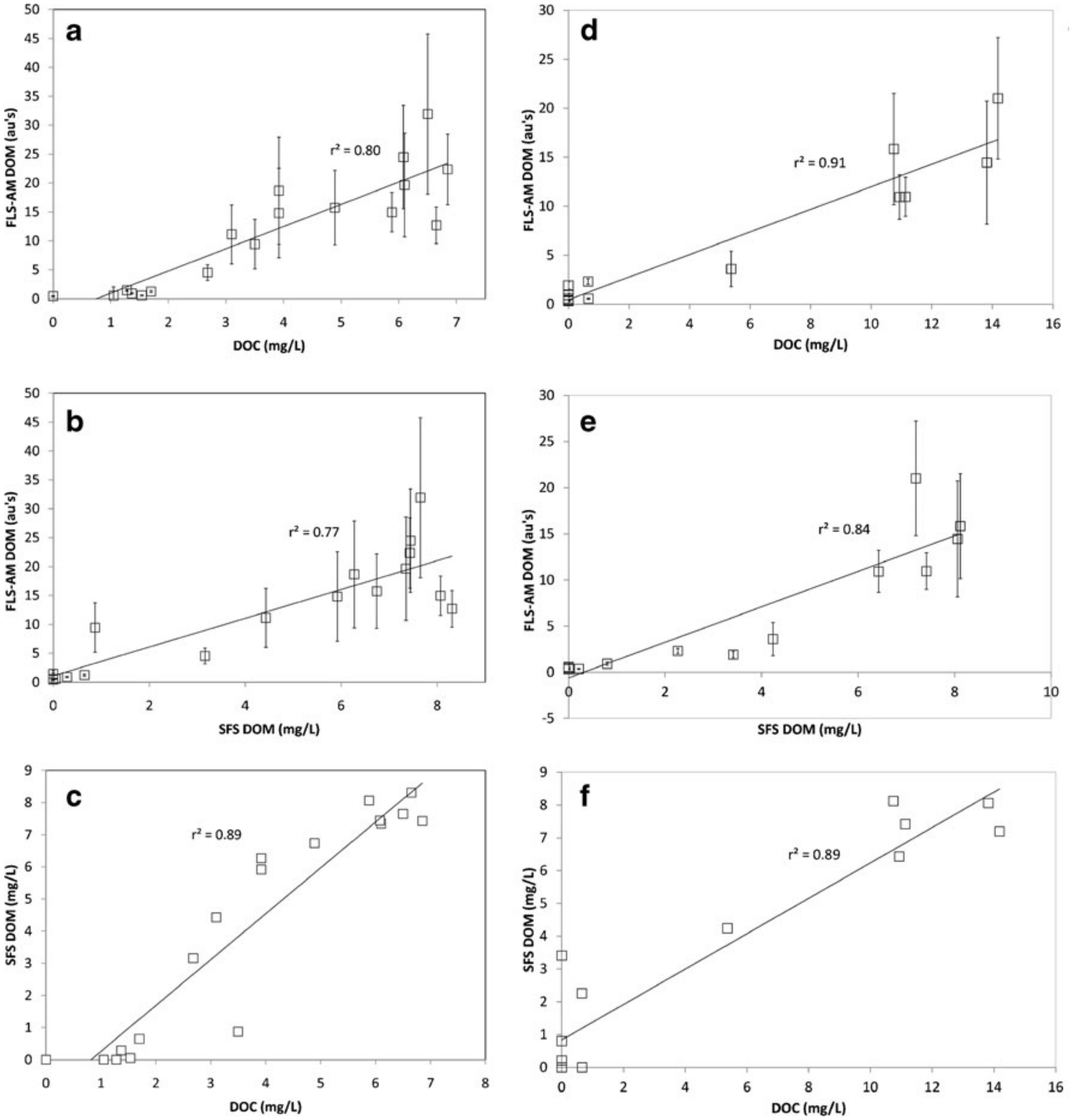

**Fig. 4** Scatterplots for all Annapolis values are shown for 2008: FLS-AM DOM–DOC (**a**), FLS-AM DOM–SFS DOM (**b**), and SFS DOM–DOC (**c**) and 2009: FLS-AM DOM–DOC (**d**), FLS-AM DOM–SFS DOM (**e**), and SFS DOM–DOC (**f**). FLS-DOM is shown in arbitrary units (au's)

