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Mitigating the impact of trans-spectral processes on multivariate retrieval of water quality parameters from case 2 waters

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Abstract. This work considers the impact of inelastic trans-spectral processes (Raman scattering and fluorescence from chlorophyll and dissolved organic matter) in terms of their impacts on estimating water quality information from remote sensing of inland and coastal (case 2) waters. Well-known results from studies of the contributions of trans-spectral processes to subsurface volume reflectance and water-leaving radiance are briefly reviewed and discussed. A means of mitigating their impact on bio-optical models currently in use and previously developed for optically complex waters (without deliberation of inelastic processes per se) is suggested in terms of the manner in which the inherent optical properties (optical cross section spectra) required for their use are determined. In situ determinations of volume reflectance are consequences of all elastic and inelastic processes occurring within the water column. Hence, values of the local inherent optical properties determined in situ already incorporate impacts of trans-spectral processes. Therefore, remotely sensing natural waters whose pertinent optical cross section spectra were determined in situ would not be subject to the same degree of retrieval uncertainty as remotely sensing waters whose pertinent optical cross-section spectra were determined under controlled laboratory conditions. Expansion of the currently meager catalogue of field-acquired optical cross section data, therefore, is once again strongly endorsed.

Résumé. Ce travail concerne l'impact des processus trans-spectraux inélastiques (diffusion Raman et fluorescence de la chlorophylle et de la matière organique dissoute) en termes de leurs impacts sur l'estimation de l'information sur la qualité de l'eau à l'aide de la télédétection pour les eaux intérieures et côtières (case 2). Des résultats publiés d'études sur la contribution des processus trans-spectraux à la réflectance de volume de la sous-surface et à la radiance ré-émise par l'eau sont succinctement passés en revue et discutés. Une façon de réduire leur impact sur les modèles bio-optiques utilisés présentement et développés au départ pour les eaux optiquement complexes (sans délibération sur les processus inélastiques comme tels) est suggérée relativement à la manière par laquelle les propriétés optiques inhérentes (spectres de la section efficace optique) requises pour leur utilisation sont déterminées. Les déterminations in situ de la réflectance de volume dépendent de tous les processus élastiques et inélastiques se manifestant à l'intérieur de la colonne d'eau. Ainsi, les valeurs des propriétés optiques inhérentes locales déterminées in situ incorporent déjà les impacts des processus trans-spectraux. Ainsi, la télédétection des eaux naturelles dont les spectres pertinents de la section efficace optique ont été déterminés in situ ne serait pas assujettie au même degré d'incertitude d'inversion que la télédétection des eaux dont les spectres pertinents de la section efficace optique ont été déterminés dans des conditions contrôlées en laboratoire. Étant donné que le catalogue actuel de données de section efficace optique acquises au sol est plutôt mince, nous souscrivons à notre tour à l'idée d'en accroître le contenu.
[Traduit par la Rédaction]

Volume reflectance

The colour of a natural water body is a consequence of the absorption and scattering of visible downwelling solar and sky radiation by organic and inorganic colour-producing agents (CPAs) residing within the water column. Historically, perhaps owing to the optical complexity of case 2 waters, bio-optical models developed for the retrieval of water quality parameters from the colour of inland and coastal waters have considered only the effects of elastic scattering and absorption on the water-leaving radiance (e.g., Bukata et al., 1981a; 1985; 1995). In addition to Raman inelastic scattering, however, fluorescence by both phytoplanktonic pigments and dissolved organics can impact the spectral distribution of upwelling radiance, thereby modifying water colour (e.g., Sugihara et al., 1984; Fischer and Kronfeld, 1990; Coble and Brophy, 1994; Waters, 1995). Therefore, models have been developed simulating the aforementioned processes initially for mid-ocean waters (Gordon, 1979; Marshall and Smith, 1990; Haltrin and Kattawar, 1993) and recently for coastal and inland waters (Sathyendranath and Platt, 1998; Vodacek et al., 1994; Lee et al., 1994). Models that consider inelastic scattering and (or) fluorescence are referred to as trans-spectral, since

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stimulation at wavelength λ_1 leads to emissions at λ_2, where, in general, $\lambda_2 > \lambda_1$.

Spectral water-leaving radiance, $L_u(0^+, \lambda)$, and spectral volume reflectance (upwelling irradiance normalized to the downwelling irradiance) just beneath the air–water interface, $R(0^-, \lambda)$, are readily obtainable from knowledge of the inherent optical properties (IOPs) of the indigenous CPAs.

$R(0^-, \lambda)$ and $L_u(0^+, \lambda)$ are governed by absorption and by both elastic energy transfer processes (scattering wherein the wavelength of a scattered photon has remained unaltered) and inelastic energy transfer processes (fluorescence and scattering wherein a scattered photon has undergone a change in wavelength).

$R(0^-, \lambda)$, at least for the approximation of single scattering, can be conveniently expressed as the additive consequences of each energy transfer process occurring within the water column, namely,

$$R(0^-,\lambda) = R_{es}(0^-,\lambda) + R_r(0^-,\lambda) + R^f_{chl}(0^-,\lambda) + R^f_{DOM}(0^-,\lambda) \tag{1}$$

where R_{es} is the contribution from elastic scattering, R_r is the contribution from inelastic Raman scattering, R^f_{chl} is the contribution from trans-spectral fluorescence from chlorophyll, and R^f_{DOM} is the contribution from trans-spectral fluorescence from dissolved organic matter.

