UV LED Fluorescence Based Method For Detecting Organic Contaminants In Water: A Review

Julius Okache, Barry Haggett, Tahmina Ajmal
Computer Science and Technology
University of Bedfordshire
Luton, Beds., United Kingdom
julius.okache@beds.ac.uk , barry.haggett@beds.ac.uk, tahmina.ajmal@beds.ac.uk

ABSTRACT: *Analysis of water quality monitoring technique based on fluorescence and UV LED is discussed. Exposing water sample to ultraviolet light induce fluorescence for detecting human faecal contaminants. Fluorometry identifies human faecal contamination in open water bodies. Existing systems make use of manual methods and incandescent filament-based sources combined with narrow-band interference filters. Such systems suffer from problems of stability, bulk, cost and degradation with time. This paper review some techniques used for monitoring bacterial contaminants in water and also looked at the feasibility of developing a UV LED fluorescence based device capable of detecting organic contaminants in water.*

Keywords: Water Quality, Monitoring, UV LED, Fluorescence, Bacteria, Sampling, Organic Contaminants, DOMS

Received: 27 December 2014, Revised 17 January 2015, Accepted 20 January 2015

1. Introduction

Water is essential for life. It is a prerequisite for many of man's activities and as such it must be managed and protected accordingly. The amount of fresh water on earth is limited, and its quality is under constant pressure. Preserving the quality of fresh water is important for the drinking water supply, food production and recreational water use. Water quality can be compromised by the presence of infectious agents, toxic chemicals, and radiological hazards.

The failure to provide water of good quality to all people is conceivably the greatest development failure of the 20th century. The most glaring consequence of this failure is the high rate of mortality among young children from preventable water-related diseases. Although water-related diseases have been eliminated in most developed nations, they remain a major concern in the developing world.

Water quality monitoring in most developing countries still uses manual methods that result in complex detection process knowing that any error of the steps in the detection process will affect the result of the final data [1, 2]. Manual methods of water monitoring processes includes; water quality sampling, transportation and preservation of sample, artificial regular or irregular sampling which are time consuming, strenuous as well as complicated for an extensive and objective response to changes of water quality [3-5].

Water-related diseases are typically placed in four classes: waterborne, water-washed, water-based, and water-related insect vectors. The first three are most clearly associated with lack of improved domestic water supply. Table 1 lists the diseases associated with each class. This life-threatening public health issue would benefit from improved detection methods.

Waterborne diseases: caused by the ingestion of water contaminated by human or animal faeces or urine containing pathogenic bacteria or viruses; include cholera, typhoid, amoebic and bacillary dysentery and other diarrheal diseases.	Water-washed diseases: caused by poor personal hygiene and skin or eye contact with contaminated water; include scabies, trachoma and flea, lice and tick-borne diseases.
Water-based diseases: caused by parasites found in intermediate organisms living in contaminated water; include dracunculiasis, schistosomiasis, and other helminths.	Water-related diseases: caused by insect vectors, especially mosquitoes, that breed in water; include dengue, filariasis, malaria, onchocerciasis, trypanosomiasis and yellow fever

Table 1. Water-Related Diseases [6]

Most private well and spring water supplies as well as small water bodies in modern rural areas are contaminated by coliforms, faecal contamination, Staphylococcus aureus, and standard plate count bacteria [7], as well as water borne diseases caused by bacterial e.g. typhoid and paratyphoid fevers, ear infections resulting from bacteria transmitted from faeces to ingestion. Escherichia coli and faecal streptococci are used as indicators of faecal contamination [8].

Obtaining standard counts of faecal coliforms takes in excess of 30 hours which needs skilled training and laboratory conditions for the preparation of the samples [7, 8]. Consequently, their use is problematic and infrequent, even though rapid drinking water quality checks are essential to prevent swift spread of disease and death. Also, these techniques are beyond the reach of the poorest nations who are in urgent need of good quality water and sanitation improvements.

Changes in intrinsic fluorescence of organic matters can be used to monitor structural changes of bacteria in water. The serious consequences of organic contamination of water have resulted in the widespread use of total organic carbon (TOC) monitoring in addition to resistivity as key indicators of water purity. Drinking water is treated to remove microorganisms and, increasing in many cases, chemical contaminants.

The paper is divided into two sections, the introductory aspect which is found in section I and the literature review with several sub-sections A to F found in section II and looks at organic contaminants as well as LEDs available. This work reviews existing systems to explore the feasibility of designing a suitable UV LED fluorescence based low cost device of for laboratory and in-field testing for bacterial contamination in water.