dilution pattern was found in all three of the PEI sites as water flowed out of the river and into the estuary (Fig. 2). This is consistent with similar discoveries made by Barbini et al. (1999) in the Venice Lagoon using shipborne LIF LiDAR. The highest DOM concentrations (> 45 mg $L^{-1}$) in the Venice Lagoon were found adjacent to the land and were caused by high levels of anthropogenic runoff. Dilution occurred when the water flowed out of the lagoon into the open ocean decreasing the DOM concentration (10 mg $L^{-1}$). It is likely that the higher DOM values in the upstream portions of the rivers result from increased nutrient inputs from anthropogenic and agricultural activities such as industrial wastes from urban areas. In our study, we also observed a dilution process of the DOM–DOC within the estuaries similar to that of Barbini et al. (1999). Our study is one of the first to demonstrate that an airborne LIF LiDAR (FLS-AM) is capable of detecting variations in DOM within estuaries that are influenced by agricultural land use. These findings have demonstrated the potential application of FLS-AM data to quickly assess and quantify the amount of DOM in estuaries. This type of information is important to resource managers concerned with water quality related to shellfish aquaculture sites where DOM influences the light attenuation through the water which affects the decay of harmful bacteria.

Results from spatial analysis in 2008 showed that FLS-AM DOM means and standard deviations ranged from 0.44±0.06 to 31.92±13.86 (Table 1). The highest FLS-

**Table 2** Statistical analysis results including correlation coefficients along with r² and p values from linear regression analysis are provided in this table

| Location | FLS-AM DOM vs. DOC | | | | FLS-DOM-AM vs. SFS DOM | | | | SFS DOM vs. DOC | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2008 | | 2009 | | 2008 | | 2009 | | 2008 | | 2009 | |
| | $r^2$ | *p* value | $r^2$ | *p* value | $r^2$ | *p* value | $r^2$ | *p* value | $r^2$ | *p* value | $r^2$ | *p* value |
| Annapolis Basin | 0.30 | 0.263 | 0.18 | 0.313 | 0.20 | 0.379 | 0.84 | **0.001** | 0.29 | 0.266 | 0.02 | 0.748 |
| Annapolis River | 0.50 | **0.010** | 0.78 | **0.019** | 0.41 | **0.025** | 0.59 | 0.075 | 0.70 | **<0.001** | 0.69 | **0.041** |
| All Annapolis | 0.80 | **<0.001** | 0.91 | **<0.001** | 0.77 | **<0.001** | 0.84 | **<0.001** | 0.89 | **<0.001** | 0.89 | **<0.001** |
| Dunk River/Estuary | 0.44 | 0.154 | na | na | 0.76 | **0.024** | na | na | 0.22 | 0.346 | na | na |
| Souris River/Estuary | 0.20 | 0.230 | na | na | 0.79 | **0.001** | na | na | 0.34 | 0.098 | na | na |
| Trout River/Estuary | 0.78 | **0.004** | na | na | 0.92 | **<0.001** | na | na | 0.79 | **0.003** | na | na |
| All PEI | 0.06 | 0.250 | na | na | 0.78 | **<0.001** | na | na | 0.13 | 0.094 | na | na |

*p* values presented in bold indicate significant relationships for regression analysis where $p<0.05$ ($\alpha=0.05$)

AM fluorescence means were found in the Annapolis River along with very high standard deviations with site 08-ANN20 having the highest variability (4.52±1.37 to 31.92±13.86). The high mean values in the Annapolis River were uncharacteristic of other water bodies that were analyzed in this study and could be attributed to contamination from outlier points caused by near-shore returns. The high standard deviation indicated that the unfiltered data are relatively inconsistent. The 2009 results for the Annapolis River showed lower FLS-AM DOM mean values and standard deviations ranging from 3.59±1.81 to 21.02±6.21. The increased accuracy of the fluorescence sensor and the lower standard deviation values for 2009 indicate that the high values in 2008 can be attributed to poor georeferencing during the first mission. The inability to properly align the data to the river in 2008 had introduced error due to the use of erroneously sampled pixels from the land or near-shore. The 2009 results suggested that with improved georeferencing, there was better agreement between FLS-AM DOM and DOC for the Annapolis River ($r^2=0.78$ in 2009 and 0.50 in 2008).

