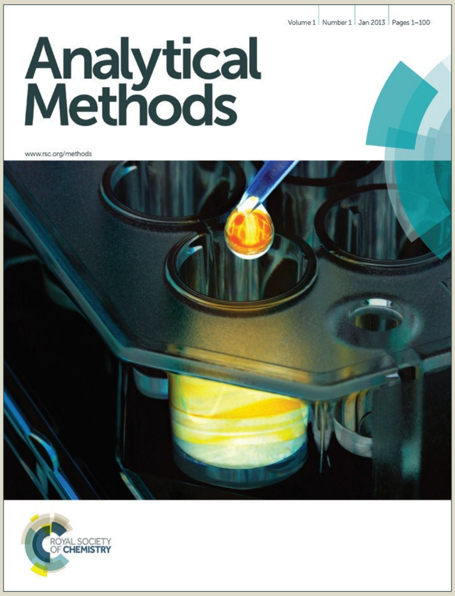
Analytical Methods



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ASSESSMENT OF PHOTO-OXIDATIVE ALTERATIONS TO NATURAL ORGANIC MATTER IN WATER USING FLUORESCENCE EXCITATION EMISSION MATRICES AND THE LIQUID CHROMATOGRAPHY-ORGANIC CARBON DETECTION TECHNIQUES

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Abstract

The fluorescence excitation emission matrices (FEEM) and the liquid chromatography-organic carbon detection (LC-OCD) are relatively novel techniques currently used in analysing natural organic matter (NOM) in water. Regardless of the complexity of the natural water matrices, the LC-OCD is able to characterize and quantify NOM as five fractions; biopolymers, humic substances, building blocks, low molecular weight neutrals, low molecular weight acids. The FEEM on the other hand characterises chromophoric dissolved organic matter and maps out their emission and excitation spectral contours. In the current study, these techniques were used to characterize and quantify NOM fractions in raw water used for cooling at Eskom power stations, as well as monitor the changes in their composition when irradiated with different intensities of sunlight using a sun simulator. The effect of hydrogen peroxide (H_2O_2) (an oxidant) together with exposition to light on NOM was also investigated. Firstly, results showed that humic substances decreased with increased sunlight intensities. Secondly, a similar trend was observed with the introduction of an oxidant such as H_2O_2. The dissolved organic carbon (DOC) in irradiated samples decreased from 9.100 ppm (in raw water) to 8.832, 8.838 and 8.175 ppm for *0.6-sun*, *1.2-sun* and *2.0-sun,* respectively. At constant sunlight intensity (of 1.2-sun), addition of increasing amounts of 30% H_2O_2 showed that the distribution of NOM fractions changed significantly. Generally, a decreasing trend in molecular weight of NOM was observed with increased irradiation intensity as well as increased oxidant amounts. The fluorescent signature peaks showed that the humic substances (HS) contours changed but remained relatively stable with an increase in light intensity. The results of the peroxide effect on humic substances showed disappearing spectral signature peaks. No spectral contours in the HS region were formed for samples illuminated by near natural sunlight intensity in the presence of H_2O_2. These results are particularly important in understanding NOM in water used for cooling in power generation stations.

Keywords: Fluorescence excitation emission matrices; Humic substances; Natural organic matter, Liquid chromatography-organic carbon detection; Sunlight

1. INTRODUCTION

Natural organic matter (NOM) research has witnessed ground breaking studies over the last 10 years. This decadal research has generated valuable information on NOM characterisation and fractionation in soils and natural waters (1-4). Over these years, NOM is reported to play an important role in chemical interactions in water (5, 6). However, NOM being a highly complex matrix, only studies on its fractions will give useful information on how it chemically interacts with other dissolved components in water. It is therefore necessary, to characterise and discuss individual fractions of NOM and their chemical behaviour. For example, humic acid (which dissolves in alkaline conditions) and fulvic acid can control a number of chemical interactions in natural water. These include dissolution, mineralization, precipitation, adsorption, chemical transport and complexation (7-9). Therefore, the NOM fractions ought to be well characterized and quantified. In addition, their alterations due to chemical changes need to be addressed.

