EPA Public Access

Author manuscript

Mar Pollut Bull. Author manuscript; available in PMC 2020 June 25.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Mar Pollut Bull. 2017 January 30; 114(2): 995–1006. doi:10.1016/j.marpolbul.2016.11.030.

Characterizing light attenuation within Northwest Florida Estuaries: Implications for RESTORE Act water quality monitoring

Robyn N. Conmy^a, Blake A. Schaeffer^b, Joseph Schubauer-Berigan^a, Jessica Aukamp^c, Allyn Duffy^c, John C. Lehrter^c, Richard M. Greene^c

^aU.S. Environmental Protection Agency, Office of Research and Development NRMRL Land Remediation & Pollution Control Division, 26 W. MLK Drive, Cincinnati, OH 45268, United States

^bU.S. Environmental Protection Agency, Office of Research and Development NERL Exposure Methods and Measurement Division, 109 T.W. Alexander Dr., RTP, NC 27711, United States

^cU.S. Environmental Protection Agency, Office of Research and Development NHEERL Gulf Ecology Division, 1 Sabine, Island, Drive, Gulf Breeze, FL 32561, United States

Abstract

Water Quality (WQ) condition is based on ecosystem stressor indicators (e.g. water clarity) which are biogeochemically important and critical when considering the Deepwater Horizon oil spill restoration efforts under the 2012 RESTORE Act. Nearly all of the proposed RESTORE projects list restoring WC as a goal, but 90% neglect water clarity. Here, dynamics of optical constituents impacting clarity are presented from a 2009–2011 study within Pensacola, Choctawhatchee, St. Andrew and St. Joseph estuaries (targeted RESTORE sites) in Northwest Florida. Phytoplankton were the smallest contribution to total absorption ($a_{t-w}PAR$) at 412 nm (5–11%), whereas colored dissolved organic matter was the largest (61–79%). Estuarine $a_{t-w}PAR$ was significantly related to light attenuation (K_dPAR), where individual contributors to clarity and the influence of climatic events were discerned. Provided are conversion equations demonstrating interoperability of clarity indicators between traditional State-measured WQ measures (e.g. secchi disc), optical constituents, and even satellite remote sensing for obtaining baseline assessments.

Keywords

Deepwater Horizon oil spill; RESTORE Act; Northwest Florida Estuaries; Water quality & clarity; Light attenuation

1. Introduction

Light attenuation, or water clarity, within natural water bodies is central to the health and function of ecosystems. Many biogeochemical processes are predicated on the number of photons and the spectral makeup of light filtering through a water column (Davies-Colley et al., 1993). Water clarity is influenced by light scattering and absorption due to phytoplankton, colored dissolved organic matter (CDOM, or color) and detritus (Kirk, 1994, Mobley, 1994). Measurements typically focus on the inherent optical properties (IOPs):

absorption (a) and scattering (b) coefficients; and apparent optical properties (AOPs), such as the diffuse attenuation coefficient. IOPs are a function of components within the water alone (Kirk, 1994), are additive, linear, and proportional to concentration. The sum of absorption coefficients for a particular wavelength (λ) due to water (a_w), detritus (a_d), CDOM (a_g) and phytoplankton (a_p) equal total absorption (a_t) as shown in Eq. (1).

$$a_t(\lambda) = a_w(\lambda) + a_d(\lambda) + a_g(\lambda) + a_p(\lambda) \quad (1)$$

AOPs, however, are not additive. They depend on constituents within the water in addition to the ambient underwater light field, thus are biased by waves, sun angle, depth and cloud cover (Morel and Smith, 1982). The diffuse attenuation coefficient, $K_d(\lambda)$, describes the loss of light through the water column (Preisendorfer, 1986). IOP and AOP coefficients can be defined at specific wavelengths, or integrated over pertinent ranges, such as PAR (Photosynthetically Active Radiation, 400–700 nm) (Mobley, 1994, Anastasiou, 2009, Durako et al., 2010). Calculating coefficients at certain wavelengths, for example 412 nm, allows for comparing field measurements to satellite-based measures of water quality from ocean color sensors such as NASA's MODerate Resolution Imaging Spectroradiometer (MODIS) and ESA's MEDium Resolution Imaging Spectrometer (MERIS), or planned sensors Ocean and Land Colour Instrument (OLCI) or Visible Infrared Imaging Radiometer Suite (VIIRS).

In some open ocean waters, optically active constituents co-vary with phytoplankton, where phytoplankton are the dominant light-attenuating substances (attenuators) and contribution of remaining attenuators is minimal (Lorenzen, 1972). In coastal waters, however, generalizations regarding attenuators are impeded by the inherent variability and complex physical / biogeochemical nature of these environments (Gallegos, 2005, Kelble et al., 2005, Anastasiou, 2009, Durako et al., 2010, Gallegos et al., 2011, Keith, 2014). In estuaries, the presence of attenuators influences the amount of light available to seagrasses and benthic algae (Kirk, 1994), as well as nutrient and pollutant fate (Aiken et al., 2011). CDOM and detritus are supplied to estuaries via terrestrial runoff and their distribution in some cases can be correlated with river discharge, precipitation, temperature and extreme weather events (Eimers et al., 2008, Osburn et al., 2016). Anthropogenic land alteration and nutrient loading also impact fluxes of attenuators (Bauer et al., 2013, Le et al., 2015). Beyond ecosystem health, water clarity is tied to local economies, where the aesthetics of water bodies influence tourism, recreational fishing and housing prices (CENR, 2003). In Florida, each acre of seagrass has an estimated value of \$22,573, or \$61 billion statewide (FDEP, 2008). Thus, characterizing light-attenuating constituents and their role in water clarity and quality is both ecologically and economically important.

Resource managers utilize light attenuation-relevant indicators (chlorophyll *a*, color, secchi depth, water clarity) to establish and monitor Optical Water Quality (OWQ) targets within Gulf of Mexico (GoM) estuaries (Smith et al., 2006, U.S. EPA (Environmental Protection Agency), 2008, Yarbro and Carlson, 2015). Clarity ratings are based on (1) variations in turbidity levels, (2) expectations for light penetration related to submerged aquatic vegetation (SAV) distribution and (3) waterbody management goals. Though to evaluate

OWQ, IOPs are often not measured, but rather proxy-IOPs (chlorophyll *a*, color, turbidity), which can be correlated with IOP coefficients but do not have an explicit analytical relationship to K_d . Anastasiou (2009) termed these ‘quasi-IOPs’, however, Kirk (2011) used the term to describe diffuse scattering and absorption coefficients. To avoid confusion, chlorophyll *a*, color, turbidity are described here as proxy-IOPs. The use of proxy-IOPs can be problematic as establishing impairment and initiation of management actions require not only documenting changes in light attenuation, but also identifying and quantifying the root causes of light limitation (Anastasiou, 2009, Fitzhugh, 2011, Schaeffer et al., 2012).