2. Literature Review

2.1 Organic Contamination

Water quality monitoring is the process of sampling and analysis of water conditions and characteristics; it is the foundation on which water quality management is based. Monitoring of water quality helps in the provision of data that allows for rational decisions to be made on water criteria [9]. The Water Framework Directive (WFD) specifies the quality elements that are used to assess the ecological and chemical status of a water body, quality elements are generally biological (e.g. fish, invertebrates, macrophytes) or chemical (e.g. heavy metals, pesticides, nutrients) [10] . Classifications indicate where the quality of the environment is good, where it may need improvement, and what may need to be improved. They can also be used, over the years, to plan improvements, show trends and to monitor success.

A large number of techniques exist for the determination of the various parameters in water. Each technique has its own particular advantages and disadvantages. When choosing the most suitable technique and apparatus for a particular situation the performance characteristics should be considered as well as cost and size. Some examples of the techniques are summarized below.

Fluorescence spectroscopy is an established analytical method used to identify dissolved organic matter (DOM), trace organics and pollutants in marine, surface and ground-waters. Fluorimeters have been used for many years in the field of water quality monitoring and are established and trusted technique for reliably measuring DOM, chlorophyll and algae. Fluorimeters work by illuminating at one wavelength and detecting light emitted by the target at another wavelength. Only certain substances exhibit this property and at very specific pairs of wavelengths – this means that fluorescence can be a very selective and sensitive optical technique [11].

DOM is made up of decaying animal or vegetable matter. In many cases DOM in a water body will also be accompanied by an active microbial community. It is this microbial community that consumes oxygen – leading to high levels of biochemical oxygen demand (BOD) and the subsequent crashes in oxygen levels that can be so devastating to aquatic ecosystems. Proteins found in the cell walls of these micro-organisms have been shown to fluoresce in the same region as the amino-acid, tryptophan. '*Tryptophan-like*' fluorescence(TLF) can be used as a measure of the microbial activity within a water body and therefore as an indicator of BOD [12, 13].

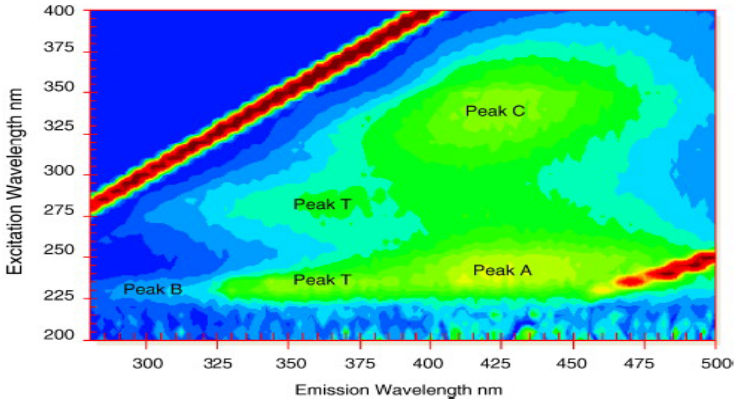

Figure 1. Example of fluorescence excitation-emission matrix (EEM) Showing position of T1, T2, C and A peaks [14]

Common sources of polluting DOM such as silage liquor, cattle and pig slurries and human sewerage all fluoresce when excited at the same short ultra violet wavelengths (~280 nm) [14, 15]. This means that fluorimeters 'adjusted' to this wavelength could be a uniquely useful tool for a wide range of monitoring applications in both rural and urban catchments. Measuring TLF gives a direct measure of the potential for DOM in the watercourse to cause harmful oxygen crashes, in the same way as the BOD 5-day test – but of course results are available instantly. This allows potential problems to be identified much earlier and for the sources of polluting DOM to be identified more quickly and with more certainty. Figure 1 shows that, each fluorophores distinct fluorescent spectra from a single fluorescent compound or overlapping spectra from a range of fluorescent moieties, appears on the EEM as a peak or series of peaks associated with specific excitation and emission wavelength. Peak A, B and C arise due to terrestrial organic matter and dissolve organic carbon present in the water environment while Peak T arise due to tryptophan-like materials. The intensity of the peak can be used as a measure of the concentration of the fluorophore to ppm or ppb levels, depending upon the fluorophore [12]