Raman scattering and fluorescence, characterized by nearly isotropic phase functions, result in multiple downward-scattering events that may restrict the single-scattering compartmentalization of R suggested previously. However, Sathyendranath and Platt (1998), who separate first-order Raman scattering from Raman–elastic and Raman–Raman events, have shown that, typically, the contribution to Raman scattering by photons undergoing second-order Raman scattering would only be about 10% that of first-order Raman scattering, with each successive order adding a further 10% of the prior order. It is not unreasonable to assume that this multiple scattering relationship should also hold for fluorescence by chlorophyll and dissolved organic matter.

Elastic scattering

Many workers (Gordon and Brown, 1973; Gordon et al., 1975; Kirk, 1981; 1984; Jerome et al., 1988; Stavn and Weidemann, 1989; Morel and Gentili, 1993; Sathyendranath and Platt, 1997; and others) have used Monte Carlo analyses to mathematically expand $R(0^-, \lambda)$ in terms of the concentrations of the aquatic colourants (chlorophyll, suspended minerals, dissolved organic matter) and their inherent optical properties (coefficients of absorption $a(\lambda)$, scattering $b(\lambda)$, and beam attenuation $c(\lambda)$). For example, for each wavelength λ, Jerome et al. (1988) obtained the following relationships (which have been shown to be effective in analyzing the optical heterogeneity of the Laurentian Great Lakes):

$$R_{es}(0^-) = \frac{1}{\mu_0}\,\frac{0.319 b_b}{a} \qquad \text{for} \qquad 0 \le \frac{b_b}{a} \le 0.25 \tag{2a}$$

and

$$R_{es}(0^-) = \frac{1}{\mu_0}\left(0.013 + \frac{0.267 b_b}{a}\right) \qquad \text{for} \qquad 0.25 \le \frac{b_b}{a} \le 0.50 \tag{2b}$$

where $\mu_0 = \cos\theta_0$, in which θ_0 is the in-water refracted angle; and $b_b = Bb$, in which B is the backscattering probability. Equations (2a) and (2b), however, do not *specifically* consider trans-spectral processes.

Inelastic Raman scattering

Sathyendranath and Platt (1998) mathematically described the contribution of Raman scattering to the volume reflectance in natural water as

$$R_r(\lambda_{em}, \lambda_{ex}, 0^-) = \frac{b_{br}(\lambda_{ex})E_d(\lambda_{ex}, 0^-)}{\mu_d[K_u(\lambda_{em}) + K_d(\lambda_{ex})]E_d(\lambda_{em}, 0^-)} \times \left[1 + \frac{b_b(\lambda_{ex})}{\mu_u[K_u(\lambda_{ex}) + K_d(\lambda_{ex})]} + \frac{b_b(\lambda_{em})}{2\mu_u K_u(\lambda_{em})}\right] \tag{3}$$

where $b_{br}(\lambda)$ is the Raman backscattering coefficient ($= B_r b_r(\lambda)$, where $B_r(\lambda)$ and $b_r(\lambda)$ are the inelastic backscattering probability and Raman scattering coefficient, respectively); $K_d(\lambda)$ and $K_u(\lambda)$ are attenuation coefficients for downwelling and upwelling irradiances, respectively; $E_d(\lambda, 0^-)$ is the downwelling irradiance of wavelength λ just below the surface; μ_d and μ_u are the average cosines for the downwelling and upwelling irradiances, respectively; and λ_{ex} and λ_{em} are the Raman scattering excitation and emission wavelengths, respectively.

Sugihara et al. (1984) approximate the relationship between the excitation wavelength, λ_{ex} (in nm), and the emission wavelength displaying maximum intensity in the Raman emission spectrum, $\lambda_{em,max}$, as

$$\lambda_{em,max} = \frac{\lambda_{ex}}{1 - 3.357 \times 10^{-4}\lambda_{ex}} \tag{4}$$

Kirk (1984) mathematically defined the attenuation coefficients for direct incident solar radiation, $K_{sun}(\lambda, \theta_0)$, and diffuse incident sky radiation, $K_{sky}(\lambda)$, as

$$K_{sun}(\lambda, \theta_0) = \frac{1}{\mu_0}\left[a(\lambda)^2 + (0.473\mu_0 - 0.218)a(\lambda)b(\lambda)\right]^{0.5} \tag{5}$$

and

$$K_{\mathrm{sky}}(\lambda) = 1.168[a(\lambda)^2 + 0.168a(\lambda)b(\lambda)]^{0.5} \tag{6}$$

where $a(\lambda)$ and $b(\lambda)$ are the absorption and scattering coefficients, respectively, of the water column; θ_0 is the in-water refraction angle; and $\mu_0 = \cos\theta_0$.