Characterizing OWQ metrics is also important for proposed restoration projects stemming from the 2012 RESTORE Act (Resources and Ecosystems Sustainability, Tourist Opportunities, and Revived Economies of the Gulf Coast Act). The 2010 GoM Deepwater Horizon spill (DWH) released an unprecedented amount of oil (Report Oil Budget Calculator, 2010), negatively impacting Gulf State communities, local economies, protected natural resources, fisheries, ecological health and ecosystem services (Sumaila et al., 2010, Carriger and Barron, 2011, Mendelssohn et al., 2012, NOAA Report, 2015). Five years after the spill, the presence of tar balls and mats continue to be a problem along Gulf beaches, particularly after major storm events (Plant et al., 2013, Mulabagal et al., 2013, Hayworth et al., 2015). To provide restitution to the Gulf Coast region, the RESTORE Act was passed, diverting 80% of civil and administrative Clean Water Act (CWA) penalties from the spill to the Gulf Coast for ecological and economic restoration. Gulf Coast Restoration Trust Funds include a Council-Selected Restoration Component to develop and implement the Comprehensive Plan (COMPREHENSIVE PLAN: Restoring the Gulf Coast’s Ecosystem and Economy, 2013). In 2014, States and Federal Agencies proposed projects (publically available) to the Gulf Coast Ecosystem Restoration Council to address five RESTORE goals: restore and conserve habitat, restore water quality, restore and revitalize the Gulf economy, replenish and protect living coastal and marine resources, and enhance community resilience. Nearly all of the proposed projects focus on watershed restoration and list restoring water quality as a goal (www.restorethegulf.gov). Yet, discussion on water clarity, or the influence of phytoplankton pigments, color and detritus as contributors to water quality is absent from 90% of the proposed projects. Water clarity is a critical physical indicator and of great economic (Gibbs et al., 2002, Major and Lusht, 2004) and ecological importance (Kirk, 1994). Thus, it should be a key variable during water quality restoration, particularly for projects that will assess estuarine baseline data for comparative analyses of watershed, loadings and land use alterations. Approaches that correlate inherent, apparent and proxy-optical properties are critical for project success. Such is the case for the RESTORE projects within Florida waters that cite restoring water quality as a primary goal.

The estuarine systems of Northwest Florida: Pensacola, Choctawhatchee, St. Andrew and St. Joseph Bays are targeted within the proposed projects. Reported here are absorption and diffuse attenuation coefficients, and proxy-IOPs of these systems collected during a 3-year study from 2009 to 2011. This paper aims to (1) describe dynamics of optical constituents that impact water clarity in four NW Florida estuaries and (2) make a case for the total absorption coefficient ($a_{t-w}PAR$) as a valuable management parameter that can be quantitatively linked to the concentration of attenuating materials within these systems. This paper does not investigate changes in water quality due to the DWH spill. Rather, it presents

OWQ parameters over space and time that are valuable for RESTORE Act restoration efforts and concurrent Early Restoration Plans (ERP) under DWH Natural Resource Damage Assessment (NRDA) efforts. Results offer a means to translate and utilize data routinely collected by researchers and managers. Such approaches are needed for future monitoring, as these parameters can be supplemented with space-based satellite estimates allowing for long-term high resolution monitoring (Schaeffer et al., 2015) and measured from in situ sensors which are commonly used in oil spill response and restoration (Conmy et al., 2014). Benefits of our work to the RESTORE projects are three-fold – the findings can guide sampling and monitoring designs, serve as baselines for watershed restoration efforts, and provide interoperability between WQ monitoring measurements for resiliency and future hazard preparedness within Florida waters.

2. Methods

2.1. Setting

The northwest Florida coast of the United States comprises the ‘forgotten’ and ‘emerald’ coasts and includes four estuarine systems: Pensacola, Choctawhatchee, St Andrew and St Joseph bays (Fig. 1). The coastal waters in this region were impacted by the 2010 DWH oil spill (NOAA PDARP, 2015) and retain a score of ‘fair condition’ on the Gulf Coast Water Quality Index (U.S. EPA, 2012). Land Development Index scores (Brown and Vivas, 2005) for the watersheds are all low (< 2), indicating less developed land use, in this case dominated by forest and wetlands (Le et al., 2015). Yet, residing counties of these estuaries exhibit population growth rates between 5–33%, which are some of the highest in the state (US Census Bureau, 2000). High rates of development coupled with the regional ‘fair’ water rating emphasizes the need to evaluate light attenuation and potential stressors that could threaten or impact natural attributes of these coastal systems.

Pensacola and Choctawhatchee bays are river-dominated estuaries. Pensacola Bay is a large, lobed river-fed system that is supplied by three main rivers with a mean annual freshwater discharge of $324 \text{ m}^3 \text{ s}^{-1}$ (Bianchi et al., 1999). Choctawhatchee Bay has one main river (3rd largest in the state) that feeds the top of the estuary with mean annual discharge of $204 \text{ m}^3 \text{ s}^{-1}$ (Kenner et al., 1971). These systems also possess large watershed areas, $18,125 \text{ km}^2$ and $13,835 \text{ km}^2$ for Pensacola and Choctawhatchee Bays, respectively. River discharge of these systems exhibits large interannual variability, with maximum discharge occurring in winter / spring months. Conversely, fresh water delivery to St Andrew and St Joseph bays is substantially lower. St Andrew Bay is supplied by a series of small creeks that drain to Deer Point Lake Reservoir before discharging to the estuary via dam. The base flow for these creeks is high because they are sourced from spring networks of the Floridan Aquifer. Ecofina Creek for example has a base flow of $16 \text{ m}^3 \text{ s}^{-1}$ (Brown, 2009). Conversely, St. Joseph Bay is supplied by a small canal and limited freshwater makes this system a coastal lagoon.

2.2. In situ / electronic sampling

Water samples and in situ measurements were collected during boat-based surveys between September 2009 and November 2011 (Fig. 1). Hydrographic profiling measurements were

collected using a Seabird CTD package. NW Florida estuaries are shallow with abrupt vertical gradients, hence the CTD was deployed sideways and lowered at a rate of $\sim 10 \text{ cm s}^{-1}$. The CTD profiling package provided for measures of water column temperature, salinity, density, dissolved oxygen, depth, turbidity, light attenuation, and chlorophyll and CDOM fluorescence (Sea-Bird WetLabs, Inc. sensors). Data processing followed manufacturer recommended procedures. Secchi depth measurements were also collected and reported in units of inverse meters.

A free-falling hyperspectral profiling system (HyperPRO, Satlantic, Halifax, NS, Canada) provided in-water hyperspectral (400–735 nm, interpolated every 1 nm) measures of downwelling irradiance [$E_d(z, \lambda)$], upwelling radiance [$L_u(z, \lambda)$], and depth (z). The instrument was allowed to drift approximately 5 to 10 m away from the boat to avoid shading interference, and three profiles were conducted at each sampling. Pressure tare was completed on deck prior to each instrument deployment. Procedures for HyperPRO profiling are based on methods detailed in National Aeronautics and Space Administration Ocean Optics Protocols for Satellite Ocean Color Sensor Validation (Mueller, 2000). HyperPRO data were quality controlled by excluding data with a tilt and roll $> 5^\circ$. Data from the profile was used to calculate [$K_d\text{PAR}$] from a linear regression of $\ln[E_d(z, \text{PAR})/E_d(0, \text{PAR})]$ and depth. $K_d\text{PAR}$ characterizes the averaged (over a water column) vertical decrease in natural light in the PAR. For these calculations irradiance values were plotted against depth (for the 0.1–3 m layer) and $K_d\text{PAR}$ was found as the exponent of the least-squares regression line through these points (Paavel et al., 2011).

2.3. Discrete sampling

Water samples were collected 0.5 m below the air-water surface (hereafter referred to as surface) for absorption (phytoplankton pigment, detritus, CDOM) and extracted chlorophyll analyses. Water was kept on ice and in the dark and then processed upon return to the laboratory within six hours of collection. To avoid contamination during sample processing, all samples were handled using polypropylene gloves.

