



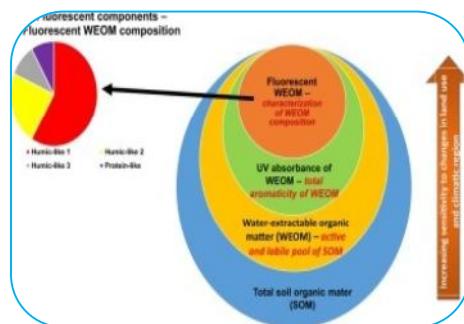
FLUORESCENCE SPECTROSCOPY IS PERFECT TOOL FOR DETECTION OF POLLUTED SAMPLES IN THE FIELD OF AGRONOMY

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ABSTRACT

Water contamination is a global problem that affects both developed and under-developed countries. Groundwater pollution in particular, as a result of human activities and natural contamination, has become one of the most controversial environmental issues. At the United Nations Millennium Summit in 2000 and the World Summit on Sustainable Development in Johannesburg in 2002, world leaders from rich and poor countries alike recognized the critical importance of surface and groundwater fresh water for human development and committed themselves to precise, timely - A committed agenda to meet the world's current and future water resource and sanitation needs.



KEYWORDS : global problem , human activities and natural contamination.

INTRODUCTION

Drinking water is continuously affected by common problems that include toxic inorganics, exposure to heavy metals, bacteria and other pathogens, elevated nitrogen concentrations, and other trace chemicals and micronutrients. Chemical contamination is often considered a lower priority than microbial contamination, because adverse health effects from chemical contamination are usually associated with long-term exposure, while the effects of microbial contamination are usually immediate. Chemicals in water supplies can cause serious health problems, whether the chemicals are naturally occurring or derived from pollution sources. Groundwater pollution is generally traced to four main sources: natural (or environmental), agricultural, industrial, and residential (or domestic) pollution.

Some groundwater pollution occurs naturally even if it is not affected by human activities. The types and concentrations of natural contaminants depend on the subsurface through which the groundwater moves and the quality of the recharged water. For example, groundwater moving through sedimentary rocks and soils can carry a wide range of compounds such as magnesium, calcium and chlorides. Some aquatic organisms have high natural concentrations of dissolved elements such as arsenic, boron, and fluoride. The impact of these natural sources of contamination on groundwater quality depends on the type of contaminant and its concentration. Agricultural sources of groundwater contamination include pesticides, fertilizers, herbicides, and animal waste. Manufacturing and service industries have high demand for cooling water, process water and cleaning water. Groundwater pollution occurs when used water returns to the hydrological cycle. Residential wastewater systems

can be a source of many types of contaminants, including bacteria, viruses, nitrates from human waste, and organic compounds. Similarly, landfilled or buried waste can contaminate soil and leach into groundwater.

Water contamination can be an important factor in limiting available water resources. Its degradation represents a serious problem that affects the environment leading to socio-economic imbalance. For this reason, a strategy to better understand these processes is presented by appropriate and convenient analytical techniques and monitoring activities with time and space actions. In particular, fluorescence spectroscopy can be applied to a wide range of problems, and advances in fluorescence technology are reducing the cost and complexity of previously complex instruments. The implementation of instruments capable of direct use in the field that can provide immediate analysis of the sample to be examined is a request arising from the scientific or legal operator. In this context the new laser spectrofluorometric device CASPER (Compact and Advanced Laser Spectrometer - ENEA Patent) can be a useful device whose measurement has emerged as an effective, fast and low-cost technique to monitor groundwater quality.

Fluorescence occurs when a loosely held electron in an atom or molecule is excited to a higher energy level by the absorption of energy, for example, a photon, and energy is lost as light when the electron returns to its original energy level. (Native state). Figure 1 shows a representation of the energy transfer involved in the fluorescence process: the energy of the excited state S2 is partially dissipated, yielding a relaxed singlet excited state (S1) from which fluorescence is emitted; Not all molecules excited by absorption return to the ground state (S0) by fluorescence emission. Other processes such as collisional quenching, fluorescence resonance energy transfer, and intersystem crossing may also be reduced. The energy of the emitted photon is lower than the excitation energy (Stokes shift), because some of the energy is 'lost' from the excited electron by potential interaction groups with its molecular environment. The fluorescence quantum yield, which is the ratio of the number of emitted fluorescence photons to the number of absorbed photons, is a measure of the extent to which these processes occur. Emission spectra, in particular, vary widely and depend on the chemical structure of the fluorophore and the solvent in which it is dissolved.

Typically, the attenuation of fluorescence intensity measurements is characterized by fluorescence quenching. In dilute solutions or suspensions, fluorescence intensity is linearly proportional to parameters such as molar extinction coefficient, optical path length, solute concentration, as well as the fluorescence quantum yield of the dye and the intensity of the excitation source and fluorescence in the collection. When the sample absorbance exceeds about 0.05 in a 1 cm pathlength, the relationship becomes nonlinear and measurements can be distorted by artifacts such as self-absorption and inner-filter effects. Primary inner-filtration is the absorption of the excitation beam before it reaches the interrogation zone and secondary inner-filtration is the absorption of the emitted fluorescence photons.

Specifically, fluorescence quenching refers to the reduction of fluorescence intensity by another molecule, so that some of the excited fluoresces return to their ground state without emitting photons; This can be due to transient excited-state interactions (collision quenching) or the formation of nonfluorescent ground-state species. Self-quenching is the quenching of one fluorophore by another; This is therefore the case when high loading concentrations or labelling densities are used. Many other environmental factors influence fluorescence properties, particularly the fluorescence intensity and wavelength of organic matter dissolved in soil extracts and natural waters. For example, the wavelength at which molecules fluoresce and the intensity of fluorescence can be affected by changes in pH, chelation with metal ions, and changes in temperature.