Fluorophores in natural surface waters are humic-like derived from the breakdown of plant material (peak C and A, [16]). The fluorophores exhibit fluorescence at excitation/emission wavelengths λ_{ex} 304–347 nm /λ_{em} 405–461 nm (Peak C) and λ_{ex} 217–261 nm/λ_{em} 395–449 nm (Peak A) [12]. In addition to humic-like material tryptophan-like and tyrosine-like material as "free" molecules or bound in amino acids and proteins (commonly referred to as peaks T and B respectively, [16]) also exhibit fluorescence at distinctive wavelengths in natural waters. In the above figure, tryptophan-like fluorescence (peak T1) occurs at $\lambda_{ex/em}$ 275–296/330–378 nm while tyrosine-like fluorescence (peak B) was not commonly seen so it was not addressed in their work. Peak T also has a shorter wavelength excitation/emission pair (named T2) with excitation at between λ_{ex} 216–247 nm and emission at between λ_{em} 329–378 nm. Tryptophan-like fluorescence may be exhibited by natural waters where tryptophan is present as 'free' molecules or is bound in proteins, peptides or humic structures. Peaks T and B are related to microbial activity and may be transported in a system (allochthonous) or be created by microbial activity within a system (autochthonous) and this is reflected in the EEM showing fluorophores common in natural waters as seen in figure I. When considering monitoring organic contaminants in water, it is suggested attention be centered on Peak T and B as well as Peak C and M because of their microbial activities in the water.

2.2 Fluoroscence Application In Determination Of Bacteria Contamination In Water

Exposing water sample to ultraviolet light help improves fluorometry for detecting faecal contamination in water. All water fluoresces, although the insensitivity of the human eye to the appropriate wavelengths renders fluorescence invisible to us [17-19]. However, off-the-shelf equipment can detect this fluorescence, and a large body of research [17, 18, 20-23] has shown that water fluorescence is particularly good at identifying faecal contamination (both human and animal). Fluorometry identifies human faecal contamination through the detection of optical brighteners in open water bodies as optical brighteners are sensitive to sunlight [24, 25]. Due to the fact that, optical brighteners are sensitive to sunlight, we decided if exposing water samples to ultraviolet (UV) light to differentiate between optical brighteners and other fluorescing organic compounds could improve fluorometry.

Studies that identified the different constituents of the fluorescence EEM (as shown in [12, 26]) was carried out in the laboratory using a sophisticated bench-top scanning fluorimeter. Once the specific excitation and emission wavelengths of the tryptophan-like peak were identified, and then lower cost portable instruments could be developed that focused solely on that excitation/emission pair (280 nm/340 nm). Due to the short wavelengths required to provide the correct excitation, high power xenon flash lamps were used as the source in early portable tryptophan-like fluorimeters. This meant that they could not be submerged – instead the sample was introduced via a quartz cuvette, and that they were still relatively large and expensive. The breakthrough recently occurred when light emitting diodes (LED) were developed that could attain shorter wavelengths required.

2.3 Wavelengths considerations

Researchers' identified different specific wavelengths of excitation and emission in the study of fluorophore T1 (tryptophan-like materials) and its relationship with BOD [22, 26-29], the wavelength variation is likely to be due to the physical characteristics of individual samples such as pH, metal ions, sample concentration, these factors have not been analysed in a sample by sample basis for any previous work [26].

The disposition and size of this fluorescence are a function of the fluorophores present. Simultaneous scanning of a range of excitation and emission wavelengths generates an excitation-emission matrix (EEM) within which fluorescence peak intensities can be identified with certain ranges [17]. Fluorescence in specific range may be indicative of different organic matter, for example, in fresh waters; fluorescence in the regions as is seen in (Table 2) could be attributed to different organic materials [17, 30].

Fluorescence Peak	Excitation(λ_{ex})	Emission (λ_{em})	Attributed Organic Matter (OM)
Peak A	230-260 nm	400-500 nm	Terrestrial derived OM
Peak C and M	300-370 nm	400-500 nm	Dissolved Organic Carbon
Peak B	230-275 nm	310 nm	Tyrosine
Peak T_1	275 nm	340 nm	Tryptophan-like material
Peak T_2	225 and 235 nm	340 and 360 nm	Tryptophan-like material

Table 2. Fluorescence peak within different regions as indicative of different organic matter [14, 17, 18, 22]

Peak A fluorescence are often attributed to terrestrially derive organic matter and peak C and M are mostly dissolve organic carbon. Peak T1 and T2 are attributed to the tryptophan-like material found within living and dead cellular material, and these are indicative of microbial activity in water.