It is noteworthy that NOM serves as microbial food and the resulting by products of organic nature termed as autochthonous (microbial) NOM [10]. Furthermore, NOM is important in many other processes including UV-visible light attenuation, buffering pH and binding metals, among others (10-16). The NOM metal binding processes control the transport and bio-cycling of carbon and nitrogen compounds (17). These could be in the form of organometallic and coordination compounds. Compared to allochthonous (terrestrial) NOM (25−30% aromatic carbon), autochthonous NOM has a lower aromaticity degree (12−17% aromatic carbon). In addition, autochthonous NOM is more labile and has a lower capability to block UV-radiation (18, 19).

However, the phenomenon of UV-penetration into surface waters has an impact on NOM fractions. Changes in UV light penetration and NOM lability needs to be investigated in our natural surface water that serve domestic and industrial purposes. Power generating companies in South Africa (Eskom), for example, use water for conventional cooling of turbines. Their cooling chambers are supplied by raw water from the rivers with NOM inputs and other chemical constituents. When metals such as Ca and Mg combine with inorganic anions in the raw water to form salts at specific physicochemical conditions, the salts precipitate on pipe walls forming scale deposits, which are very difficult to remove. This forces the power generation companies to replace their water pipes from time to time (20).

It is important to note that the presence of certain NOM fractions in a higher proportion, may be a solution to problems such as scaling in pipes. This is because, some NOM fractions are large organic molecules (such as humic acid (HA) and fulvic acid (FA)) and could act as excellent ligands that coordinate with metals to form relatively stable complexes. Other literature expresses this in terms of chelate effect (21). However, the complexation capacity will depend on the physico-chemical conditions (such as pH, temperature, light penetration, presence of oxidants and their composition. This study seeks to show the changes in composition of raw water as a function of changing sunlight intensities. Furthermore, the changes to NOM in the presence of an oxidant were investigated. This 'photo-oxidation' of natural organic matter was determined using raw water obtained from Vaal River, which serves Lethabo and Kriel power stations (of Eskom, South Africa) with cooling water.

2. EXPERIMENTAL

2.1. Sampling and sample pre-treatment

Raw water samples from Vaal River were collected at the points feeding Lethabo and Kriel power stations and immediately filtered through a 0.45 µm PES membrane and stored at 4 °C. Cooling water was collected at Lethabo and Kriel and similar treatment to that of raw water applied and stored for analysis.

2.2 Instrumental analysis

The FEEM measurements were conducted using the fluorescence AquaLog Spectrometer (Horiba, New Jersey, USA). The NOM fractions were characterized and quantified by the LC-OCD (DOC-Labor, Karlsruhe, Germany). Prior to LC-OCD chromatographic separation, samples were passed through 0.45 µm filters and all the soluble organics were identified by the LC-OCD system and the FEEM.

2.2.1 Light simulation studies

The UV-visible light used in this study was obtained from a light simulator (**Fig. 1**) that producing light that was measured with the equivalent of natural sunlight. Accordingly, an equivalent of natural sunlight was termed *1-sun*; twice the natural sunlight termed *2-sun*; thrice termed as *3-sun*; and so on. These intensities are obtained by adjusting the sample distance between **a** and **b** at a power of 400 to 500W (**Fig. 1**).

Fig. 1

2.2.2 LC-OCD analysis

The LC-OCD technique, developed to identify fractions natural organic matter in water, gives quantitative information and qualitative results regarding molecular size distribution of organic matter in water (22). This technique separates components on the basis of their molecular size. The separated fractions include humic substances, biopolymers, building blocks, low molecular weight organic acids, neutrals and hydrophobic organic carbon. In addition, it generates an improved diagram for the characterisation of aquatic humic substances (HS-diagram) (7). The HS-diagram is a plot of the spectral absorption coefficient (SAC) to the organic carbon (OC) ratio (aromaticity) of HS fractions against their nominal molecular weights. The spectral absorption coefficient (SAC) is obtained with the ultra-violet detection. The SAC/OC ratio describes the specific UV absorption of the HS peak, and a measure of HS aromaticity, since the response in UVD reflects aromatic and unsaturated structures. As shown, a close correlation exists between HS aromaticity and HS-molecularity (7).

Water samples were injected into a column filled with a chromatographic gel material where large molecules are eluted first followed by the smaller compounds (22). To achieve quantification of organic carbon, organic nitrogen and specific UV absorbance at λ-254, their signal responses in the samples at different retention times were measured with an online organic carbon detector, organic nitrogen detector and UV detectors, respectively (**Fig. 2**) (7). The LC-OCD analysis was carried out following the procedure described by Huber *et al*. (7).