2.4. Spectroscopic analyses

Water samples were filtered through Whatman 47 mm GF/F filters (nominal pore size = 0.7 μm) into combusted glass flasks for CDOM analysis. CDOM absorption was measured in a 10 cm cuvette using a Shimadzu UV1700 dual-beam spectrophotometer at 1 nm intervals between 200–700 nm with Milli-Q deionized water as a reference. Spectra were normalized by subtracting from each wavelength the absorption value at 700 nm CDOM absorption coefficient $a_g(\lambda)$ and spectral slopes (S) were calculated (Pegau et al., 2003). Total particulates were collected on Whatman 25 mm GF/F filters and analyzed with a Shimadzu UV1700 dual-beam spectrophotometer at 1 nm intervals between 400–800 nm with 0.2 μm filtered seawater as the reference standard (Pegau et al., 2003). Pigments were extracted from filters with warm methanol and rescanned to measure the detritus absorption (Kishino et al., 1985). Phytoplankton absorption coefficients $a_p(\lambda)$ were calculated as the difference between total particulate absorption and detritus absorption $a_d(\lambda)$. Spectra were corrected for baseline noise by subtracting each wavelength from the mean measured value between

790–800 nm (Pegau et al., 2003). Absorption coefficients were integrated over PAR range from 400 to 700 nm.

2.5. Extracted chlorophyll

Water samples for chlorophyll *a* were filtered onto a 25 mm Whatman GF/F filter (nominal pore size 0.7 μm), with water volume recorded. Filters were immediately frozen at $-20\text{ }^{\circ}\text{C}$ or colder in a 50 ml polypropylene centrifuge tube and kept in the dark in preparation for spectrophotometric analysis. Frozen GF/F filters were sonicated in 10 ml of 0.5 M ammonium acetate buffered methanol and then allowed to extract for 30 min in a dark refrigerator, followed by analysis with a Turner Designs (TD700) fluorometer. Associated pigment interferences from chlorophyll *b* and phaeopigments were minimized using a 436 nm excitation filter, 680 nm emission filter, and two neutral density reference filters with a blue lamp (Welschmeyer, 1994).

3. Results

3.1. IOPs

Of the systems sampled, Pensacola and Choctawhatchee Bays receive larger contributions of freshwater via river discharge. The discharge regimes for the Escambia (Pensacola Bay) and Choctawhatchee Rivers during this study are illustrated in Fig. 2. Salinity ranged between 0 and 35.14 for Pensacola, Choctawhatchee and St. Andrew estuaries, with a narrower range of 21 and 34.25 for St. Joseph Bay. CDOM and detritus absorption coefficients at 412 nm (a_{g412} and a_{d412}) were inversely proportional to salinity (Fig. 3; Supplemental Table S1), with majority of a_{g412} values ranging between $0.1\text{--}12\text{ m}^{-1}$ for river-fed estuaries. Median, minimum and maximum values separated by salinity zones are presented in Table 1. Values above 14 m^{-1} were observed for near zero salinity waters, with the largest in Choctawhatchee Bay (17.2 m^{-1} ; Station 10) in May 2010. St. Joseph Bay exhibited lower a_{g412} values of $0.1\text{--}3.9\text{ m}^{-1}$. In all systems, the relative contribution of detritus was smaller compared to that of CDOM, where a_{d412} ranged between $0.02\text{--}6.9\text{ m}^{-1}$, with largest values in Pensacola and Choctawhatchee Bays. Absorption due to phytoplankton pigments (a_{p412}) was the least dominant contributor to total absorption in all systems as evidenced by ternary diagrams (Fig. 4; Table 2) with the largest contribution by phytoplankton observed in St. Joseph Bay (median % $a_{p412} = 11\%$). Conversely, CDOM was the largest contributor to total absorption in all estuaries (median % a_{g412} between 61–79%).

A strong linear fit exists between a_{g412} , a_{d412} and a_{p412} and the absorption coefficients integrated over PAR wavelengths ($a_{x\text{PAR}}$; where *x* represents any of the attenuator subscripts) as indicated by Fig. 5. Regression slopes are not 1:1. The lowest correlation of determination was observed for a_{p412} due to low phytoplankton concentrations, some near the limit of detection, in these systems. In general, absorption coefficients, whether measured at one wavelength or integrated, can be estimated from one another with high confidence as indicated by the r^2 values.

NW Florida estuaries exhibit variability not only in the magnitude of the absorption coefficients, but also in spectral quality of the colored dissolved organic matter, as evident

from the spectral slope ($S_{280-312\text{ nm}}$ and $S_{350-412\text{ nm}}$) values (Fig. 6). Higher a_{g412} values correspond to lower $S_{280-312\text{ nm}}$ (Fig. 6 inset), with slopes ranging between 0.0118–0.0287 m^{-1} . Stations in the eastern lobe (East Bay) of St. Andrew Bay with the highest a_{g412} values, however, did not exhibit the lowest slopes. The a_{g412} and spectral slope relationship at longer wavelengths, $S_{350-412\text{ nm}}$ is more variable, where at times lower slopes were observed for some St. Joseph and St. Andrew Bay stations with low a_{g412} values.

3.2. Proxy-IOPs

The relationships between proxy-IOPs to absorption coefficients are shown in Fig. 7. Turbidity and FDOM (CDOM measurement collected via in situ fluorometry) were correlated to a_{d412} and a_{g412} , with correlation coefficients of $r^2 = 0.527$ and 0.669 , respectively. A weak correlation between extracted chlorophyll a and $a_{\phi412}$ was observed ($r^2 = 0.212$) for these systems with low pigment concentration that ranged within one order of magnitude.

3.3. Light attenuation and $a_{t-w}\text{PAR}$

The PAR-integrated diffuse attenuation coefficient, $K_d\text{PAR}$, is inversely related to secchi depth, Z_{SD} (Fig. 8). Secchi depth ranged between 0.4 and 8 m^{-1} , with deepest values observed in St. Andrew Bay in January 2010, near the mouth of the bay. $K_d\text{PAR}$ ranged between 0.08 and 0.98 m^{-1} , with the largest variability observed in waters with decreased transparency, or shallower Z_{SD} . The PAR-integrated total absorption coefficient, $a_{t-w}\text{PAR}$, is positively correlated to $K_d\text{PAR}$ for all estuaries (Fig. 9). Variability exists in the relationship due the wide range in values amongst the estuaries, with lowest values observed in St. Andrew and St. Joseph Bays.

3.4. Optical properties by station

Median $K_d\text{PAR}$, $a_{t-w}\text{PAR}$, salinity, spectral slope and absorption coefficient values are plotted by estuary station (Fig. 10, Fig. 11, Fig. 12, Table S1). In general, $K_d\text{PAR}$ and $a_{t-w}\text{PAR}$ follow similar patterns. Absorption coefficients are represented by shaded gray areas where $a_{\phi412}$, a_{d412} and a_{g412} are shown from lightest to darkest. The river-fed Pensacola and Choctawhatchee Bay data are separated between low flow and high flow (January–June 2010, El Niño event) regimes to illustrate the influence of discharge on the OWQ within these systems. High flow conditions were coincident with elevated AOP and IOP values and decreased salinity. Higher relative contribution of detrital particles (a_{d412}) and lower spectral slopes were also observed due to contribution of riverine materials. Systems with multiple drainage watersheds (Pensacola and St. Andrew Bays) exhibit OWQ values unique to segments within the estuary. Optical properties were less variable for St. Joseph Bay stations with the exception of Station 8 near a canal.