2.4 Characteristics of suggested dyes to mimic the behaviour of the identifed organic contaminants

Tryptophan, tyrosine and humic acid are the dyes suggested to be used to mimic the behavior of the identified bacteria. Table 3 summarizes the fluorescence characteristics of the three aromatic residues:

The three residues have distinct absorption and emission wavelengths. The fluorescence of a folded protein is a mixture of the fluorescence from individual aromatic residues. Protein fluorescence is generally excited at 280 nm or at longer wavelengths, usually

dyes	Lifetime	Absorption		Fluorescence	
		Wavelengths (nm)	Absorptivity	Wavelengths (nm)	Quantum
Tryptophan	2.6	280	5,600	348	0.20
Tyrosine	3.6	274	1,400	303	0.14
Humic acid	6.4	275	200	330	0.04

Table 3. Fluorescence characteristics of the three aromatic residues

at 295 nm. Most of the emissions are due to excitation of tryptophan residues, with a few emissions due to tyrosine and humic acid. They differ greatly in their quantum yields and lifetimes. Due to these differences and to resonance energy transfer from proximal humic acid to tyrosine and from tyrosine to tryptophan, the fluorescence spectrum of a protein containing the three residues usually resembles that of tryptophan. Concentrations of these aromatic residues are traditionally estimated out of concentrations of organic matter (typically from concentrations of total organic carbon (TOC) or dissolved organic carbon (DOC).

2.5 Potable organic measurement system

Intrinsic fluorescence techniques can be used in developing a UV fluorescence system for detecting organic contamination in a water body. Such a system would employ UV LEDs to illuminate the water sample and detect the resulting fluorescence using a simple photodetector. This would draw on the benefits of LEDs such as stability compared to incandescent sources, their small size, long lifetimes, and low power consumption. Lasers were previously preferred for fluorimetric techniques because of the high intensity and narrow bandwidths but new digital spectroscopic, filtering techniques have made LEDs more popular. LEDs have the additional capability to be coupled with waveguides or optical fibers to a wide variety of detectors such as, photodiode-arrays (PDA), photomultiplier tubes (PMT) etc that allows easy amplification of signal [31]. Other examples of the applications of LEDs systems in the past are described below;

The first LED based photometer was proposed by Barnes in 1970 [31], they applied the system for chemical sensing. The most common use of LEDs in chemical sensing has been with photometric methods, i.e., measurement of spectral attenuation of the LED by a sample. Traditionally incandescent sources and filters have been used for these tests. However, this arrangement has inherent stability problems associated with filter degradation and bulb stability. Recently LEDs have been favoured, as alternative tight sources, for the reasons outlined in the LED characteristics above. Light-Emitting Diodes (LEDs) are reliable means of indication compared to light sources such as incandescent and neon lamps. LEDs have long operating lifetimes, small size, low power consumption, low heat, fast switching speeds, shock and vibration resistant. It disadvantage is that it has limited cooler (monochromatic) narrow viewing angle, current limiting resistor required and it is a polarised device. LEDs are available from narrow angle to wide angle and compound LEDs.

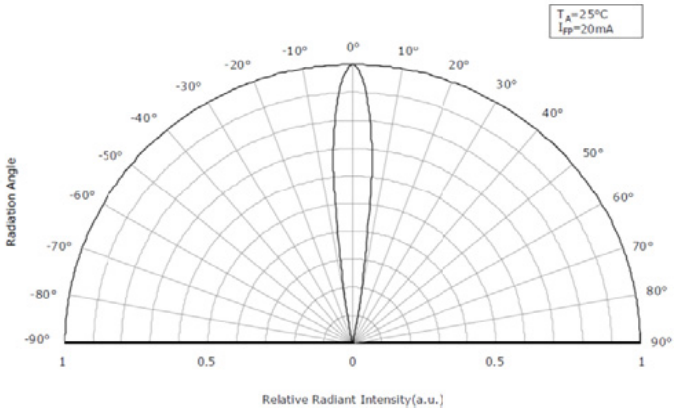

Figure 3. optical characteristics of LEDs [32]

A wide angle viewing angle is good when you have a large data sample. A viewing angle is where the contrast is 50% of maximum contrast directly in front of the sample host. This is where the degradation starts to be noticeable. LEDs are measured so that the line along half the viewing-angle from directly forward is half the brightness as at directly forward. LED performance is based on

some few primary characteristics such as LED colours showing LEDs to be highly monochromatic emitting pure colour in narrow frequency range.