Fig. 2

2.1 Fluorescence excitation emission matrices (FEEM)

The FEEM spectrometer used a xenon excitation flash lamp with excitation and emission slits set to a 10 nm band pass. To obtain excitation emission maps, excitation wavelengths were varied from 200 nm to 600 nm at 3 nm band pass. For each excitation wavelengths, the emission was detected at longer wavelengths (0.3 nm steps). A 1 cm quartz fluorescence cuvette held the water samples during analysis. To account for Rayleigh scattering, a blank solution (Type 1 water) response was subtracted from the fluorescence spectra of the sample to be analysed. All Spectra were then corrected by Rayleigh 1st and 2nd (10 band slits) order masking and inner filter effect corrections were made. Spectral correction of fluorescence EEMs was done to reduce instrumental and sample biases as a result of wavelength-dependent variability. Processed FEEM spectra were then plotted using Origin Lab. FEEM distinguishes chromophoric dissolved organic compounds by assessing the absorption/emission wavelength spectral information for different groups of molecules. These are classified into spectral groups based on excitation and emission wavelengths where the molecules fluoresce (**Fig. 3**) (23). The simultaneous working setup of the FEEM technique incorporates a light source (usually a xenon lamp and a detector. Overall, a FEEM measurement is a rapid, quantitative evaluation (15 seconds to 2 minutes) that determines all the species independent of fluorescent properties.

Fig. 3

3.0 RESULTS AND DISCUSSION

The LC-OCD results (in which all the fractions identified in water were quantified in terms of organic carbon concentration) are presented in tabular, chromatogram and HS-diagram forms (**Table 1**, **Fig. 4-6**). The FEEM spectral signatures for raw, cooling, irradiated and oxidized raw water samples are shown in **Fig. 7-8**.

3.1 LC-OCD results

The dissolved organic carbon (DOC) concentrations in raw water was found to be 9.106 ppm. Results showed that light irradiation of a 50 mL sample of raw water decreased the DOC after the 4 hours of measurement. The DOC in irradiated samples decreased from 9.100 ppm to 8.832, 8.838 and 8.175 ppm for *0.6-sun*, *1.2-sun* and *2.0-sun*, respectively. On the other hand, the oxidation experiment results (at constant sunlight intensity of 1*.2-sun*) showed that the distribution of NOM fractions changed on addition of hydrogen peroxide (H_2O_2), from the original distribution in raw water. This is expected as oxidation leads to increased dissolved organic compounds, due to the decomposition of organic particles. On the other hand, sunlight has an effect on NOM as it results in its breakdown. Combining light and an oxidant, as done in this study shows that NOM will change and this could be attributed to the breakdown of NOM and or aggregation of molecules which r-arrange to form new organic compounds. At *1.2-sun*, the corresponding DOC values for 250, 500 and

750 µL of H_2O_2 were 16.81, 9.946 and 8.832 ppm, respectively. Generally, exposition to light conditions showed decreased DOC values from those of raw water, whereas combined exposition to light and H_2O_2 showed an increase in DOC values. Apparently, the dissolved organic nitrogen distribution in the various samples did not show any particular trend. However, the dissolved organic nitrogen values were relatively reduced in the samples with hydrogen peroxide.

The average molecular weights of HS in all the analysed water samples are shown in **Table 1**. These nominal molecular weights were plotted in the humic substances-diagram (HS-diagram) alongside the aromaticities of the HS, to give a picture of how hydrophobic/hydrophilic NOM was in the various water samples. The highest molecular weight of HS was observed in raw water samples (523 g mol L^{-1}). A decreasing trend in molecular weights was observed with increased exposition to light and increased H_2O_2 amounts. The range of molecular weight was found to be 204-510 g mol L^{-1}. The observed decrease in molecular weights when samples were exposed to light in the presence of H_2O_2, was significantly different from the values of photo-irradiation in absence of H_2O_2 ($P<0.05$, one-way ANOVA, generated by Origin Lab V8 at 0.05 confidence limits).