The resultant downwelling attenuation coefficient, $K_{\mathrm{d}}(\lambda, \theta_0)$, for the global irradiance is then given by

$$K_{\mathrm{d}}(\lambda, \theta_0) = F_{\mathrm{w}}K_{\mathrm{sky}}(\lambda) + (1 - F_{\mathrm{w}})K_{\mathrm{sun}}(\lambda, \theta_0) \tag{7}$$

where

$$F_{\mathrm{w}} = \frac{F(1 - \rho_{\mathrm{sky}})}{F(1 - \rho_{\mathrm{sky}}) + (1 - F)[1 - \rho_{\mathrm{sun}}(\theta_{\mathrm{s}})]} \tag{8}$$

and ρ_{sky} is the reflectivity of sky irradiance for a flat air–water interface; $\rho_{\mathrm{sun}}(\theta_{\mathrm{s}})$ is the Fresnel reflectivity of solar irradiance at a solar zenith angle θ_{s}; and F is the diffuse fraction of the downwelling global irradiance at the air–water interface, i.e., $F = E_{\mathrm{sky}}/(E_{\mathrm{sky}} + E_{\mathrm{sun}})$, where E_{sky} and E_{sun} are the sky and solar irradiance, respectively.

Fluorescence of chlorophyll and dissolved organic matter

Incorporating fluorescence into radiative transfer calculations requires knowledge of the fluorescence quantum yield of fluorescing components, $\eta(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}})$, where λ_{ex} and λ_{em} are the excitation and emission wavelengths of the fluorescence process, respectively. Although precise values of $\eta(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}})$ are currently unavailable for many specific species of fluorescing matter, typical values of η for chlorophyll, η_{chl}, generally range from 0.005 to 0.050 (IOCCG, 2000). Typical values of η for dissolved organic matter, η_{DOM}, generally range from 0.005 to 0.030 (Green and Blough, 1994; IOCCG, 2000). The term η_{DOM} is generally represented as a three-dimensional function following a log-normal distribution in both λ_{ex} and λ_{em} (Hawes, 1992), and η_{chl} is generally considered to possess a Gaussian shape factor (Gordon, 1979; Culver and Perry, 1997). Incorporating fluorescence from algal pigment and dissolved organic matter into inland and coastal water quality models is further complicated by the need to also estimate quenching effects from the same compounds that produce the fluorescence.

Gordon (1979) mathematically expressed the contribution of chlorophyll fluorescence to water volume reflectance, $R^{\mathrm{f}}_{\mathrm{chl}}(\lambda_{\mathrm{em}})$ as

$$R^{\mathrm{f}}_{\mathrm{chl}}(\lambda_{\mathrm{em}}, \lambda_{\mathrm{ex}}) = \frac{0.5}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\lambda_{\mathrm{em}} - \lambda_{\mathrm{em0}})^2}{2\sigma^2}\right]$$

$$\times \left[\int_{\lambda_{\mathrm{ex}}} \frac{\eta_{\mathrm{chl}}(\lambda_{\mathrm{ex}})a_{\mathrm{chl}}(\lambda_{\mathrm{ex}})E_{\mathrm{d}}(0^-, \lambda_{\mathrm{ex}})f(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}})\mathrm{d}\lambda_{\mathrm{ex}}}{K_{\mathrm{d}}(\lambda_{\mathrm{em}})\mu_0 E_{\mathrm{d}}(0^-, \lambda_{\mathrm{em}})\lambda_{\mathrm{em}}}\right] \tag{9}$$

where $a_{\mathrm{chl}}(\lambda_{\mathrm{ex}})$ is the chlorophyll absorption coefficient at the excitation wavelength, $\eta_{\mathrm{chl}}(\lambda_{\mathrm{ex}})$ is the chlorophyll fluorescence quantum yield at the excitation wavelength, λ_{em0} is the chlorophyll fluorescence emission peak wavelength (685 nm), σ^2 is the variance of the chlorophyll fluorescence emission band (σ being the standard deviation), and $f(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}})$ is a function of downwelling irradiance attenuation coefficients K_{d} defined by

$$f(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}}) = \frac{K_{\mathrm{d}}(\lambda_{\mathrm{em}})}{K_{\mathrm{d}}(\lambda_{\mathrm{ex}})}\left\{1 - \frac{K_{\mathrm{d}}(\lambda_{\mathrm{em}})}{K_{\mathrm{d}}(\lambda_{\mathrm{ex}})}\ln\left[1 + \frac{K_{\mathrm{d}}(\lambda_{\mathrm{ex}})}{K_{\mathrm{d}}(\lambda_{\mathrm{em}})}\right]\right\} \tag{10}$$

Culver and Perry (1997) expressed the contribution of dissolved organic matter fluorescence to volume reflectance, $R^{\mathrm{f}}_{\mathrm{DOM}}(\lambda_{\mathrm{em}})$ as

$$R^{\mathrm{f}}_{\mathrm{DOM}} = \frac{0.5}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\lambda_{\mathrm{em}} - \lambda_{\mathrm{em0}})^2}{2\sigma^2}\right]$$

$$\times \left[\int_{\lambda_{\mathrm{ex}}} \frac{\eta_{\mathrm{DOM}}(\lambda_{\mathrm{ex}})a_{\mathrm{DOM}}(\lambda_{\mathrm{ex}})E_{\mathrm{d}}(0^-, \lambda_{\mathrm{ex}})\mathrm{d}\lambda_{\mathrm{ex}}}{\mu_0[K_{\mathrm{d}}(\lambda_{\mathrm{ex}}) + 2\mu_0 K_{\mathrm{d}}(\lambda_{\mathrm{em}})]E_{\mathrm{d}}(0^-, \lambda_{\mathrm{em}})}\right] \tag{11}$$

where $a_{\mathrm{DOM}}(\lambda_{\mathrm{ex}})$ is the dissolved organic matter (DOM) absorption coefficient at the excitation wavelength, $\eta_{\mathrm{DOM}}(\lambda_{\mathrm{ex}})$ is the DOM fluorescence quantum yield at the excitation wavelength, λ_{em0} is the DOM fluorescence emission peak (490–520 nm), and σ^2 is the variance of the DOM fluorescence emission band.