Different LED compounds emit light in specific regions of the visible light spectrum and therefore yields high intensity levels. The exact choice of the semiconductor material used will determine the overall wavelength of the photon light emissions and therefore the resulting colour of the light emitted.

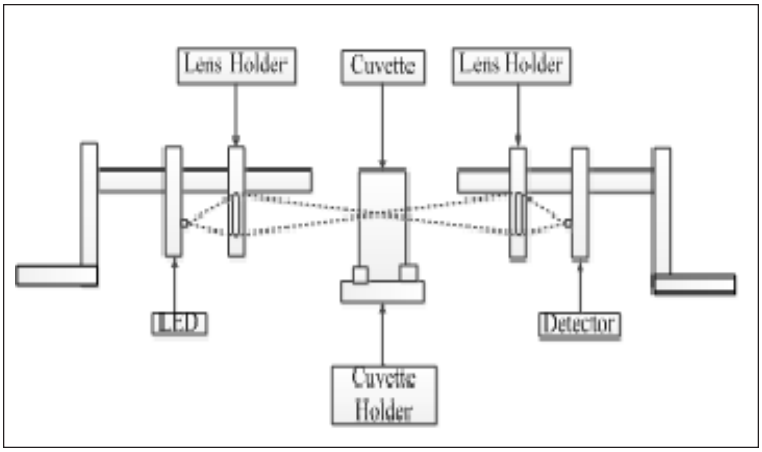

Figure 2. An example of LED based system for absorption measurements [33]

Colour/Center Wavelength (nm)	Manufacturer/ Model #	Cone Half Angle (°)	Operating Current (mA)	Forward Voltage (V)	Luminous Intensity (mW)	Diameter of FOV (mm)
UV 260	THORLABS	60	30	6.5-8.0	0.300	15
UV 275	THORLABS	60	30	6.2-7.5	0.8	15
UV 300	THORLABS	60	30	5.5-7.5	0.50	15
UV 315	THORLABS	60	30	5.5-7.5	0.600	15

Table 4: suggested Optical Output of Individual 1 LED Modules

LEDs are made from exotic semiconductor compounds such as Gallium Arsenide (GaAS), Gallium Phosphide (GaAsp), Silicon Carbide (SiC) or Gallium Indium Nitrite (GaInN) all mixed together at different ratio to produce a distinct wavelength of colour [34]. Different LED compounds emit light in specific regions of the visible light spectrum and therefore yields high intensity levels. The exact choice of the semiconductor material used will determine the overall wavelength of the photon light emissions and therefore the resulting colour of the light emitted.

The wavelength of the light emitted that is determined by the actual semiconductor compound used in forming the PN junction determines the actual colour of the LED, therefore the colour of the light emitted by an LED is not determined by the colour of the LED's plastic body. From the table above we can see that the main P-type dopant used in the manufacture of LEDs which is Gallium (Ga, atomic number 31) and that the main N-type dopant used is Arsenic (As, atomic number 31) giving the resulting compound of Gallium Arsenide (GaAs) crystal structure. An LED's brightness or luminous intensity is dependent upon the amount of forward bias current applied to the diode and the viewing angle. An LED specified for certain brightness with 20mA current will provide less illumination at 10mA. Luminous intensity is usually characterized in terms of millicandelas (mcd).

The figure above shows different types of LEDs and they are; Gallium Arsenide (GaAs) – infrared, Gallium Arsenide Phospide

Typical LED Characteristics			
Semiconductor Material	Wavelength	Colour	V_F @ 20mA
GaAs	850-940nm	Infra-Red	1.2v
GaAsP	630-660nm	Red	1.8v
GaAsP	605-620nm	Amber	2.0v
GaAsP:N	585-595nm	Yellow	2.2v
AlGaP	550-570nm	Green	3.5v
SiC	430-505nm	Blue	3.6v
GaInN	450nm	White	4.0v

Table 5. Light Emitting Diodes colours [34]

