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Impacts of land-use on surface waters at the watershed scale in southeastern China: Insight from fluorescence excitation-emission matrix and PARAFAC

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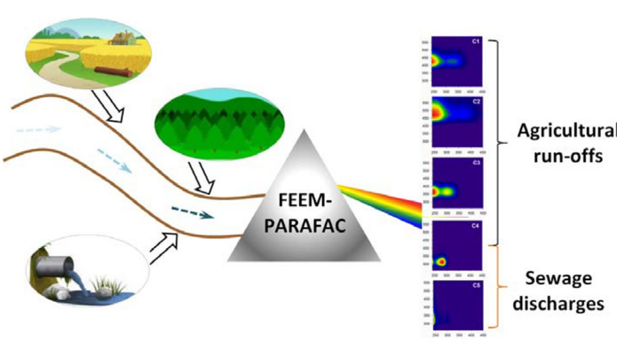
HIGHLIGHTS

- Impacts of land use on water quality were evaluated at the watershed scale in southeastern China.
- Fluorescence EEM combined with PARAFAC was employed for pollutant source tracking.
- Significant effects of agriculture on stream water quality were reflected by multiple indices.
- Anthropogenic discharges can be indicated with sensitivity by a PARAFAC component.
- The approach of fluorescence technique shows great potential for watershed management.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, the Chinese government has strengthened its efforts in surface water protection and restoration through strict policies and heavy investments. A clear understanding of the impacts of land use on water quality is necessary in order to ensure an effective and efficient implementation of the ongoing surface water restoration program in China. To this end, four small watersheds (less than 5000 ha) in southeastern China, which have clear gradients in the intensities of agriculture (17.0–45.4%), forest (35.2–73.6%) and built-up area (3.3–8.5%), were investigated regarding the impacts of land use on water quality. In addition to the general water quality indices, characteristic components derived by fluorescence excitation-emission matrices (FEEMs) coupled with parallel factor analysis (PARAFAC) were employed to explore a more accurate association between land use and water quality. The results show that agricultural intensity has significant effects by elevating the concentrations of dissolved organic carbon (DOC, an approximate six-fold increase) and total phosphorous (TP, an approximate four-fold increase) in the surface waters. A total of five PARAFAC components representing terrestrial (three components) and protein-like (two components) substances were identified. The PARAFAC results indicate that land-use patterns affected the dissolved organic matter (DOM) in the aspects of both amount and composition. The intensity (R.U.) of the terrestrial components showed a strong correlation ($r^2 = 0.95$, $p = 0.01$) with

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agricultural land percentage. Moreover, although the proportion of built-up area varies with a relatively small range, a protein-like component could predict its impact with excellent sensitivity ($r^2 = 0.94$, $p = 0.02$), whereas the general water quality indices were incapable of predicting the impact due to their multiple sources. The results of this study demonstrate that the FEEMs-PARAFAC technique provides an inexpensive and effective tool for policy makers to overcome the insensitivity of general water quality indices, particularly for the restoration of watersheds with complex land-use patterns.

1. Introduction

After more than three-decades of rapid economic development, an extensive challenge has arisen for the surface waters in China (Jiang, 2009; Lu et al., 2015; Wang et al., 2008; Yang et al., 2017), particularly for highly populated regions such as southeastern China (Qin et al., 2010; Wen et al., 2016; Zhang et al., 2010). This challenge is considered to be part of the price to be paid for the rapid economic development (Liu and Diamond, 2005). In recent years, the Chinese government issued a series of strict management policies for water pollution control (Lu et al., 2016), such as the Water Pollution Prevention and Control Action Plan (The State Council of China, 2015), and has also dedicated a large amount of resources to the restoration of deteriorated watersheds (Liu et al., 2013; Zhou et al., 2017). For example, Zhejiang Province, in southeast China, has made significant efforts to improve water quality in recent years. A primary goal is to restore the water quality of surface waters at watershed scale, rather than just the remediation of a few concerned watercourses. However, the historical factors of development models and management strategy, particularly land use management policy, are hindering the achievement of this goal. For instance, like most provinces of southeast China, this region has a high intensity of agriculture (Hao and Ren, 2009; Qiu et al., 2017; Wu et al., 2003), and intensive agriculture is a major source of non-point source pollutants (Carpenter et al., 1998; Ju et al., 2009; Kleinman et al., 2011; Zhou et al., 2018). In addition, a large proportion of rural villages within these watersheds still lack enough efficient sewage collection and treatment facilities, leading to a direct discharge of sewage into receiving rivers (Mostofa et al., 2010; Yu et al., 2015a). Therefore, the situation of this intensive, multiple-source pollution makes watershed restoration practices here much more difficult compared to the western countries with much smaller agricultural and population pressures (Donohue et al., 2006; Hampson et al., 2010; Tu, 2011).