Equations (2a) or (2b), (3), (9), and (11) can then be summed to provide the cumulative volume reflectance just beneath the air–water interface, $R(0^-, \lambda)$, resulting from the spectral and trans-spectral processes occurring within the water column.

Impact on $R(0^-, \lambda)$ of Raman scattering

Since suspended organic and inorganic matter are the principal participants in the elastic scattering processes in most inland and coastal waters, it is logical to expect inelastic Raman scattering to be most significant in oligotrophic (case 1) waters and fluorescence to be most significant in mesotrophic waters devoid of suspended inorganics, this significance decreasing as the waters become more turbid.

Extensive work on Raman scattering in mid-oceanic and coastal-oceanic waters (Waters, 1995; Haltrin and Kattawar, 1993; Babin et al., 1996; Sathyendranath and Platt, 1998; Bartlett et al., 1998; others) has shown the following:

(1) Maximum impacts of Raman scattering occur in water devoid of chlorophyll, suspended minerals, and dissolved organic matter.

(2) Raman scattering decreases with increasing visible wavelength. However, its *percent* impact on pure water volume reflectance increases with increasing wavelength

across the entire visible spectrum. Maximum impacts occur at values of λ greater than ~635 nm, where Raman scattering accounts for nearly 35% of the volume reflectance at $\lambda \approx 685$ nm.

(3) Addition to pure water of increasing concentrations of chlorophyll *a*, suspended minerals, or dissolved organic matter reduces the impact of Raman scattering, with the resulting subsurface volume reflectance spectrum ($R_{es} + R_r$) rapidly becoming equal to the elastic volume reflectance R_{es}.

(4) Of the three possible optically binary water columns (i.e., chlorophyll-pure water; suspended mineral-pure water; dissolved organic matter-pure water), the greatest impact of Raman scattering would occur in natural waters devoid of particulate elastic scatterers, i.e., those optically binary in pure water and DOM.

(5) Small impacts of Raman scattering occur in natural water bodies containing a low to moderate concentration (see later in the paper) of either chlorophyll, suspended minerals, or dissolved organic matter. In case 2 water bodies containing admixtures of the three colourants, the influence of Raman scattering would be even more dramatically reduced.

Therefore, Raman scattering would be of consequence to the water-leaving radiance from mid-oceanic waters and perhaps from the most oligotrophic of inland and coastal waters, but of little or no consequence to any water body displaying at least small organic and (or) inorganic concentration.

To numerically quantify the impacts of inelastic Raman scattering, chlorophyll fluorescence, and DOM fluorescence on water-leaving radiance for waters of differing compositions, it would be desirable to suggest ranges on either the concentrations of the resident aquatic matter or their inherent optical properties (e.g., specific absorption and scattering coefficients for chlorophyll, suspended minerals, and dissolved organic carbon (DOC) at a designated wavelength). We have not performed experimental determinations of these impacts under either field or laboratory conditions. However, the inherent optical properties of molecular water and the elastic and inelastic equations reviewed in these discussions (coupled with the inelastic numerical values and mathematical relationships in the work cited herein, and the elastic inherent optical properties for Lake Ontario that we have reported in the literature) can readily yield the following approximate concentration ranges:

(1) At $R(0^-, 685)$, Raman scattering in "pure" molecular water makes up ~35% of the total volume reflectance. However, the value of $R(0^-, 685)$ is $<2 \times 10^{-4}$. By contrast, for water containing no suspended mineral or DOC but a chlorophyll concentration of 1.0 µg/L, the value of $R(0^-, 685)$ is $\sim 6 \times 10^{-2}$, with fluorescence accounting for over 99% of this reflectance.

(2) The impacts of Raman scattering on $R(0^-, \lambda)$ for $\lambda > 560$ nm are infinitesimal for binary waters of suspended mineral concentrations of 0.1 mg/L and for binary waters of dissolved organic matter concentrations of 0.1 mg C/L.

Impact on $R(0^-, \lambda)$ of fluorescence from chlorophyll

Fluorescence from chlorophyll manifests as a tightly knit Gaussian distribution centred on the peak chlorophyll fluorescence emission wavelength $\lambda_{em0} = 685$ nm. Therefore, it would be expected that (*i*) this spectral distribution would be a prominent feature of the volume reflectance and water-leaving radiance spectrum within (from) optically binary waters rich in chlorophyll, and (*ii*) this feature would increase in prominence as the concentration of chlorophyll increases. Such a feature is readily observed in ocean waters and those inland waters that satisfy this optically binary criterion. **Figure 1** illustrates reflectance data from the Institute of Ocean Sciences spectrometer in and around Saanich Inlet, Vancouver Island. Clearly seen is the chlorophyll fluorescence distribution centred at 685 nm.