The processed FLS-AM data were analyzed to determine how well we could predict DOM and DOC in water bodies as compared to traditional in situ water sampling methods. The results ranged from site to site, but all sites showed positive, although some weak and not significant, correlation values in the 2008 and 2009 surveys. For the FLS-AM DOM–DOC relationship, the Annapolis River (2008, $p=0.010$, $r^2=0.50$, $n=12$; 2009, $p=0.019$, $r^2=0.78$, $n=6$) and Trout River ($p=0.004$, $r^2=0.78$, $n=8$) were the only two sites to have significant relationships with moderate to high positive regression values. In 2008, the remaining three sites did not have significant relationships and had weak to moderate regression values ranging from 0.20 to 0.44. In the Annapolis Basin in 2008, the poor correlations between FLS-AM DOM and DOC were thought to be explained by the temporal differences in sampling as there was a delay, ranging from approximately 6 to 8 h, between when the water samples were collected and when the aircraft collecting FLS-AM data points flew over the water body. The temporal delay was due to poor visibility for the flight and miscommunication between the air and ground crews. However, in 2009 the water sampling was synchronous with the FLS-AM flight, and weak correlations were still observed between FLS-AM DOM and DOC indicating that the time lag did not have a direct result on the 2008 results. Improvements in correlations may be possible through reduction of sample lag-time errors. However, given that the effect of the time difference is already incorporated into the correlation the conclusions are still correct. The weak correlations from both years may indicate that at lower levels of DOM and DOC, the limited precision of FLS-AM may cause lower correlations; however, the general patterns of DOM and DOC can still be sufficiently observed. In PEI, without the temporal difference in sampling during the 2008 survey, the patterns in the statistical analysis suggest that the relationship between FLS-AM DOM and DOC was not strong ($p=0.250$, $r^2=0.06$, $n=23$) and was similar to the results in the Annapolis River and Basin.

The relationship between the two laboratory methods, SFS DOM–DOC, was significant in two of five sites in 2008 and in one of two sites in 2009. Trout River had strong positive correlation ($p=0.003$, $r^2=0.79$, $n=8$) and the Annapolis River in had significant relationships with high correlations in 2008 ($p<0.001$, $r^2=0.70$, $n=12$) and 2009 ($p=0.041$, $r^2=0.69$, $n=6$). The results in 2008 for the FLS-AM DOM–SFS DOM relationship were stronger than the relationships between FLS-AM DOM–DOC and SFS DOM–DOC. Four out of five sites had significant positive correlations between FLS-AM DOM and SFS DOM relationship indicating that the FLS-AM sensor is better at measuring DOM than DOC and can be used as an efficient