FLUORESCENCE SPECTROSCOPY:

Fluorescent organic materials, compounds that absorb light are called chromophores and those that absorb and re-emit light energy are called fluorophores. Fluorophores can be divided into two main classes: intrinsic and extrinsic. The former, referring to naturally occurring fluorophores, include aromatic amino acids, NADH, flavins, derivatives of pyridoxal, and chlorophyll. The latter are added to

the sample to provide fluorescence when none is present or to change the spectral properties of the sample; Dansyl, fluorescein, rhodamine and numerous other substances are included. Aromatic organic compounds provide particularly good subjects for the study of fluorescence due to the energy sharing, unpaired electron structure of the carbon ring. Dissolved organic matter (DOM), in particular, is a complex and poorly understood mixture of organic polymers that play an influential role in aquatic ecosystems and have specific spectrophotometric properties in terms of both absorption and fluorescence. Organic matter in natural water exists in dissolved, colloidal and particulate forms. DOM can originate from a range of sources. Some are transported within hydrologic systems and are derived from and influenced by the geology, land-use, and hydrology of their origin. Some are produced in situ by microbial activity that may be independent sources of organic matter or recycling mechanisms carried into the system.

Fluorescence in natural waters is mainly produced by organic acids (humic and fulvic) and amino-acid groups in proteins, mainly derived from decaying plant material in the soil; Humic acids (HA) have longer fluorescence emission wavelengths than fulvic acids (FA), due to increased aromaticity, carboxylic group content, and polycondensed aromatic and conjugated structures in HA. In addition, the most commonly studied fluorescent organic components of natural waters include amino acids from proteins and peptides. Three fluorescent amino acids tryptophan, tyrosine, and phenylalanine are indicators of proteins and peptides. The fluorescence of this particular amino acid is due to the presence of an indole group a fused ring heterocycle containing both a benzene ring and a heterocyclic aromatic ring in which a nitrogen atom is found as part of the ring or some other aromatic ring structure. Which electrons are 'shared' rather than forming opposite spin pairs and are therefore loosely held and available for promotion to higher energy levels.

These groups of fluorophores are commonly named humic-like, fulvic-like, and protein-like because of the difficulties in definitively identifying individual fluorescent compounds in water, because their fluorescence occurs in the same region of optical space as the standards of these materials. Anthropogenic DOM sources such as farm waste, wastewater treatment outfalls or sewage overflows are all characterized by high levels of protein-like fluorescence. Fluorescence can be used to detect DOM in 'natural' water bodies through differences in fluorescence wavelengths such as fulvic and the ratio of tryptophan to fulvic acid has been used to identify different potential sources of DOM based on characteristic ratios found in different source words.

Fluorescence spectroscopy has also been used to obtain estimates of aromatic hydrocarbon contamination in estuarine and seawater and fluorescent whitening agents (FWA) content as part of most laundry detergent formulations. Fluorimetric methods are commonly used for the determination of chl a and phe a in marine environments. The fluorescence technique also proves to be a good tool for finding information about phytoplankton community composition. Determination of chlorophyll a (chl a) is routinely performed in marine surveys. Chlorophyll concentration correlates with phytoplankton concentration and is thus used to estimate ocean primary productivity and biomass. Besides chl a in marine samples, chlorophyll b (chl b), and chlorophyll c (chl c) are also present with their respective degradation products; Phaeophytin A (PHE A), Pheophytin B (PHE B) and Phaeoporphyrin C (PHE C). Knowledge of accessory pigments (chl b and chl c) and degradation products provides useful information on the taxonomic structure and status of algal communities.

Phytoplankton, with its chlorophyll concentration, is the first level of the aquatic food chain and can be considered a very sensitive indicator of the ecological status of an aquatic system. Numerous studies have demonstrated that changes in phytoplankton taxonomic composition can occur due to organic pollution or enhanced nutrients. In particular, it has been observed that the presence of Cyanophyceae blooms can indicate poor water quality. Toxic phytoplankton blooms harmful algal blooms (HABs) – have increased in frequency and severity in coastal areas over the past two decades. Human activity and human population growth are commonly cited as the main factors for this. Photosynthetic pigments of phytoplankton have the role of capturing sunlight at specific wavelengths for photosynthesis. Chlorophylls are green pigments that contain a stable porphyrin ring-shaped molecule around which electrons are free to migrate. The ring can easily gain or lose an excited

electron, supplying energized electrons to nearby molecules. In this process chlorophyll captures the energy of sunlight and transfers it to other molecules that are responsible for successive steps in the photochemical chain.

Improvements in technology, particularly light-source wavelength range and stability, scanning speed, and data processing capabilities, have made fluorescence spectroscopy a more flexible, rapid, and portable diagnostic tool. It is possible, using simple equipment, to target a single excitation and emission wavelength pair, diagnostic of a specific molecule useful in determining the presence or absence and character of the target compound. Other available techniques include fluorescence emission spectrometry, in which emission is scanned at a fixed excitation wavelength, and synchronous fluorescence scanning (SFS) over a range of wavelengths. Today, excited emission matrix fluorescence spectroscopy (EEMS) is a state-of-the-art technique used, if not as a portable diagnostic tool.

CONCLUSION:

The use of fluorescence spectrometry in water quality studies reveals specific wavelengths associated with specific contaminants. These techniques can be used to map properties and contaminants from water samples collected during routine sampling events, without requiring additional field work. In fact, as technology has improved, fluorescence spectroscopy has become a flexible, rapid, and portable diagnostic tool.

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