The presence of suspended minerals and (or) dissolved organic matter in the water column reduces and can quench chlorophyll fluorescence. Quenching refers to an altering of the lifetime of an excited state or the generation of an alternate emission–reabsorption process or de-excitation pathway. Reducing refers to the attenuation of the incoming excitation radiation (whereby photons are prevented from reaching the phytoplankton and exciting the fluorescing molecules) and the attenuation of the outgoing emitted radiation (thereby preventing the emitted photons from escaping the air–water interface). Chlorophyll both quenches and reduces its own fluorescence. Thus, increasing concentrations of inorganic and organic matter (inclusive of chlorophyll itself) resident within the water column would decrease the prominence of chlorophyll fluorescence. **Figure 2** illustrates remote sensing reflectance (ratio of the water-leaving spectral radiance to the downwelling spectral irradiance) recorded by the National Water Research Institute WATERS system of upwelling and downwelling spectrometers in Lake Waskesiu, Saskatchewan, during the Boreal Ecosystem–Atmosphere Study (BOREAS). No obvious fluorescence peak is discernible.

Hence, the impact of chlorophyll fluorescence on volume reflectance (and on water-leaving radiance) will be of most consequence to case 1 waters and to those oligotrophic to mesotrophic case 2 waters wherein chlorophyllous pigments are the overwhelmingly dominant aquatic CPAs. For example, Culver and Perry (1997) report that solar-induced chlorophyll fluorescence can account for 10%–40% of the upwelling irradiance centred on 685 nm at the surface in case 1 waters.

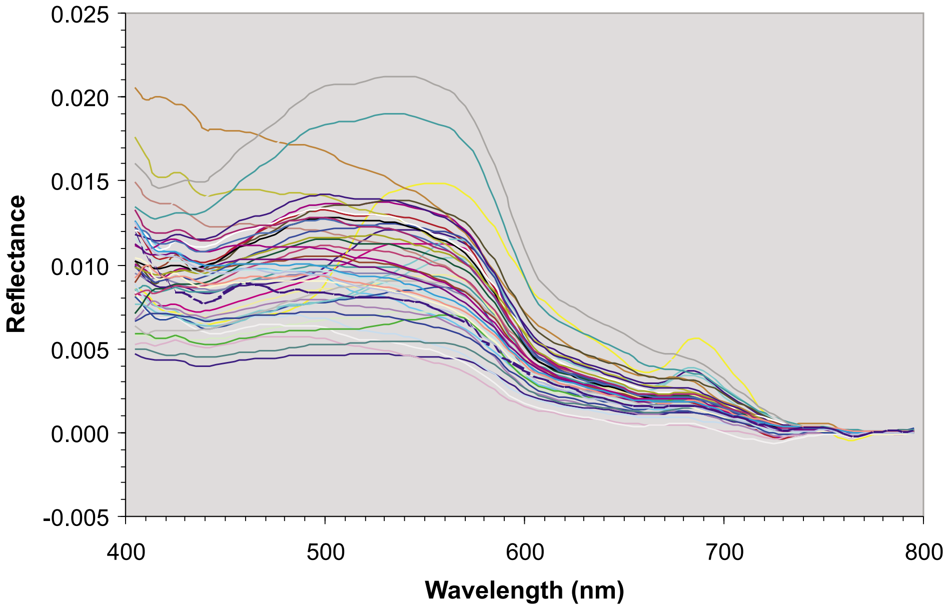

Figure 1. Reflectance data from the Institute of Ocean Sciences spectrometer in and around Saanich Inlet.

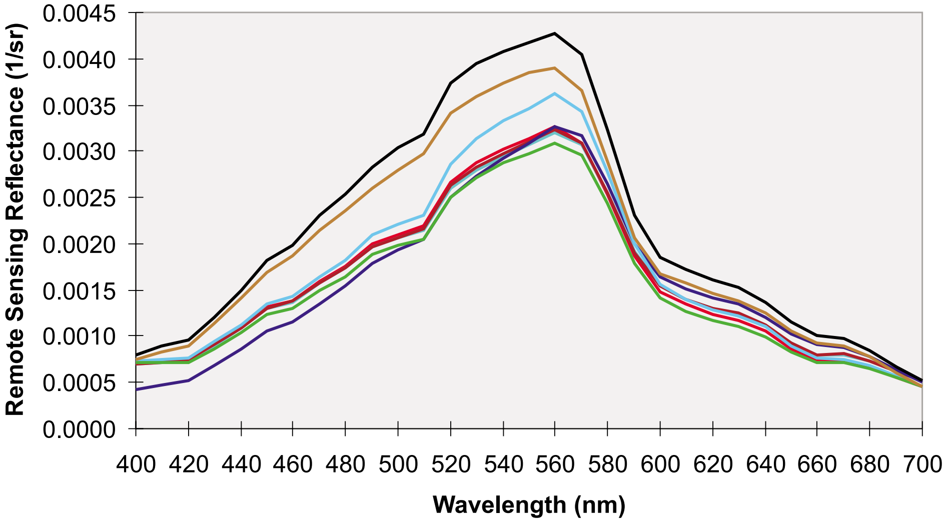

Figure 2. Remote sensing reflectance recorded by the National Water Research Institute WATERS system of upwelling and downwelling spectrometers in Lake Waskesiu.