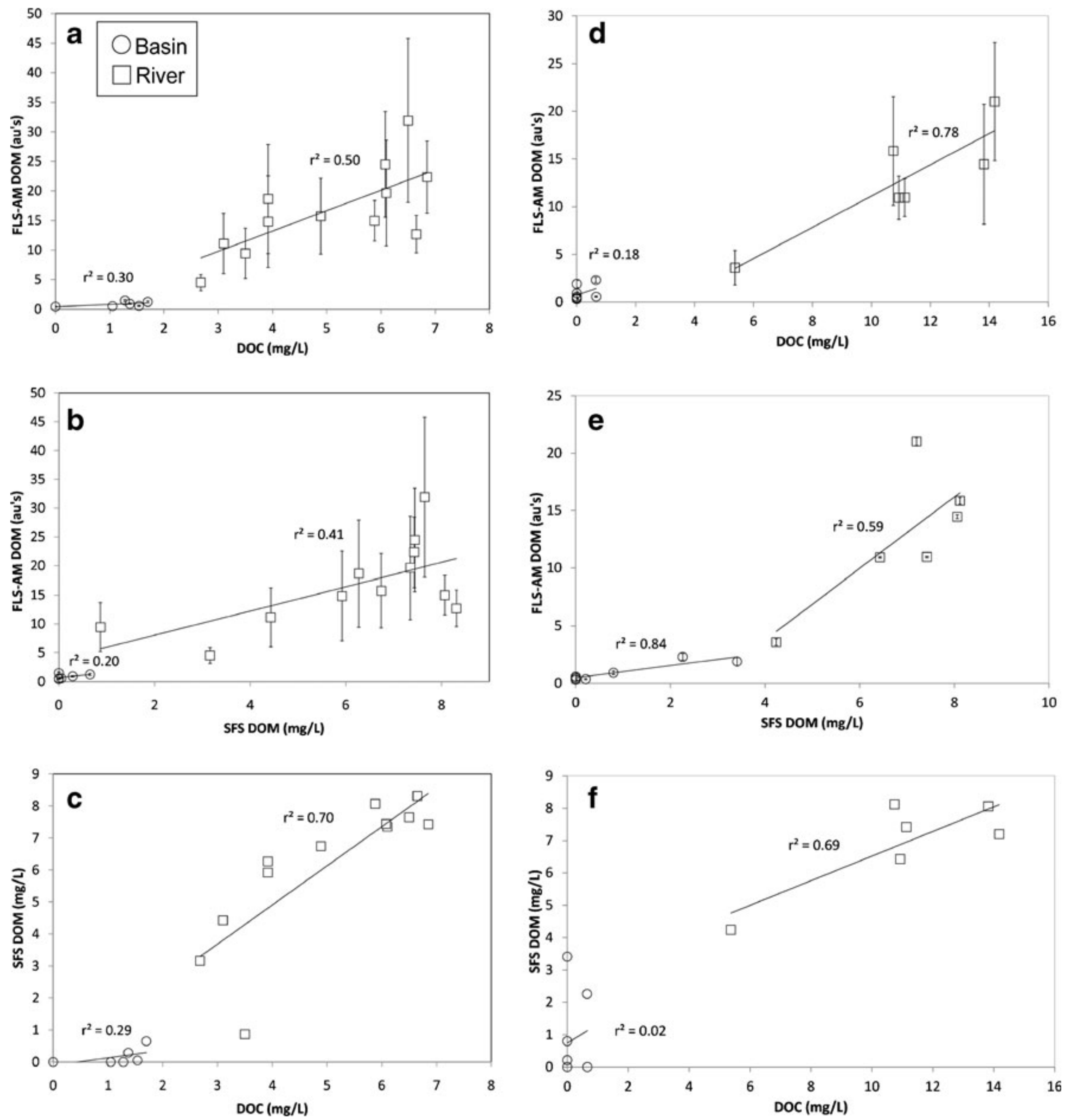

**Fig. 5** Scatterplots for Annapolis River (*square*) and Basin (*circle*) values are shown for 2008: FLS-AM DOM–DOC (**a**), FLS-AM DOM–SFS DOM (**b**), and SFS DOM–DOC (**c**) and 2009: FLS-AM DOM–DOC (**d**), FLS-AM DOM–SFS DOM (**e**), and SFS DOM–DOC (**f**). FLS-DOM is shown in arbitrary units (au's)

surrogate tool for traditional DOM water sampling methods. The Annapolis Basin was the only site that did not show a significant relationship for linear regression ($p$=0.379, $r^2$= 0.20, $n$=6) for FLS-AM–SFS DOM in 2008. In 2009, we found a significant positive correlation between FLS-AM DOM and SFS DOM ($p$=0.041, $r^2$=0.69, $n$=6) in the Annapolis River but a very weak regression in the basin ($p$=0.748, $r^2$=0.02, $n$=8) due to the majority of in situ DOC readings resulting in zeros (six out of eight sites).