4. Discussion

4.1. IOPs

Pensacola and Choctawhatchee (river-fed), and St. Andrew (dam / groundwater-fed) estuaries exhibit a wide range in salinity compared to St. Joseph Bay which receives the lowest freshwater discharge (Fig. 3; Table S1). These systems drain watersheds with LULC

(land use land cover) dominated by evergreen forest and wetlands (47–60%; Le et al., 2015). The relationship of a_{g412} and a_{d412} with salinity is driven largely by freshwater input for the river-fed systems, and correlated with river discharge. This is also apparent in the OWQ distribution by estuary station (Fig. 10, Fig. 11) for high flow versus base flow conditions. For example, the largest a_{g412} value observed was 17.2 m^{-1} (not shown in Fig. 2) in Choctawhatchee Bay (Station 10) in May 2010 occurring after record river discharge during January–May 2010 (Fig. 2) associated with an El Niño event. The State of Florida reports that increased CDOM and turbidity resulting from heavy rainfall contributed to seagrass losses in the eastern portion of the bay, which has already experienced a baywide 55% acreage reduction since 1992 (Yarbro and Carlson, 2015). Fig. 3, Fig. 10, Fig. 11 illustrate that a_{g412} and a_{d412} values for river-fed systems during this season were elevated compared to the following season (2011 drought year). State-collected color, turbidity and $K_d\text{PAR}$ values suggest a two to four-fold increase within Choctawhatchee Bay between 2009 and 2011, consistent with our values (Yarbro and Carlson, 2015). Pensacola Bay has also suffered from historic declines in seagrasses, but has recently experienced (2003 – 2010) a 51% increase in acreage attributed to improved water clarity, despite exposure to DWH weathered crude oil residues beginning in June 2010 (Harvey et al., 2015). Pensacola Bay segments exhibit unique OWQ due to drainage of multiple watersheds within the estuary. The western bay section drains the Escambia River and is closest to urban areas, and exhibits the highest contribution of particles (a_{d412}) particularly after high discharge (Fig. 10). Conversely, the Blackwater and Yellow rivers deliver to the eastern section (East Bay) a higher contribution and more labile CDOM (supported by spectral slope values) from drainage of forested areas.

Elevated a_{g412} and a_{d412} were observed for some high salinity waters, such as Choctawhatchee Bay samples from July and September 2011 during a period of drought. Previous studies have demonstrated a reversal of the CDOM - salinity relationship at high salinities, attributed to concentration of material due to evaporation, new production of marine CDOM (Conmy et al., 2010, Milbrandt et al., 2010), or wind driven resuspension events (Boss et al., 2001). Although difficult to discern the specific source, new production and/or wind resuspension may have been the case here, as river discharge was the lowest recorded during this study (587–1393 cfs), warm summer conditions prevailed, and stations are located mid-estuary in shallow water with productive sediments (Stations 7, 8, 9). State-collected OWQ data show elevated total suspended solids for this portion of the bay during 2011 (Yarbro and Carlson, 2015).

Given the ecological significance of light penetration, it could be stated that the requirements governing Florida WQ standards transparency criteria (water clarity) are PAR-centric. Characterizing absorption coefficients, not only at specific wavelengths, but also integrated over PAR wavelengths is key to demonstrating the relevance of IOP measurements to existing criteria. A strong positive correlation exists between a_g , a_d , a_ϕ for $\lambda = 412 \text{ nm}$ and integrated over PAR wavelengths ($a_{x\text{PAR}}$) (Fig. 7). Lowest coefficient of determination was observed for a_ϕ due to minimum dynamic range and very low concentrations, some near the limits of detection. In general, absorption coefficients, whether measured at one wavelength or integrated, can be estimated from one another. Thus

either is sufficient when attempting to correlate IOPs to OWQ parameters, such as chlorophyll *a*, color, secchi depth and water clarity.

4.2. Relative contribution of IOPs

Regardless of seasonality and climatic events, CDOM is typically the largest contributor to light attenuation at 412 nm with median values ranging between 61–78% (Fig. 6, Fig. 10, Fig. 11, Fig. 12). The relative contribution of detritus is typically smaller (16–29%), with lowest median a_{412} values observed in St. Andrew Bay. The contribution by phytoplankton was low in all systems ($a_{412} = 5\text{--}11\%$), but was greatest in St. Joseph Bay during the 2011 drought period. This is consistent with the State monitoring, where St. Joseph Bay has experienced improved OWQ and stable seagrass coverage in recent years (Yarbro and Carlson, 2015). This system has minimal freshwater contribution and less variability in salinity and attenuators (Fig. 12). In contrast, St. Andrew Bay has experienced, substantial seagrass declines (65–75%) in the middle and western portions of the bay from 2009 to 2011, coincident with poor OWQ water clarity values, despite efforts to improve water quality. Suspected causes are severe land development pressure, large precipitation / runoff events, increased nutrients and wastewater treatment discharges (Yarbro and Carlson, 2015). Our data suggest that elevated absorption coefficient values during 2010 El Niño may also have contributed to reduced water clarity for this system. The relative contribution of attenuators within coastal systems can be influenced by alterations to watershed (Bauer et al., 2013, Le et al., 2015) and climatic events (Eimers et al., 2008). Although resuspension or rain events can increase the contribution of detritus to light attenuation in these systems, typically the contribution of CDOM remains predominant in these estuaries. In systems where dissolved materials are the dominant attenuator and scattering by particles is minimal, absorption coefficients are substantially larger than scattering coefficients. To that end, absorption coefficients and not scattering coefficients were the focus of our study. However, in situations where scattering by phytoplankton or non-algal particles could be a significant fraction of light attenuation, monitoring of scattering coefficients is essential (Kelble et al., 2005, Anastasiou, 2009).

4.3. CDOM quantity and quality

Higher a_{412} values correspond to lower $S_{280-312\text{nm}}$ (Fig. 6 inset) and represent riverine sources of CDOM with high lignin content (Helms et al., 2008, Fichot and Benner, 2012). As material moves through estuaries, CDOM concentration decreases and spectral slope increases due to photochemical transformations and aging (Vodacek et al., 1997), where greater loss of chromophores at longer wavelengths occurs relative to shorter wavelengths. Alterations to watershed and climatic shifts can influence not only the amount of DOM entering a system, but the chemistry as well (Stedmon et al., 2006, Spencer et al., 2013, Le et al., 2015). In St. Andrew Bay, highest a_{412} was not coincident with lowest $S_{280-312\text{nm}}$ for stations in the central bay or eastern lobe (East Bay) which drains a smaller, less forested watershed compared to Choctawhatchee and Pensacola Bays. Lower slopes suggest material with lower lability existed in the eastern portion of St. Andrew Bay. Lowest $S_{350-412\text{nm}}$ ($0.008\text{--}0.014\text{ m}^{-1}$) was observed in St. Andrew and St. Joseph Bay. These stations also exhibited low a_{412} indicating an alternate, less refractory source of CDOM, independent from the aged riverine material. Previous studies have reported on seagrass-derived

(Stabenau et al., 2004) or phytoplankton-derived CDOM production (Rochelle-Newall and Fisher, 2002) which were discerned by lower slopes. Our data implies that a source other than aged terrigenous material was present, likely seagrass beds or productive sediments. This is further supported by the fact that East Bay is the only section of this system that has experienced constant seagrass beds for the past five decades (Yarbro and Carlson, 2015).