Impact on $R(0^-, \lambda)$ of fluorescence from dissolved organic matter (DOM)

Fluorescence from DOM results from a much more loosely knit and broader Gaussian distribution centred on peak DOM fluorescence emission wavelengths within the range $\lambda_{\mathrm{em}0}$ = 490–520 nm. Hence, fluorescence from DOM would manifest as a broad Gaussian-shaped increase over most of the midvalue wavelengths of the visible spectrum.

From the literature cited earlier, the following is known:

(1) The spectral region most affected by fluorescence from DOM is an extended range from ~430 nm to ~580 nm.

(2) Since DOM absorbs but does not elastically backscatter visible radiation, addition of DOM to the water column will decrease the volume reflectance attributable to elastic processes as it increases fluorescence. Hence, for a fixed concentration of suspended minerals and (or) chlorophyll, the *percent* impact of DOM fluorescence on the subsurface volume reflectance will increase as the DOM concentration increases.

(3) Very small amounts of chlorophyll and suspended minerals added to a water column do not dramatically reduce the impact of DOM fluorescence on the volume reflectance.

(4) Suspended inorganics (particularly in inland waters where suspended mineral concentrations are routinely in the concentration range 1–10 mg/L) provide effective attenuating agents, while suspended organics (i.e., chlorophyll) and dissolved organic matter provide both effective attenuating and effective quenching agents. Increasing concentrations of both suspended minerals and chlorophyll rapidly and effectively reduces the impacts of DOM fluorescence on the upwelling spectra.

Comparable to the maximum impact of chlorophyll fluorescence on volume reflectance and water-leaving radiance of waters optically binary in chlorophyll, significant mid-wavelength impacts of DOM fluorescence on the spectral distribution of volume reflectance and water-leaving radiance can be detected in waters optically binary in DOM. For example, Vodacek et al. (1994) report that fluorescence from dissolved organics in the blue-green to green spectral region may account for as much as 70% of the water-leaving radiance from optically binary waters essentially devoid of both suspended minerals and phytoplankton (i.e., for waters wherein the suspended mineral concentration is much less than 0.1 mg/L and the chlorophyll concentration is much less than 0.1 µg/L). For case 2 waters containing admixtures of inorganic and (or) organic particulates, however, no such dramatic impact of fluorescence on volume reflectance would be observed.

Extracting water quality information from water-leaving radiance

Inverse modeling is used to deconvolve water colour (water-leaving radiance) into the co-concentrations of organic and inorganic colourants responsible for its generation. A variety of water quality algorithms have been and are being developed to retrieve these concentrations from the upwelling radiance recorded by a remote sensing device (IOCCG, 2000). We have long advocated (see discussions in Bukata et al., 1981a; 1991; 1995) that to retrieve the concentration of a desired aquatic colourant (e.g., chlorophyll), the coextant concentrations of *all* other aquatic colourants (e.g., suspended minerals, dissolved organic matter) *must be simultaneously retrieved*. To perform such retrieval we have also consistently advocated the use of a multivariate optimization technique such as that attributed to Levenberg (1944) and Marquardt (1963) that has been shown to provide very good agreement between directly measured and remotely inferred values of chlorophyll *a*, suspended minerals, and dissolved organic matter (Bukata et al., 1981a; 1985; 1991) for the optically complex waters of the Laurentian Great Lakes.

As discussed previously, impacts of fluorescence on the spectral distribution of volume reflectance can be detected in waters rich in either phytoplankton or dissolved organics but containing only small amounts (<1 mg/L) of suspended minerals. Similarly, impacts of Raman scattering are of consequence to waters devoid of elastic scatterers. Logically, therefore, the water-leaving radiance from case 1 waters would display more prominent impacts of inelastic processes than would the water-leaving radiance from most case 2 waters.

Grassl et al. (2002) have recently utilized Equations (1)–(11) along with a variety of coexisting organic and inorganic concentrations and input optical parameters to forward model hypothetical composite spectra of $R(0^-, \lambda)$ that incorporated absorption, elastic scattering, and trans-spectral processes. Equations (2a) and (2b) were then used in conjunction with Levenberg–Marquardt multivariate optimization analyses to inversely model the CPA concentrations from these hypothetical spectra. These concentrations were then compared with the preselected concentrations used in the forward modeling, thereby assessing the water quality retrieval uncertainty arising from the neglect of Raman scattering and fluorescence by chlorophyll and dissolved organic matter. The results of such a comparison suggested that for inland and coastal waters containing chlorophyll, suspended minerals, and dissolved organic matter, retrieval uncertainties for extracting concentrations of chlorophyll, suspended minerals, and dissolved organic matter without due deliberation given to trans-spectral processes for most waters are generally contained within the range –50% to +50%.