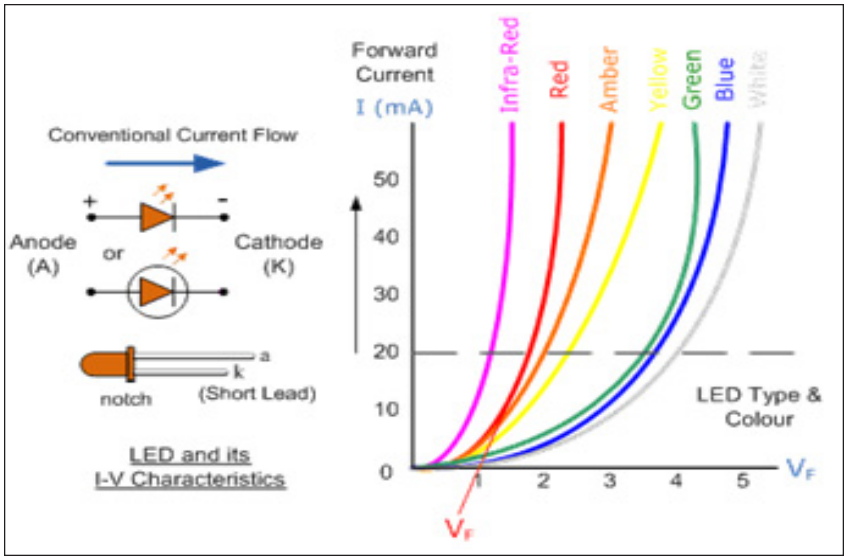

Figure 4. Light Emitting Diode (LED) Schematic symbol and I-V Characteristics Curves showing the different colours available [34]

(GaAsP) – red to infra-red, orange, Aluminium Gallium Arsenide Phosphide (AlGaAsP) - high-brightness red, orange-red, orange,and yellow, Gallium Phosphide (GaP) - red, yellow and green, Aluminium Gallium Phosphide (AlGaP) – green, Gallium Nitride (GaN) - green, emerald green, Gallium Indium Nitride (GaInN) - near ultraviolet, bluish-green and blue, Silicon Carbide (SiC) - blue as a substrate, Zinc Selenide (ZnSe) – blue, Aluminium Gallium Nitride (AlGaN) – ultraviolet [34]. Few other examples of the applications of LEDs systems in the past are described below;

In situ and remote sensing measurements of optical properties of CDOM are easy to conduct and make the use of CDOM absorption and fluorescence as a substitution for DOC concentration. Current methods for the analysis of water often require the use of reagents and may require extensive sample preparation. Below are some of the systems that use optical sensing.

Fluorescence spectroscopy was used in measurements of ocean water by Coble and he showed that deep-UV excitation of naturally occurring organic compounds in water can yield significant and unique fluorescence signals in the near UV to visible wavelengths [16, 35]. As a result of Cobles work, Sharikova and Killinger used deep-UV laser-induced-fluorescence techniques to detect trace organic compounds in drinking water and distilled spirits and were able to show readings within the time span of few seconds [36], their system is been used to detect ppb trace level of plasticizer Bisphenol-A (BPA) that leached into drinking water and the system detected and monitored trace levels of DOCs within ocean currents.

UV LED and laser induced fluorescence was used to monitor trace organic contaminants in portable water by Killinger et al., their system measured fluorescence of portable liquids contained within an optical quartz cell that includes a UV laser which generates a light beam [37]. Their system was built with a concave mirror that collects fluorescence signal; The 266 nm UV laser used for excitation in their work cost $10,000 [37]. Accordingly, there is a need for a low cost, compact LED to replace the known expensive lasers

Currently, no real time or reagentless laser-induced-fluorescence systems have been authorized for use by water treatment plants. However, for the past several years, some water agencies have been testing a selected range of UV absorption and fluorescence water monitoring instruments. One such device is a UV-visible (200 nm-750 nm) absorption instrument from S-CAN in Austria that can detect small changes in the optical absorption properties of Water. Another fluorescence-based test is used to monitor water for the e-coli bacteria. This involves growing a culture obtained from a water sample, using a fluorescence dye or stain, and counting the organisms by either visual micro scopes or laser readers. Fluorescence is also used in liquid chromatography laser-induced fluorescence, or LC-LIF, a technique in which a capillary tube is used to separate the chemical species and a laser reads the separated column.

UV-LEDs are good alternative light sources for the novel LIF system, because they make the apparatus less expensive and more compact than conventional systems. This review is focused toward the development of new optical spectroscopic measurement techniques having the potential to provide enhanced capabilities over conventional water monitoring. The sensitivity of the novel laser and LED induced fluorescence system is several orders of magnitude better than that of a conventional spectrophotometer that often uses UV lamps and wavelength selecting spectrometers for its emission source, with a single or double monochromators with photo-multiplier tubes for fluorescence detection.