4.4. Proxy-IOPs

Absorption coefficients a_{412} and a_g were significantly correlated to turbidity and FDOM (proxy-IOPs; Fig. 7). Such strong correlations have been demonstrated in other systems, where a_g can serve a good indicator of color with high degree of accuracy (Gallegos, 2005). A weaker correlation between extracted chlorophyll and a_{412} was observed, in part due to low pigment concentrations and small dynamic range in these estuaries but also because the peak absorption wavelength of the pigment is not at 412 nm. For systems with higher concentrations a stronger correlation would be expected (Gallegos, 2005, Le et al., 2015). These data demonstrate the interoperability value in collecting these parameters in RESTORE monitoring plans, as state and local monitoring programs include proxy-IOPs and in limited cases absorption coefficients. FDOM, turbidity and chlorophyll fluorescence can be measured in situ via moored stations, thereby improving the temporal resolution of data. Furthermore, these parameters are used to validate WQC estimates from space-based satellites, improving on the spatio-temporal coverage. This will serve to strengthen the RESTORE Comprehensive Plans and enable managers to discern the causes of water impairment and shifts in OWQ metrics.

4.5. Light attenuation and $a_{t-w}PAR$

Secchi depth, Z_{SD} , is routinely used as a water clarity indicator (Preisendorfer, 1986). However, measurements are influenced by observer subjectivity, disc variability and above-water light conditions (Davies-Colley and Smith, 2001). Our data suggest that K_dPAR is inversely proportional Z_{SD} , in agreement with Lee et al., 2015 and the well-cited references therein. When examining the relationship between Z_{SD} and K_dPAR , greatest K_dPAR variability exists for a given Z_{SD} value in optically shallow waters (less transparent). For example, $Z_{SD} = 2$ m, equates to a K_dPAR range 0.13–0.46 m^{-1} , or a 63% difference in these systems. Variability in the Z_{SD} to K_dPAR relationship occurs in waters with high absorption or scattering, consistent with previous findings (Kirk, 1994 and references therein), thus illustrating the limitations and/or complications of Z_{SD} as a quantitative index. Beyond this, the use of secchi disc measurements is also limited in shallow, yet clear waters where the disc is still visible over the entire water column (sediments visible by observer) so a Z_{SD} value cannot be determined.

Estuarine values of $a_{t-w}PAR$ were positively correlated to K_dPAR (Fig. 9), where variability exists in the relationship most likely due to differences in the parameter definitions. Ship shadow, sun angle, and clouds can bias K_dPAR values, but not $a_{t-w}PAR$, an IOP. Additionally contributing to variability, K_dPAR is a function of materials that both absorb and scatter light (phytoplankton and detritus). Whereas $a_{t-w}PAR$ is a function of absorbers alone, like CDOM, that contributes negligibly to scattering (Mobley, 1994). River-fed and dam / groundwater-fed estuaries exhibited highest $a_{t-w}PAR$ and K_dPAR . Systems with less

freshwater input exhibited higher a_{t-w} PAR relative to K_d PAR compared to the river-fed systems, most likely due to the presence of fewer river-derived particulates (less scattering). A larger percentage of seagrass beds in St. Joseph Bay may also diminish bottom resuspension events, reducing the influx of sediment to the water column (Gacia and Duarte, 2001). Fig. 9 highlights that a_{t-w} PAR may be a good predictor of light attenuation in these systems, allowing for discerning the root cause of changes (Fig. 4). Although there have been a handful of studies presenting numerous approaches on sophisticated mechanistic models to characterize absorbers and scatters (IOPS and proxy-IOPS) to derive robust light attenuation values, these efforts have been for systems with consistent and substantial particulate contributions (Gallegos, 2005, Kelble et al., 2005, Durako et al., 2010). Light attenuation within the NW Florida estuaries, however, is so heavily dominated by CDOM (absorber), with the exception of large discharge events, that simply relying on absorption coefficients, and not scattering, may suffice in estimating light attenuation in these systems. For cases where scattering is small relative to absorption, K_d should be related to the absorption coefficient divided by the average cosine of the radiance field (Berwald et al., 1995). Thus, accounting for variations in the sun angle and surface water conditions may improve this relationship.

4.6. Relevance to RESTORE projects

The proposed RESTORE projects that target Pensacola, Choctawhatchee, St. Andrew and St. Joseph Bays offer a unique opportunity to better assess OWQ in order to verify achievement of project goals. Efforts in these systems aim to update water management plans, restore coastal habitats, improve wastewater treatments and initiate urban stormwater retrofit projects. Pensacola Bay watershed restoration includes the installation of oyster reefs and breakwaters within Blackwater Bay, East Bay (Stations 10–14), and behind White Island (Bayou Grande and Davenport Bayou; near Station 8); the creation of 25 acres of emergent marsh and seagrasses behind the White Island breakwater; wastewater diversions to reduce nutrient loadings and other pollutants; and stormwater reduction and dredging of contaminated sediments within Bayou Chico (near Station 7). Our findings suggest that a_{t-w} PAR, along with component coefficients (a_g , a_ϕ and a_d) can provide an index for discerning sources of OWQ impairment and the impact of climatic patterns on OWQ. Our work provides valuable baseline data, supplementing those of State entities to better characterize the optical constituents impacting water clarity within these systems. Further, it demonstrates the application of IOPS for water quality monitoring. This work is relevant to RESTORE as planned stormwater diversions, dredging and reef construction will impact localized light attenuation, possibly negatively in the short term during development and positively in the long term via reduced resuspension events and pollutant loading. Additionally, establishing natural variability in OWQ can also help determine risks for planned seagrass plantings. These findings can help establish natural variability in OWQ, teasing out the effect of climate as compared to the impact of any management actions. OWQ can help evaluate expected outcomes from the planned RESTORE and NRDA ERP activities and demonstrate achievement of long and short-term water quality goals. The dynamic nature of estuaries requires assessment over finer spatial and temporal resolution, which can be achieved by combining discrete bottle samples, in situ moored observations and satellite estimates of OWQ parameters presented here. Such a multi-pronged approach is

essential for discerning influences of natural hazards, climatic shifts and other environmental hazards such as oil spills, thereby enhancing resiliency through adaptive management plans. Relationships defined in this report allow for the interoperability of measures from the recommended multi-pronged approach within these estuarine systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

The authors would like to thank NASA Applied Sciences Program for financial support of this work. The information in this document has been partially funded by the U.S. Environmental Protection Agency Office of Research and Development. It has been subjected to quality assurance and peer review by the National Risk Management Research Laboratory (NRMRL) and approved for publication. Approval does not signify that the contents reflect the views of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. This a contribution of the EPA NRMRL Land Remediation and Pollution Control Division and the National Health and Environmental Effects (NHEERL) Gulf Ecology Division. Additional thanks to EPA staff Dianne Yates for data management, George Craven for boat operation, James Hagy for sensor processing and Michael Murrell for field logistics. For more details on the RESTORE Act and the Council go to www.restorethegulf.gov.