In 2008, the Annapolis River had relatively weak regression results ($p$=0.025, $r^2$=0.41, $n$=6) relative to the three significant PEI sites: Souris ($p$=0.001, $r^2$=0.79, $n$=9), Dunk ($p$=0.024, $r^2$=0.76, $n$=6), and Trout ($p$=<0.001, $r^2$=0.92, $n$=8) for the FLS-AM DOM–SFS DOM relationship in those rivers. The low correlation results for the FLS-AM DOM–DOC relationship suggest that the FLS-AM DOM data are limited in its ability to universally predict absolute DOC concentration. Similar results were found in laboratory fluorescence studies (Coble 1996) and shipborne fluorescence studies (Barbini et al. 1999; Babichenko et al. 1999; 2000). Moderate to high positive regression values for four out of five sites in the FLS-AM DOM–SFS DOM analysis in 2008 and for the Annapolis River in 2009 suggest that the FLS-AM LiDAR more accurately represents the

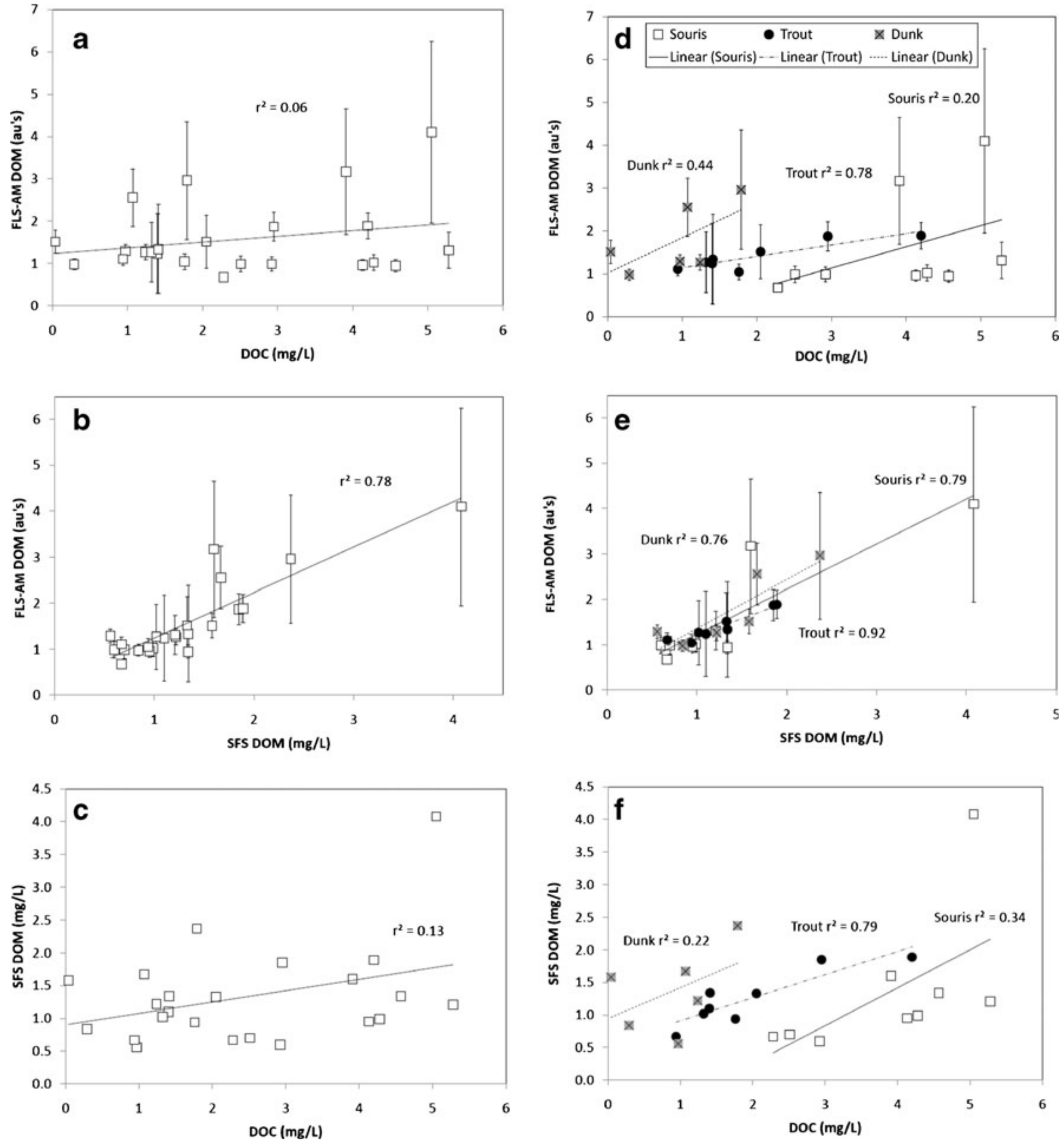

**Fig. 6** Scatterplots for all PEI site values are shown for FLS-AM DOM–DOC (**a**), FLS-AM DOM–SFS DOM (**b**), and SFS DOM–DOC (**c**) and scatterplots for Dunk (*gray square with x*), Souris (*white square), and Trout (black circle) Rivers values are shown for 2009: FLS-AM DOM–DOC (***d***), FLS-AM DOM–SFS DOM (***e***), and SFS DOM–DOC (***f***) FLS-DOM is shown in arbitrary units (au's)*

relationship between fluorescence and DOM levels or concentration. Quantitatively, we have a high degree of variability between FLS-AM DOM values and water sample results. However qualitatively, the FLS-AM DOM shows the spatial pattern of relative amounts of DOM especially in estuaries whose watersheds are influenced by agricultural land use.

From the information provided by Coble (1996), we believe that the low correlation values found between FLS-AM DOM and DOC and the high correlation values found between FLS-AM DOM and SFS DOM in this study indicate that the FLS-AM is a better predictor of DOM composition than it is of DOC concentration. Coble (1996) identified