Under this condition, a clear understanding of the specific correlation between land use pattern and water quality will be required in order to ensure an effective water quality restoration implementation for the provinces such as Zhejiang in China. Correlation analysis between the proportions of land-use types and the water quality indices can provide useful quantitative information on how land use affects a watercourse (Allan, 2004). For instance, the effects of agriculture (Wilcock et al., 2011), pasture (Donohue et al., 2006) and urbanization (Hampson et al., 2010; Yu et al., 2015b) for various aquatic environments across the world have been assessed. The available data for watersheds in southeastern China, however, are limited, and the relationship between land use and water quality at watershed scale is still poorly understood. An investigation based on long-term (1947–1996) monitoring data indicated that 94% of the variability in water quality is explained by industrial land area in Shanghai (Ren et al., 2003). Zhao et al. utilized buffer circles (with diameters from 100 to 1500 m) to characterize the relationship between land use and the water quality of a reticular river network in Shanghai. Their results suggested that land use and hydrological variables could explain >50% of the variability in water quality (Zhao et al., 2015). These studies have shown the general impacts of land use on water quality, and further analysis focusing on the specific mechanisms using advanced methods is required (Wan et al., 2014).

A large variety of water chemical indices have been applied to characterize the responses of rivers to land use changes (Liu et al., 2017). A general classification can be drawn as follows: organic substances (e.g., DOC and COD), nutrients (e.g., ammonium, nitrate, nitrite, and total phosphorus), metals (e.g., Mg^{2+}, Ca^{2+} and Mn^{2+}), UV spectrum parameters (e.g., UV_{254} and $SUVA_{254}$), anions (e.g., SO_4^{2-}, Cl^{-1} and Br^-), and other indices such as pH, turbidity and conductivity, etc. The objective for the introduction of these indices is to select some sensitive indicators to assess the impacts of land-use change. However, with the increase of the mixing extent of land use composition, these indices have been found to be not sensitive enough to characterize the influence of various land uses individually due to the nature of multiple-source pollution (Ye et al., 2009). The combination of fluorescence excitation-emission matrix (EEM) and parallel factor (PARAFAC) analyses has proven to be a powerful tool to rapidly quantify and characterize chromophoric dissolved organic matter (CDOM) across a range of environments (Stedmon and Bro, 2008). PARAFAC enables the mathematical separation of chemically independent but spectrally overlapping fluorescence components, which derive from different sources. By the large number of applications across the world (Nimptsch et al., 2015) and the build-up of an online spectral database (Murphy et al., 2014), some robust PARAFAC components with clear origins have been established, such as terrestrial components (e.g., humic-acid and fulvic-acid) associated with agriculture run-off, and protein-like components (e.g., tryptophan and tyrosine) associated sewage/septic effluent, etc. PARAFAC components have been successfully applied as new indicators to investigate the impacts of land use on aquatic environments. For example, the impacts of agricultural practices (Nimptsch et al., 2015), urbanization (Hosen et al., 2014; Meng et al., 2013; Yang et al., 2012), and wetlands (Chen and Jaffe, 2016) have been studied. The predictive accuracy of PARAFAC components has been supported by some advanced analysis such as ultrahigh-resolution mass spectrometry (FT-ICR-MS) (Herzsprung et al., 2012; Stubbins et al., 2014). A combination of general water quality indices and PARAFAC components has the potential to impart a deeper understanding of the relationship between land-use and water quality (Osburn et al., 2012; Osburn et al., 2016; Xu et al., 2016).

In this study, four independent watersheds in Ningbo, Zhejiang Province, China, sharing similar climate and soil types but varying significantly in the compositions of land-use, were investigated. The land-use gradient among these watersheds, which is mainly formed by their landform features, enables a quantitative assessment of the effects of land use in the absence of a long-term water quality monitoring dataset for this region. PARAFAC components derived from an EEM dataset of 723 water samples were used as indicators in addition to the general water quality indices. The goals of this study are as follows: (1) explore the quantitative relationships between water quality and the highly concerning land-use patterns in this region, such as intensive farming practices and untreated rural sewage; and (2) examine whether any PARAFAC components are capable of indicating the impacts of land use on rivers with greater sensitivity than the general water quality indices. This study is intended to provide useful guidance for policymakers that are implementing water quality restoration programs for watersheds with complex land use compositions.