References

- Aiken GR, Hsu-Kim H, Ryan JN (2011) Influence of dissolved organic matter on the environmental fate of metals, nanoparticles and colloids. *Environ. Sci. Technol*, 45, 3196–3201. [PubMed: 21405118]
- Anastasiou CJ (2009) Characterization of the underwater light environment and its relevance to seagrass recovery and sustainability in Tampa Bay, Florida. Ph.D. Dissertation, University of South Florida, Tampa, 132 pp.
- Anonymous (1959) Venice system for the classification of marine waters according to salinity. *Limnol. Oceanogr*, 3, 346–347.
- Bauer JE, Cai WJ, Raymond PA, Bianchi TS, Hopkinson CS, Regnier PAG (2013) The changing carbon cycle of the coastal ocean. *Nature*, 504, 61–70. [PubMed: 24305149]
- Bianchi TS, Pennock JR, Twilley RR (1999) *Biogeochemistry of Gulf of Mexico Estuaries*. John Wiley and Sons, New York. 428 pp.
- Boss E, Pegau WS, Zanaveld JRV, Barnard AH (2001), The spectral particulate attenuation and particle size distribution in the bottom boundary layer of a continental shelf, *J. Geophys. Res*, 106, 9509–9516, doi:10.1029/2000JC900077.
- Brown MT, Vivas B. (2005) Landscape Development Index. *Environ. Monit. Assess*, 101, 289–309. [PubMed: 15736887]
- Brown P. (2009) Saint Andrew Bay Watershed: A look into one of Florida's most diverse watersheds. Thesis, Environmental Science Department, University of Florida, Gainesville, FL, 81 pp.
- Carriger JF, Barron MG (2011) Minimizing Risks from Spilled Oil to Ecosystem Services Using Influence Diagrams: The Deepwater Horizon Spill Response. *Environ. Sci. Technol*, 45, 7631–7639. [PubMed: 21875054]
- COMPREHENSIVE PLAN: Restoring the Gulf Coast's Ecosystem and Economy (2013) Draft submitted by Gulf Coast Ecosystem Restoration Council, 20 pp.
- Conmy RN, Coble PG, Cannizzaro JP and Heil CA (2010) Influence of extreme storm events on West Florida Shelf CDOM distributions. *J. Geophys. Res. – Biogeosci.* doi:10.1029/2009JG000981.
- Conmy RN, Coble PG, Parsons R, Walsh I, Koch C, Miles MS, Abercrombie M, Farr J, Wood AM, Lee K, Pegau S, Kelble C. (2014) Performance of submersible fluorometers exposed to chemically-dispersed crude oil: wave tank simulations for improved oil spill monitoring and

evaluation of Deepwater Horizon spill measurements. *Environ. Sci. Technol.* 48, 3: 1803–10. [PubMed: 24377909]

- Davies-Colley RJ, Smith DG (2001) Turbidity, Suspended Sediment, and Water Clarity: A Review. *J. American Water Resources Assoc.* 37, 1085–1101.
- Durako MJ, Kowalczyk P, Mallin MA, Cooper WJ, Souza JJ, Wells DH (2010) Interannual variation in photosynthetically significant optical properties and water quality in a coastal blackwater river plume. *Est. Coasts*, doi: 10.1007/s12237-010-9302-5.
- U.S. EPA, 2012 U.S. EPA National Coastal Condition Report IV, Washington, D.C., EPA/842-R-10-003, 334 pp.
- Eimers MC, Buttle J, Watmough SA (2008) Influence of seasonal changes in runoff and extreme events on dissolved organic carbon trends in wetland and upland draining systems. *Can. J. Fish. Aqu. Sci.* 65, 796–808.
- FDEP (2008) St. Joseph Bay Aquatic Preserve Management Plan: 2008–2018. Tallahassee, FL, Department of Environmental Protection, 176 pp.
- Fichot CG, Benner R. (2012) The spectral slope coefficient of CDOM (S_{275–295}) as a tracer of terrigenous DOC in river-influenced ocean margins. *Limnol. Oceanogr.* 57(5), 1453–1466.
- Fitzhugh LM (2011) Using Changes in Biomass and Productivity to Discern Anthropogenic Impacts in Aquatic Systems. Ph.D. Dissertation, Florida State University, Tallahassee, 157 pp.
- Gacia E, Duarte CM (2001) Sediment Retention by a Mediterranean *Posidonia oceanica* Meadow: The Balance between Deposition and Resuspension. *Est. Coast. Shelf Sci.* 52, 505–514.
- Gallegos CL (2005) Optical water quality of a blackwater river estuary: the Lower St. Johns River, Florida, USA. *Est. Coast. Shelf Sci.* 63, 57–72.
- Gallegos CL, Werdell PJ, McClain CR (2011) Long-term changes in light scattering in Chesapeake Bay inferred from Secchi depth, light attenuation, and remote sensing measurements. *J. Geophys. Res.* 116, doi:10.1029/2011JC007160.
- Gibbs JP, Halstead JM, Boyle KJ, Huang J-C (2002) An Hedonic Analysis of the Effects of Lake Water Clarity on New Hampshire Lakefront Properties. *Agricult. Res. Econ. Rev.* 31: 39–46.
- Hayworth JS, Clement TP, John GF, Yin F (2015) Fate of Deepwater Horizon Oil in Alabama's Beach System: Conceptual Framework for Physical Evolution Based on Observational Data. *Marine Pollution Bulletin* 90: 95–105 doi: 10.1016/j.marpolbul.2014.11.01625496697. [PubMed: 25496697]
- Helms JRStubbins A, Ritchie JD, Minor E, Kieber DJ, Mopper K. (2008) Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of CDOM. *Limnol. Oceanogr.* 53(3), 955–969.
- Keith DA (2014) Coastal and Estuarine Waters: Behavior of Light. *Encycl. of Nat. Resources* doi: 10.1081/E-ENRW-120049158.
- Kelble CR, Ortner PB, Hitchcock GL, Boyer JN (2005) Attenuation of Photosynthetically Available Radiation (PAR) in Florida Bay: Potential for Light Limitation of Primary Producers. *Estuaries*, 28, 4, 560–571.
- Kenner WE, Hampton ER, and Conover CS (1971) Average flow of major streams in Florida, map of the Interior, Washington, D.C. and the Florida Department of Natural Resources, Bureau of Geology, Tallahassee, FL.
- Kirk JTO (1994) *Light and Photosynthesis in Aquatic Ecosystems*. Cambridge University Press, New York, 509 pp.
- Kishino M et al. 1985 Estimation of the spectral absorption coefficients of phytoplankton in the sea. *Bulletin of Marine Science.* 37(2): 634–642.
- Le C, Lehrter JC, Hu C, Schaeffer BS, MacIntyre H, Hagy JD, Beddick DL (2015) Relation between inherent optical properties and land use and land cover across Gulf Coast estuaries. *L&O.* 60:920–933.
- Lorenzen CJ (1972) Extinction of Light in the Ocean by Phytoplankton. *J. Cons. Int. Explor. Mer.* 34, 2, 262–267.
- Major C, Lusht KM (2004) Beach Proximity and the Distribution of Property Values in Shore Communities. *The Appraisal Journal* Fall, 333–338.