various fluorescence compounds which represented different components of DOM such as anthropogenic and autochthonous sources in complex mixtures of water but were unable to determine exact concentrations of DOM from fluorescence alone. Fluorescence analysis is useful for establishing the composition of DOM in water bodies, but concentrations of DOC cannot be assumed or calculated from this information due to the variability of the relationship between DOM and DOC.

It should be taken into consideration that there are limitations when using any fluorescence method as a water quality analysis tool. For example, not all portions of DOM have fluorescence properties; therefore the non-fluorescing portions are not included in the data analysis process which can be problematic as those portions often contain revealing information about the sample (Jiang et al. 2008). Also, in natural waters, the amount of scattering is dependent on the water characteristics of the sample being studied; thus, the medium scatters most energy in the form of Mie scattering, some energy in the form of Raman scattering, and the rest of the energy is scattered according to the pigments in the water column (Exton et al. 1983). These factors give fluorescence a high unpredictability and make it difficult to compare between different water bodies with different water quality characteristics. LiDAR itself requires a source of energy, a method of transportation, and a great deal of expertise in installation and implementation of the technology which can lead to high costs. LiDAR also requires good weather and a relatively clear day as poor visibility can affect the return signals and alter the data. However, the benefit of an airborne LIF LiDAR is the ability to sample large areas in a short time period to obtain the relative spatial distribution and pattern of DOM. We have demonstrated that this technique is especially useful in highlighting estuaries that drain agricultural watersheds.