Such substantial uncertainties resulting from neglect of trans-spectral processes in multivariate retrieval of concentrations of organic and inorganic colourants from volume reflectance of natural water bodies appear both startling and discouraging. Hence, if we concede that the reported uncertainties are the results of trans-spectral process neglect, a focus on the reality of such a modeling exercise is certainly warranted. Consider the following caveats:

(1) A rigorous mathematical definition of volume reflectance in terms of concentrations of coexistent organic and inorganic aquatic colourants (Equation (1)) requires accurate spectral values of suites of absorption and elastic scattering coefficients, inelastic scattering coefficients, scattering phase functions, upwelling and downwelling attenuation coefficients, fluorescence quantum yields and spectral shape functions, downwelling solar and sky irradiance, reflectivities at the air–water interface, sea state, atmospheric conditions, and viewing orientation. All are parameters that are nonlinearly variant in both time and space and that must be known a priori, laboriously determined, or judiciously assumed.

(2) Within the robustness and precision of the selected volume reflectance models for elastic scattering (R_{es}), Raman scattering (R_{r}), fluorescence from chlorophyll $R^{\mathrm{f}}_{\mathrm{chl}}$, and fluorescence from dissolved organic matter $R^{\mathrm{f}}_{\mathrm{DOM}}$, the forward modeling of pure water containing predetermined concentrations of chlorophyll, suspended minerals, and dissolved organic matter of known elastic and inelastic specific inherent optical properties into

volume reflectance spectra just beneath the air–water interface ($R(0^{-}, \lambda)$) can be confidently considered to be mathematically sound.

(3) Using nonlinear multivariate optimization techniques (e.g., Levenberg–Marquardt) to inversely model coextant concentrations of chlorophyll, suspended minerals, and dissolved organic matter from these modeled $R(0^{-}, \lambda)$ spectra will readily yield the precise values of the preselected organic and inorganic concentrations.

(4) Using nonlinear multivariate optimization techniques (e.g., Levenberg–Marquardt) to inversely model the coextant concentrations of chlorophyll, suspended minerals, and dissolved organic matter from these modeled $R(0^{-}, \lambda)$ spectra on the assumption that $R(0^{-}, \lambda)$ may be solely attributable to $R_{\mathrm{es}}(\lambda)$ will readily yield the retrieval uncertainties of such an assumption (differences between the preselected and inversely modeled organic and inorganic concentrations) provided that the specific inherent optical properties of the indigenous chlorophyll, suspended mineral, and dissolved organic matter are known. To date there is a limited knowledge base of inherent optical properties (particularly for suspended inorganic particulates) of aquatic matter indigenous to natural waters on a global basis. Further, the limited wavelength-dependent IOPs that do exist display dissimilarities in both spectral shape and spectral intensity (Bukata et al., 1995; IOCCG, 2000).

The fourth caveat warrants further discussion. There are two ways to obtain specific inherent optical properties (IOPs or optical cross section spectra as they are referred to in the limnological literature (Bukata et al., 1981b; 1991)): (*i*) from laboratory determinations of the specific absorption and scattering properties of chlorophyll, suspended minerals, and dissolved organic matter, wherein the identity of the colourant and the nature of its containment medium are both known and controlled within precise laboratory processes and monitoring protocols; and (*ii*) from field expeditions, wherein in situ determinations of in-water volume reflectance spectra are made in concert with collection of water samples that are brought to the laboratory for accurate determination of chlorophyll, suspended minerals, and dissolved organic matter concentrations.

Since the inherent optical properties of an inland water body are influenced by the geochemical composition of its confining basin, different sets of indigenous inherent optical properties will yield different sets of "retrieval uncertainty" values when used in inverse models. So, too, however, might the sets of inherent optical properties emerging from the laboratory and field determinations *at the same time for the same water body.* Direct laboratory determinations of IOPs are invariably the result of analyses based on absorption and elastic scattering. Grassl et al. (2002) utilized IOPs appropriate for colourants of Russian lakes (Kondratyev et al., 1998) as a means of modeling $R_{\mathrm{es}}(\lambda)$, i.e., the volume reflectance with no due deliberation of inelastic scattering or fluorescence. In a similar manner they might have used IOPs previously determined for Lake Ontario (Bukata et al., 1981b; 1985) or Lake Ladoga (Bukata et al., 1991; 1995). Such IOPs, however, were determined from field excursions wherein inverse modeling was utilized to convert in situ measurements of volume reflectance spectra, $R(0^{-}, \lambda)$, and laboratory-determined concentrations of chlorophyll, suspended minerals, and dissolved organic matter into the specific optical properties of the indigenous colourants of the collected water samples.

A *Gedanken* thought process, however, leads to the realization that in situ determinations of $R(0^{-}, \lambda)$ already include the local values of $R_{\mathrm{es}}(0^{-}, \lambda)$, $R_{\mathrm{r}}(0^{-}, \lambda)$, $R^{\mathrm{f}}_{\mathrm{chl}}(0^{-}, \lambda)$, and $R^{\mathrm{f}}_{\mathrm{DOM}}(0^{-}, \lambda)$ and that inverse modeling of these colour spectra along with known concentrations of organic and inorganic colourants *do not yield the specific IOPs of solely absorption and inelastic scattering*, but rather *some possible hybrid of specific IOPs representing the combined contributions of elastic and inelastic processes attributable to the indigenous colourants.* Thus, inelastic processes such as luminescence, which have not been considered in this work, would also be represented within these hybrid IOPs.