- Mendelssohn IA, Andersen GL, Baltz DM, Caffey RH, Carman KR, Fleege JW, Joye SB, Lin Q, Maltby E, Overton EB, Rozas LP (2012) Oil Impacts on Coastal Wetlands: Implications for the Mississippi River Delta Ecosystem after the Deepwater Horizon Oil Spill. *Biosci*, 62 (6), 562–574.
- Milbrandt EC, Coble PG, Conmy RN, Martignette AJ, Siwicke JJ (2010) Evidence for the production of marine fluorescence dissolved matter in coastal environments and a possible mechanism for formation and dispersion. *Limnol. Oceanogr*, 55 (5), 2037–2051.
- Mobley CD (1994) *Light and Water Radiative Transfer in Natural Waters*. Academic Press, London, 592 pp.
- Morel A, Smith RC (1982) Terminology and units in optical oceanography, *Marine Geodesy*, 5, 335–349.
- Mueller JL (2000) SeaWiFS algorithm for the diffuse attenuation coefficient, $K(490)$, using water-leaving radiances at 490 and 555 nm, in *SeaWiFS Post launch Calibration and Validation Analyses, Part 3* Eds. Hooker SB and Firestone ER, NASA Tech. Memo., NASA TM-206892, vol. 11, 24–27.
- Mulabagal V, Yin F, John GF, Hayworth JS, Clement TP (2013) Chemical fingerprinting of petroleum biomarkers in Deepwater Horizon oil spill samples collected from Alabama shoreline. *Marine Pollution Bulletin* 70: 147–154 doi: 10.1016/j.marpolbul.2013.02.02623523118. [PubMed: 23523118]
- NOAA Report (2015) Programmatic Damage Assessment and Restoration Plan (PDARP) and Programmatic Environmental Impact Statement (PEIS) for the Deepwater Horizon Oil Spill, October 2015.
- CENR (2003) An assessment of coastal hypoxia and eutrophication in U.S. Waters National Science and Technology Technical Council Report, Committee on Environment and Natural Resources, Washington, DC, 74
- Osburn CL, Boyd TJ, Montgomery MT, Bianchi TS, Coffin RB, Paerl HW (2016) Optical proxies for terrestrial dissolved organic matter in estuaries and coastal waters. *Frontiers Mar. Sci*, DOI: 10.3389/fmars.2015.00127.
- Paavel B, Arst H, Metsamaa L, Toming K, Reinart A. (2011) Optical investigations of CDOM rich coastal waters in Pärnu Bay. *Estonian J Earth Sci*, 60(2), 102–112.
- Pegau WS, Zaneveld JR, Mueller JL (2003) Inherent optical properties: instruments, characterization, field measurements, and data analysis protocols In: Mueller JL et al. *Ocean Optics Protocols for Satellite Ocean Color Sensor Validation, Revision 4*, vol. IV Goddard Space Flight Center, Greenbelt, pp 1–76.
- Plant NG, Long JW, Dalyander PS, Thompson DM, Raabe EA (2013) Application of a hydrodynamic and sediment transport model for guidance of response efforts related to the Deepwater Horizon oil spill in the Northern Gulf of Mexico along the coast of Alabama and Florida: U.S. Geological Survey Open-File Report 2012–1234, 46 p.
- Preisendorfer RW 1986 Secchi disk science: Visual optics of natural waters. *Limnology and Oceanography* 31, 909–926.
- Report Oil Budget Calculator: Deepwater Horizon; Federal Interagency Solutions Group: 2010; p 217.
- Rochelle-Newall EJ, Fisher TR (2002) Production of chromophoric dissolved organic matter fluorescence in marine and estuarine environments: an investigation into the role of phytoplankton. *Mar. Chem*, 77, 7–21.
- Schaeffer BA, Hagy JD, Lehrter JC, Conmy RN, Stumpf R. (2012) An approach to developing numeric water quality criteria for coastal waters using SeaWiFS satellite data record. *Environ. Sci. Technol.* 46, 916–922. [PubMed: 22192062]
- Schaeffer BA, Conmy RN, Duffy AE, Aukamp J, Yates DF, Craven G. (2015) Northern Gulf of Mexico estuarine coloured dissolved organic matter derived from MODIS data. *Int. J. Rem. Sens.* 6:8, 2219–2237, DOI: 10.1080/01431161.2015.1035408.
- Spencer RGM, Aiken GR, Dornblaser MM, Butler KD, Holmes RM, Fiske G, Mann PJ, Stubbins A. (2013) Chromophoric dissolved organic matter export from U.S. rivers. *Geophys. Res. Lett.* 40, 1575–1579.
- Stabenau ER, Zepp RG, Bartels E, Zika RG (2004) Role of the seagrass *Thalassia testudinum* as a source of CDOM in coastal South Florida. *Mar. Ecol. Prog. Ser.* 282, 59–72.

- Stedmon CA, Markager S, Sondergaard M, Vang T, Laubel A, Henrk-borch N, Windelin A. (2006) DOM export to a temperate estuary: Season variations and implications of land use. *Est. Coasts*, 29(3), 388–400.
- Sumaila UR, Cisneros-Montemayor AM, Dyck A, Huang L, Cheung W, Jacquet J, Kleisner K, Lam V, McCrea-Strub A, Swartz W, Watson R, Zeller D, Pauly D. (2010) Impact of the Deepwater Horizon well blowout on the economics of US Gulf fisheries. *Can. J. Fish. Aquat. Sci*, 659, 499–510.
- U.S. Census Bureau (2000) Census of Population and Housing Population and Housing Unit Counts, PHC-3–1, Washington DC, 211 pp.
- Vodacek A, Blough NV, DeGrandpre MD, Peltzer ET, Nelson RK (1997) Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnol. Oceanogr*, 42(4), 674–686.
- Welschmeyer NA (1994) Fluorometric Analysis of Chlorophyll a in the Presences of Chlorophyll b and Phaeopigments. *Limnol. Oceanogr*. 39: 1985–1992. doi:10.4319/lo.1994.39.8.1985.
- Yarbro LA, Carlson PR Jr. (2015) Seagrass Integrated Mapping and Monitoring Program. Mapping and Monitoring Report No. 1.1, FWRI Technical Report TR-17. Summary Reports for Pensacola, Choctawhatchee, St. Andrew and St. Joseph Bays, 50 pp.

Figure 1. Map and station locations for Pensacola, Choctawhatchee, St Andrew and St. Joseph Bays in Northwest Florida. Mean estuary depth ranges between 4–5 m.

Figure 2. Monthly freshwater discharges for the Choctawhatchee and Escambia Rivers in cubic feet per second. Source, <http://waterdata.usgs.gov>.

Figure 3.
CDOM (a_g412) and detrital (a_d412) absorption coefficients as a function of salinity for each estuary. Symbols denote sampling month.

Figure 4. Ternary plots illustrating relative contribution of a_g412 , a_d412 , and $a_\phi412$ to total absorption (a_{t-w412}) for each estuary represented as percentages.

Figure 5. Relationship between absorption coefficients at 412 nm and integrated over PAR wavelengths for all bays. Note different scales for X and Y axes.

Figure 6.
Estuarine CDOM spectral slope and absorption coefficient for all stations and months.

Figure 7. Log transformed plots of absorption coefficients at 412 nm and proxy-IOP water quality parameters.

Figure 8.
 K_d PAR as a function of secchi depth, Z_{SD} , for all estuaries.

Figure 9.

Log transformed relationship between the diffuse attenuation coefficient, $K_d \text{ PAR}$, and the PAR integrated absorption coefficient, $a_{t-w} \text{ PAR}$.

Figure 10.

Median $K_d \text{ PAR}$ and $a_{t-w} \text{ PAR}$ values (a,d), salinity (b,e), absorption coefficient and spectral slope (c,f) for Pensacola Bay stations (x-axis numbers). Cap bars represent minimum and maximum values. Solid triangles denote $a_{t-w} \text{ PAR}$, open circles denote $K_d \text{ PAR}$ and closed circles denote spectral slopes or salinity. Absorption coefficients represented with colored areas, where a_g is darkest gray, and a_ϕ is lightest. Low flow (left panels) and high flow (right panels) conditions are plotted separately.

Figure 11.