### Sources of Error

Due to weather delays and communication issues, there was a discrepancy in the collection times between the DOC water samples and the FLS-AM DOM samples from the aircraft in the Annapolis Basin during the 2008 survey. DOC water samples collected on August 27, 2008 were retrieved at low tide around mid-day between 1000 and 1400 hours (AST). The FLS-AM recorded readings later in the evening from about 1600 to 2000 hours, just after high tide. While tidal effects were not specifically analyzed for in this study, we can assume that tidal effects would include a mass movement of low DOC ocean water into the basin and an opposite flushing of high DOC water from the river upon recession. We are confident in the 2008 results because the majority of data points analyzed fall in the larger basin and the central river channel, there were no precipitation events in that time span initiating runoff from DOC from the surrounding watershed, and because DOC levels in this area do not change drastically on a diurnal basis but more so on a seasonal time scale (Gorham et al. 1998) especially in the upper portion of the estuary where the tidal influence is negligible. The transitional estuary zone accounts for only a small percentage (4.0 %) of the total data analyzed. Therefore the effects of error due to tidal transitions are likely minimized, and any error would be incorporated in the correlations provided. The positive correlations found between FLS-AM DOM and SFS DOM and DOC readings also suggest that the water samples were representative. The similarity in the 2009 results for the Annapolis River and Basin add to our confidence in the 2008 results. Corrections to the 2008 swaths proved to be more effective for the larger bodies of water. For example, in the narrow upstream part of the Annapolis River, we could not be sure that adjustments were done accurately as it was impossible to line up the swath values to the water due to the small area of the river and inaccurate geographic positioning which caused uncertainty. The FLS-AM dataset was filtered to include all points indicating presence of water and may have contained data points acquired from wet substances on the ground, even though these areas may not have been the water bodies intended as targets, which was reflected in the data in the form of higher FLS-AM DOM means and standard deviation values. Without a method for removing contaminated points based on spectral filtering, we were unable to remove all outlier returns. In larger water bodies, such as the Annapolis Basin and PEI Rivers, it was clear as to how the FLS-AM DOM values should match up to the water body based on the characteristic LIF signatures of land and water, so the corrections were relatively straightforward and considered accurate compared to the Annapolis River. With the implemented of the IMU in the 2009 flight mission, the geographic positioning errors were rectified, and increased precision was attained with the FLS-AM DOM data. With the upgrades to the FLS sensor, FLS-AM surveys are appropriate for all water bodies and not just coastal and large estuarine environments but also for narrow meandering rivers, such as that of the Annapolis River.

## Conclusions

The main goal of this study was to test the applicability of the FLS-AM sensor to determine DOM levels in coastal areas of Atlantic Canada, which are affected by intensive agricultural practices, to verify and establish correlations with SFS DOM and DOC laboratory analysis. We hypothesized that FLS-AM DOM values would be significantly ($p<0.05$) and positively linearly correlated to SFS DOM measurements taken from water samples. We found that in 2008, four of five sites had significant relationships with high correlation and linear regression values and 2009 showed strong positive correlations as well, proving that the FLS-AM sensor can be used as a surrogate for traditional laboratory analysis of DOM optical character and analysis of DOM structure in coastal regions in Atlantic Canada. Results from the FLS-AM DOM have also detected higher DOM values in areas adjacent to agricultural land use and a dilution effect of DOM as water flows further into the estuary suggesting the agriculture is affecting the optical properties of the DOM (more aromatic in nature).

The relationship between FLS-AM DOM and DOC FLS-AM DOM–DOC had moderate to low correlation values in all of the study areas (not including the groups "all Annapolis" and "all PEI") for both years with the lowest correlation ($r^2$=0.20) in Souris River in 2008 and lower in the Annapolis Basin in 2009 ($r^2$=0.18). Linear regression values were also low ($r^2$<0.50) for all but Trout River in 2008 ($r^2$=0.78) and the Annapolis River in 2009 ($r^2$=0.78). Positive correlations were found between FLS-AM DOM and DOC for all sites. The relationship was significant at only two of five sites in 2008 and one of two sites in 2009, therefore, with these data, it can be stated that FLS-AM DOM and DOC are positively related, but not with strong significance at all sites, indicating that, as previously proven in laboratory and shipborne fluorescence research, it is difficult to predict DOC concentration from optical DOM measurements.

Considering the objectives of application of the FLS-AM technology in the 2008 and 2009 missions, we have determined that the implementation of the IMU was imperative and has added the element of geographic location precision to the sensor which is necessary for determining correlations with water samples. Even with the limited accuracies of the 2008 mission, the results show similarities to data obtained for 2009 indicating that correction methods in 2008 were beneficial. We found that it was most beneficial to average the FLS-AM data points in this study for a better representation of the overall optical character of DOM. Also, if the FLS-AM is to be used to determine DOC concentrations rather than spectral character, then we suggest the use of another method of in situ DOC measurement, such as water samples like those that were taken in this study, in order to obtain accurate concentrations of DOC to compare to the FLS-AM readings. It has been shown that there are quantitative discrepancies between the FLS-AM data and in situ DOC laboratory samples which could deter further research with the current system, but qualitatively, we have determined that the FLS-AM is a useful and efficient tool for establishing relative DOM and DOC levels in water bodies affected by agricultural practices in Atlantic Canada.

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