Table 1

The level of unsaturation in NOM fractions could be expressed by aromaticity levels. In the current study, the NOM aromatic character as shown in the HS-diagrams follows the order C>B>A (**Fig. 4a**) for the photo-irradiated water samples. **Fig. 4b** shows only one photo-oxidised sample data point, D, measured for 250 µL H_2O_2. The corresponding molecularities of water samples follow the order A>B>C. Generally, the aromaticity and molecularity decreased with increased radiation which implied decreased hydrophobicity. The HS-diagram showed that irradiated samples were relatively on the same position on the plot. Only one sample exposed to light and hydrogen peroxide was mapped on the HS-diagram (i.e. the 250 µL H_2O_2 irradiated sample).

The aromaticity relationship is critical in describing the NOM composition. In essence, it allows discrimination of relatively higher molecular weight humic acids and fulvic acids from water. However, aromaticity of compounds with the same molecular weight could be different depending on the source. For example, Huber *et al*. (2011) reported that aromaticity of fulvic acid was higher in brown water lakes (7). Their reports are attribute the disparity to sunlight induced bleaching of substances, which is related to the current study. The photo-bleaching however depends on the depth of water since deeper layers are not relatively accessible and hence lower impact of solar radiation.

Fig. 4

The chromatograms based on the organic carbon detector, the organic nitrogen detector and ultraviolet detector responses of samples exposed to light and those exposed to light and H_2O_2 are presented in **Fig. 6**. The NOM of raw water from Vaal River was mainly comprised of humic substances of fulvic acid character **(Fig. 4**). As a function of the intensity of radiation, the humic substances decreased in percentage from 61.5% in raw water to 57.8 and 61.4 down, for *0.6-sun*, and *2.0-sun*, respectively. At *1.2-sun*, however a slight increase in humic substances was observed (i.e from 61.5 to 61.7%). Furthermore the molecular masses decreased from 523 g mol L^{-1} to 510, 469 and 408 g mol L^{-1} for 0.6-sun, 1.2-sun and 2.0-sun, respectively. Regardless of the concentration of humic substances, the specific absorbance at λ_{254} decreased with an increase in the light intensity. The corresponding SUVA values were, 4.24, 3.77 and 3.74, for 0.6-sun, 1.2-sun and 2.0-sun, respectively. These values which deviate from the raw water SUVA (4.11), show a decreasing trend as the intensity of light was increased. The same observation was made in biopolymers with a decrease from 3.9% in raw water to 3.4%, 3.4% and 3.6% for samples exposed to sunlight of *0.6-sun*, *1.2-sun* and *2.0-sun* intensities, respectively. The decreasing SUVA values observed showed increased hydrophilicity of NOM present in the water samples (24).

In the presence of H_2O_2 and exposition to light conditions, the SUVA values were found to reduce even further to 0.81, 0.57 and 0.27 for 250, 500 and 750 µL aliquots of $H_2O_{2.}$ The molecular masses decreased from 523 g mol L^{-1} to 275, 278 and 204 g mol L^{-1} for 250, 500 and 750 µL, respectively. The concentration of humic substances decreased even further. An interesting observation was made on the behaviour of the building block peaks (42-50 min), that is, the concentration increased with the amount of radiation and concentration of the oxidant.

The biopolymer fraction and the corresponding concentrations of dissolved organic nitrogen increased with irradiation but decreased with oxidation (all oxidative processes being carried out at *1.2 sun*) (**Fig. 5**), as expected. Literature indicates that the physico-chemical treatments such as oxidation or adsorption have degradative effects on NOM. These studies have also indicated that oxidation processes such as ozonation reduce the biopolymer fraction of NOM (8, 24). The biopolymer fraction mainly consists of polysaccharides, proteins and some humic-like substances (25). These compounds are generally large molecules and henceforth their decrease suggests that advanced oxidation processes have a degradative of NOM.