2.6 Discusssion and Conclusion

Natural water analysis using fluorescence excitation and emission matrices (EEM) gives a rapid determination of the proportions of labile and refractory organic matter present. EEM analysis also facilitates a greater understanding of the oxygen depleting potential of organic matter in unfiltered samples in a shorter timescale than would be the case using BOD or other manual methods.

The literatures reviewed so far, reinforces the idea that a portable device which could measure organic contamination in water as described is feasible and potentially a way forward in the branch of this study as a portable, robust, accurate methods of analysis of organic contamination in water is much needed to help during monitoring such that the samples can be analysed in the field in real time as well as enabling results to be available faster, at low cost and minimizing the risk of contamination by eliminating the transport of the samples. Our research is focus on UV fluorescence method for surface water quality monitoring.

References

[1] Yue, R., Ying, T. (2011). A water quality monitoring system based on wireless sensor network & solar power supply, in *Cyber Technology in Automation, Control, and Intelligent Systems (CYBER), 2011 IEEE International Conference on,* 126-129.

[2] Wang, J., Ren, X., Shen, Y., Liu, S. (2010). A remote wireless sensor networks for water quality monitoring, In Innovative Computing & Communication, 2010 *Intl Conf on and Information Technology & Ocean Engineering, 2010 Asia-Pacific Conf on (CICC-ITOE), 7-12.*

[3] Wang, Z., Wang, Q., Hao, X. (2009). The design of the remote water quality monitoring system based on WSN, In *Wireless Communications, Networking and Mobile Computing, WiCom '09. 5th International Conference on,* 1-4.

[4] Othman, M. F., Shazali, K. (2012). Wireless Sensor Network Applications: A Study in Environment Monitoring System, *Procedia Engineering,* 41, 1204-1210.

[5] Stedmon, C. A., Seredyñska-Sobecka, B., Boe-Hansen, R., Le Tallec, N., Waul, C. K., Arvin, E. (2011). A potential approach for monitoring drinking water quality from groundwater systems using organic matter fluorescence as an early warning for contamination events, *Water Res.,* 45, 6030-6038, 11/15.

[6] Gleick, P. H., *Dirty-Water*. (2002). *Estimated Deaths from Water-Related Diseases 2000-2020.* Pacific Institute for Studies in Development, *Environment, and Security*.

[7] Lamka, K. G., LeChevallier, M. W., Seidler, R. J. (1980). Bacterial contamination of drinking water supplies in a modern ruralneighborhood, *Appl. Environ. Microbiol.,* 39, 734-738.

[8] Fawell, J., Nieuwenhuijsen, M. J., Contaminants in drinking water Environmental pollution and health, *Br. Med. Bull.,* 68, 199-208.

[9] Bartram, J., Ballance, R. (1996). Water Quality Monitoring: A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes. *Taylor & Francis*.

[10] (Jan 2013). *Method statement for clasification of surface water bodies v3 (2012 classification release)*. Available: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290506/LIT_5769_ed4e2b.pdf. DOI: NA/EAD/0113/pdf/v3.

[11] Foley, J., Batstone, D., Keller, D. (2007). The Challenges of Water Recycling–Technical and Environmental Horizons, 2007.

[12] Hudson, N., Baker, A., Ward, D., Reynolds, D. M., Brunsdon, C., Carliell-Marquet, C., Browning, S. (2008). Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An example from South West England, *Sci. Total Environ.,* 391, 149-158.

[13] Van den Broeke, J., Langergraberb, G., Weingartnera, A. (2006). On-line and in-situ UV/vis spectroscopy for multi-parameter measurements: a brief review, *Spectroscopy Europe,* 18, 15-18.

[14] Langergraber, G., Broeke, J. v. d., Lettl, W., Weingartner, A. (2006). Real-time detection of possible harmful events using UV/vis spectrometry, *Spectroscopy Europe,* 18, 19-22.

[15] Baker, A., Ward, D., Lieten, S. H., Periera, R., Simpson, E. C., Slater, M. (2004). Measurement of protein-like fluorescence in river and waste water using a handheld spectrophotometer, *Water Res,* 38, 2934-2938.

[16] Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy," *Mar. Chem*., 51, 325-346.