Median $K_d\text{PAR}$ and $a_{t-w}\text{PAR}$ values (a,d), salinity (b,e), absorption coefficient and spectral slope (c,f) for Choctawhatchee Bay stations (x-axis numbers). Cap bars represent minimum and maximum values. Solid triangles denote $a_{t-w}\text{PAR}$, open circles denote $K_d\text{PAR}$ and closed circles denote spectral slopes or salinity. Absorption coefficients represented with colored areas, where a_g is darkest gray, and a_ϕ is lightest. Low flow (left panels) and high flow (right panels) conditions are plotted separately.

Figure 12.

Median $K_d \text{ PAR}$ and $a_{t-w} \text{ PAR}$ values (a,d), salinity (b,e), absorption coefficient and spectral slope (c,f) for St. Andrew and St. Joseph Bay stations (x-axis numbers). Cap bars represent minimum and maximum values. Solid triangles denote $a_{t-w} \text{ PAR}$ and open circles denote $K_d \text{ PAR}$. Absorption coefficients represented with colored areas, where a_g is darkest gray, and a_ϕ is lightest.

Table 1.

Median, minimum and maximum estuarine water quality parameters calculated according to salinity zone within each estuary. The three zones are categorized by low salinity (0–15) for oligohaline and mesohaline, intermediate salinity (15–25) for Polyhaline, and high salinity (> 25) euhaline waters (Venice System, Anonymous, 1959).

Estuary	Salinity Zone	Salinity	Temp. (°C)	Turbidity (NTU)	FL _{CDOM} (QSE)	CHL (µg/L)	Z _{SD} (m)	S _{350-412 nm} (m ⁻¹)	a _g 412 (m ⁻¹)	a _d 412 (m ⁻¹)	a _g 412 (m ⁻¹)	a _w PAR (m ⁻¹)	k _d PAR (m ⁻¹)
Pensacola	0–15	Median	24.04	3.76	78.38	5.31	1.00	0.0166	0.2461	1.2848	3.4328	1.4216	0.4733
		Min	5.52	0.03	12.89	0.29	0.40	0.0143	0.0033	0.0237	0.2503	0.2962	0.1988
		Max	14.84	26.54	143.44	24.18	3.50	0.0227	2.5006	5.4148	7.5736	3.6404	0.9793
	15–25	Median	19.86	1.36	37.73	6.58	1.75	0.0172	0.2536	0.5794	1.2266	0.6727	0.2518
		Min	15.03	0.45	10.88	1.48	0.50	0.0144	0.0011	0.1153	0.2333	0.1313	0.1907
		Max	24.88	20.59	150.00	26.01	6.40	0.0215	0.7167	2.5050	8.6344	3.1040	0.9405
	> 25	Median	27.12	1.24	32.39	4.10	2.00	0.0175	0.1623	0.4425	1.0280	0.5208	0.1913
		Min	25.41	0.50	10.62	0.65	0.50	0.0135	0.0570	0.1184	0.2315	0.1576	0.1514
		Max	32.45	10.36	94.10	28.04	4.50	0.0195	0.9370	2.2708	8.1040	4.1564	0.2937
	0–15	Median	7.27	3.24	70.00	3.96	1.50	0.0163	0.1904	1.2945	3.7569	1.3815	0.3221
		Min	0.08	0.46	19.94	0.62	0.45	0.0146	0.0430	0.2263	0.8022	0.4169	0.1583
		Max	14.95	24.19	117.74	27.49	3.00	0.0194	0.7279	5.4727	17.1994	5.6150	0.7650
Choctawhatchee	15–25	Median	18.81	0.63	27.41	3.32	3.00	0.0176	0.1725	0.3380	1.1515	0.4960	0.2140
		Min	15.00	0.28	16.28	0.34	0.75	0.0130	0.0370	0.0030	0.0256	0.0626	0.1405
		Max	24.86	24.18	70.12	15.43	7.20	0.0195	0.7796	1.5835	10.8370	3.4076	0.5572
	> 25	Median	18.97	0.44	21.89	3.51	3.23	0.0175	0.1164	0.2714	0.5725	0.3275	0.1655
		Min	25.14	0.18	14.78	0.70	1.10	0.0141	0.0098	0.0697	0.3945	0.1118	0.1408
		Max	33.72	30.03	40.05	9.52	7.20	0.0189	0.4875	1.3549	2.2162	2.6410	0.2010
	0–15	Median	0.25	4.24	116.81	1.81	1.00	0.0162	0.1125	1.2062	7.2161	2.5617	0.3534
		Min	0.25	0.17	8.95	0.07	0.50	0.0149	0.0050	0.0474	0.2249	0.1196	0.1917
		Max	14.42	23.73	149.99	17.15	2.00	0.0186	2.0055	6.8840	16.3344	4.9809	0.6214
	15–25	Median	22.02	1.14	44.41	4.04	2.00	0.0168	0.1409	0.3520	2.1263	0.8005	0.2679
		Min	15.22	0.34	11.53	0.87	0.75	0.0138	0.0458	0.0521	0.4208	0.2005	0.0816
		Max	24.93	7.24	106.56	16.75	7.25	0.0205	0.3858	1.9060	7.2062	2.5618	0.4797

Estuary	Salinity Zone		Salinity	Temp. (°C)	Turbidity (NTU)	FL _{CDOM} (QSE)	CHL (µg/L)	Z _{SP} (m)	S _{350-412 nm} (m ⁻¹)	a _g 412 (m ⁻¹)	a _d 412 (m ⁻¹)	a _g 412 (m ⁻¹)	a _w PAR (m ⁻¹)	k _d PAR (m ⁻¹)
	> 25	Median	29.02	27.77	0.71	22.65	2.38	3.00	0.0172	0.0734	0.1707	0.9235	0.3982	0.2095
		Min	25.07	10.69	0.13	5.03	0.58	1.25	0.0101	0.0163	0.0200	0.1808	0.1011	0.0822
		Max	35.14	32.57	4.46	62.09	8.75	8.25	0.0193	0.2030	1.1380	10.9780	1.7390	0.3656
		Median	–	–	–	–	–	–	–	–	–	–	–	–
		Min	–	–	–	–	–	–	–	–	–	–	–	–
		Max	–	–	–	–	–	–	–	–	–	–	–	–
	0–15	Median	23.74	10.57	1.95	46.57	5.18	2.00	0.0161	0.1415	0.5199	1.9857	0.7520	0.2776
		Min	21.37	7.25	1.15	16.78	1.66	1.60	0.0155	0.0349	0.3240	0.3832	0.3435	0.1519
		Max	24.82	30.62	7.45	62.63	14.24	2.50	0.0202	0.3270	0.9184	3.9123	1.0148	0.3370
	> 25	Median	30.90	23.31	0.69	16.04	5.24	2.75	0.0166	0.1366	0.2464	0.6719	0.3732	0.2033
		Min	25.30	7.43	0.20	10.74	1.20	1.25	0.0103	0.0230	0.0126	0.1284	0.1480	0.1280
		Max	34.25	32.18	24.57	60.36	15.65	6.00	0.0335	0.5662	1.5730	3.3603	1.4004	0.3163
St. Joseph	> 25													

Table 2.

Median percent contribution of absorption coefficients within Northwest Florida estuaries. Many extracted chlorophyll values were below detection limit of the method and reported as 'nd' for non-detect.

Estuary	% a _φ 412		% a _d 412		% a _g 412	
	Median	Range	Median	Range	Median	Range
Pensacola	9	nd–43	29	< 1–62	61	34–95
Choctawhatchee	9	nd–39	23	< 1–79	69	20–92
St. Andrew	5	nd–20	16	< 1–50	79	33–98
St. Joseph	11	nd–51	22	< 1–66	65	10–90