In this regard, the limnological choice of terminology for such inherent optical properties (namely, the optical cross section spectra) is particularly appropriate. The term optical cross section (first used in Bukata et al., 1981b) was adopted from atomic and nuclear collision theory, since it rightfully implies that a specific aquatic component will act as an effective target for a photonic interaction (bombardment resulting in absorption or elastic scattering or inelastic trans-spectral scattering of the impinging photon). Consistent with this terminology, the units of optical cross sections are area per unit mass of the aquatic component (e.g., m^2/mg). Thus, using indigenous IOPs obtained from in situ measurements of volume reflectance (or of water-leaving radiance) and known organic and inorganic component concentrations will result in retrieval uncertainties of chlorophyll, suspended minerals, and dissolved organic matter that would be significantly smaller than those resulting from use of laboratory-determined indigenous IOPs in inverse models that neglect the impact of Raman scattering and fluorescence. Precisely how much smaller these retrieval uncertainties become is a matter of conjecture that certainly warrants further investigation.

Concluding remarks

The volume reflectance spectrum just beneath the air–water interface, $R(0^{-}, \lambda)$, is comprised of volume reflectance resulting from absorption, elastic scattering $R_{\mathrm{es}}(0^{-}, \lambda)$, inelastic Raman scattering $R_{\mathrm{r}}(0^{-}, \lambda)$, trans-spectral fluorescence from chlorophyllous pigments $R^{\mathrm{f}}_{\mathrm{chl}}(0^{-}, \lambda)$, and trans-spectral fluorescence from dissolved organic matter $R^{\mathrm{f}}_{\mathrm{DOM}}(0^{-}, \lambda)$, components that are sensitive to the spectral and trans-spectral optical properties of the chlorophyll, suspended minerals, and dissolved organic matter coexisting within the water column. Therefore, neglecting the impacts of inelastic scattering and fluorescence in inverse models (i.e., models that extract the coexisting concentrations of chlorophyll, suspended minerals, and dissolved organic matter from a remote measurement of aquatic colour) can result in discrepancies between inferred and actual values of chlorophyll, suspended minerals, and dissolved organic matter.

However, optical cross section spectra determined from concurrent in situ optical data and accurately determined indigenous organic and inorganic component concentrations approximate the totality of elastic and inelastic contributions to volume reflectance or water-leaving radiance. Use of such optical cross section spectra, therefore, would minimize the retrieval uncertainties of nonlinear multivariate inverse modeling. In actuality, use of these optical cross section spectra might well eliminate the need to further consider Raman scattering and fluorescence for many (albeit not necessarily all) inland and coastal waters.

We are certainly not suggesting that bio-optical models incorporating inelastic processes should be discarded. Mathematical rigor is always a valued commodity. The use of the inelastic equations reviewed herein requires precise values of a large number of inelastic input parameters that are not always readily available, and ofttimes their impact is of little consequence. Further, inversion of such mathematically intensive models may become cumbersome and possibly insoluble. However, we are suggesting that the use of field-determined optical cross section spectra provides a practical means of circumventing these difficulties for many inland and coastal water bodies. We are also aware that the use of in situ determined optical cross section spectra is itself not free from criticism. The optical cross section spectra of organic and inorganic CPAs are species dependent, as well as geographically and temporally dependent. In addition, determination of indigenous optical cross section spectra is a labour-, time-, and cost-intensive activity involving field-data collection, laboratory analyses, and mathematical modeling. The optical cross section spectra determined for one water body cannot be indiscriminately applied to another water body or possibly even applied to other regions of the same water body (this statement, however, also applies to inelastic optical properties and to laboratory determinations of spectro-optical cross sections). Because of these spatial and temporal complexities, we have long advocated that a catalogue of optical cross section spectra for all waters of environmental consequence be compiled on a global basis. To date, such a catalogue contains a limited number of entries. Although the optical cross section spectra of chlorophyll-bearing biota and dissolved organic matter display spectral dissimilarities, by far the greatest discrepancies in inland water cross section spectra are displayed by the suspended inorganic matter resulting from global geologic diversities. However, Bukata et al. (2001) have shown that a judicious selection of watersheds displaying comparable geologic origin–history enables use of surrogate inorganic optical cross section spectra. The ability to use similar optical cross section spectra for waters of geologic comparability should somewhat reduce the number of required entries in the optical cross section catalogue.

This differential in optical cross section spectra determined in naturally controlled in situ environments and in technologically controlled laboratory environments is, of course, not restricted to the interaction of visible solar and sky radiation with organic and inorganic matter co-resident within a natural water column, but rather is systemic to the cumulative and synergistic responses of ecosystems to multiple interactive stressors. The principal implication to the remote sensing of case 2 waters, however, can quite simply be stated as follows: to mitigate the impacts of trans-spectral processes in remotely estimating coexisting concentrations of chlorophyll, suspended minerals, and dissolved organic matter in case 2 waters, it is essential to employ optical cross section spectra determined from multivariate analyses performed on in situ spectro-optical data in waters of known composition.

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