[17] Bridgeman, J., Baker, A., Carliell-Marquet, C., Carstea, E. (2013). Determination of changes in wastewater quality through a treatment works using fluorescence spectroscopy, *Environ. Technol.,* 1-20.

[18] Carstea, E. M. Fluorescence Spectroscopy as a Potential Tool for in-situ Monitoring of Dissolved Organic Matter in Surface Water Systems.

[19] Zhao, Y., Zhang, X., Han, Z., Qiao, L., Li, C., Jian, L., Shen, G., Yu, R. (2009). Highly Sensitive and Selective Colorimetric and Off, On Fluorescent Chemosensor for Cu2 in Aqueous Solution and Living Cells, *Anal. Chem.,* 81, 7022-7030.

[20] *Progress on Sanitation and Drinking-Water*. (2013). Available: http://apps.who.int/iris/bitstream/10665/81245/1/9789241505390_eng.pdf.

[21] Hartel, P. G., Hagedorn, C., McDonald, J. L., Fisher, J. A., Saluta, M. A., Dickerson, J. W., Jr.,Gentit, L. C., Smith, S. L., Mantripragada, N. S., Ritter, K. J., Belcher, C. N., Exposing water samples to ultraviolet light improves fluorometry for detecting human fecal contamination, *Water Res.,* 41, 3629-3642, 8.

[22] Bridgeman, J., Bieroza, M., Baker, A. (2011). The application of fluorescence spectroscopy to organic matter characterisation in drinking water treatment," *Reviews in Environmental Science and Bio/Technology,* 10, 277-290.

[23] Baker, A., Spencer, R. G. (2004). Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy, *Sci. Total Environ.,* 333, 217-232.

[24] Hartel, P. G., Hagedorn, C., McDonald, J. L., Fisher, J. A., Saluta, M. A., Dickerson, J. W., Jr,Gentit, L. C., Smith, S. L., Mantripragada, N. S., Ritter, K. J. (2007). Exposing water samples to ultraviolet light improves fluorometry for detecting human fecal contamination, *Water Res.,* 41, 3629-3642.

[25] Cao, Y., Griffith, J. F., Weisberg, S. B. (2009). Evaluation of optical brightener photodecay characteristics for detection of human fecal contamination, *Water Res.,* 43, 2273-2279.

[26] Hudson, N., Baker, A., Reynolds, D. (2007). Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review, *River Research and Applications,* 23, 631-649.

[27] Hudson, N., Urquhart, G., Baker, A., Ward, D., Reynolds, D., Carliell-Marquet, C. (2006). Water quality monitoring using tryptophan-like fluorescence. in *AGU Fall Meeting Abstracts,* 2006, 1521.

[28] Mudarra, M., Andreo, B., Baker, A. (2011). Characterisation of dissolved organic matter in karst spring waters using intrinsicfluorescence: Relationship with infiltration processes, *Sci. Total Environ.,* 409, 3448-3462, 8/15,

[29] Bieroza, M., Baker, A., Bridgeman, J. (2010). Fluorescence spectroscopy as a tool for determination of organic matter removal efficiency at water treatment works, *Drinking Water Engineering and Science,* 3, 63-70.

[30] Leblanc, L., Dufour, É. (2002). Monitoring the identity of bacteria using their intrinsic fluorescence, *FEMS Microbiol. Lett.,* 211, 147-153.

[31] Toole, M. O'., Diamond, D. (2008). Absorbance based light emitting diode optical sensors and sensing devices, *Sensors,* 8, 2453-2479.

[32] (April 22, 2013). *Specifications for UV LED*s. Available: http://www.nichia.co.jp/specification/products/led/NSHU591B-E.pdf.

[33] Murphy, T. (1995). Development of LED-based instrumentation for the monitoring of water quality parameters. (2nd June 2014). *Light Emitting Diode*s. Available: http://www.electronics-tutorials.ws/diode/diode_8.html.

[34] Coble, P. G. (2007). Marine optical biogeochemistry: *The chemistry of ocean color*, *Chem. Rev.,* 107, 402-418.

[35] Sharikova, A. V., Killinger, D. K. UV-Laser and LED Fluorescence Detection of Trace Organic Compounds in Drinking Water and Distilled Spirits.

[36] Killinger, D. K., Sharikova, A., Sivaprakasam, V. (2013). Deep-UV LED and Laser Induced Fluorescence Detection and Monitoring of Trace Organics in Potable Liquids.