Besides the humic substances, biopolymers and building blocks, the low molecular weight acids and low molecular weight neutrals (weakly and uncharged organic compounds) identified are shown in **Fig. 5**. The low molecular weight organic responses of samples exposed to light and samples exposed to both light and H_2O_2 showed a high percentage of low molecular weight neutrals and a non-significant percentage of low molecular weight acids. In most water samples exposed to light, the low molecular weight acids were not produced. The values for the low molecular weight neutrals decreased from 1.38 ppm in raw water to 1.09, 0.918, 0.708 ppm in *0.6, 1.2* and *12.0 sun*, respectively. In the presence of H_2O_2 and exposition to light conditions, the low molecular weight neutrals showed a decreasing trend i.e. 2.32, 2.31 and 1.32 ppm for 250, 500 and 750 µL aliquots of H_2O_2 added. In the presence of an oxidant, low molecular weight acids were formed which decreased drastically with increased H_2O_2 aliquots. These acids may have been as a result of oxidation of NOM in the raw water.

Fig. 6 shows chromatograms for the various NOM fractions. The ultra-violet detector response in the HS peak was observed to reduce with intensity showing decreased levels of unsaturation and aromaticity of humic substances. We conclude that exposition to light decreases aromaticity. Combined H_2O_2 and exposition to light conditions minimise the HS peak, an indication of changing the form and structure of HS.

Fig. 5

Fig. 6

3.2 FEEM signatures of raw and cooling water

Complete NOM characterization of the raw, samples exposed to light and those exposed to combined H_2O_2 and exposition to light conditions was achieved using combined LC-OCD and FEEM techniques. In addition, the fluorescent contours of cooling water samples of two stations are discussed. The FEEM spectra of fluorescent NOM for samples of raw and cooling water collected from Lethabo and Kriel power stations are shown in **Fig. 7**. The raw water used for cooling in these stations is sourced from the same river, the Vaal. It is for this reason that the FEEM spectra of raw and cooling water used in these two stations are compared. Subsequently, the discussions on FEEM spectral signatures were based on raw water that was sampled at Lethabo power station. The results in this study show that the FEEM signatures were independent of the sampling power station but depended on the stage at which sampling took place (i.e raw and cooling water sampling stages). The cooling water showed more intense spectral contours, all of which were obtained at the primary humic-like region (excitation wavelength 280-350 nm/ emission wavelength 350-500 nm). The increase in the intensity of fluorescent signatures can be explained by the water processes that lead to concentration of fluorescing compounds in water.

The spectral analysis was performed at 0 to 1146 spectral units for raw water and 0 to 1650 units for cooling water. The effect of exposition to light conditions and combined H_2O_2 and light conditions on fluorescent organic matter are discussed in **Section 3.2.1** and **3.2.2**. The only fluorescing organic material found in this study corresponds to signatures obtained for the humic-like substances region. The FEEM signatures observed in this study, showed the changes occurring to humic substances as a result of increasing exposure to light intensities and oxidizing substances in water. The main essence of our study, therefore, is to describe the processes that bring about primary changes in raw water before use in the cooling water chambers, where recycling takes place.

Fig. 7

3.2.1 The effect of light intensity

The intensity of spectral contours (indicating humic-like substances) was dependent on the intensity of light (**Fig. 8**). The identified EEM spectra of humic substances obtained by using different light intensities showed that the spectral contours reduced with increased UV-visible radiation. In all the samples exposed to light, the spectral signatures (predominantly appearing in the humic-like region), showed a significant decrease in fluorescence. The results in this study showed that spectral response was lowest at *1.2-sun*. However, the decrease in spectral contour intensities with increasing sunlight was not linear. We noted similar signatures for *0.6-sun* and *2.0-sun*. We thus concluded that near natural or natural sunlight (that is, 1.*2 sun* ~1.0 *sun*) could be the most appropriate condition for attenuating the humic substances in water. The EEM spectra of raw water before exposition to light was in close agreement with what was reported in other studies. The effect of surface waters on the reduction of the HS peak due to exposure to sunlight, has also been reported elsewhere (2, 26). Moreover, these previous studies have shown that natural light has a significant effect on the alterations to humic-like materials, which means the total fluorescence intensity of humic-like materials could be much higher in closed water systems, such as those used in the cooling water chambers.

Fig. 8

3.2.2 Effect of H_2O_2 to NOM in surface water

The results of the peroxide effect on humic substances showed disappearing spectral signatures (**Fig. 9**). No spectral contours in the HS region were formed for samples exposed to light with near natural sunlight intensity in the presence of hydrogen peroxide. The oxidative reactions between NOM and oxidizing compounds such as peroxides, dictate the destiny of humic substances in natural water. While recycle systems produce HS-concentrates, oxidizing agents affect their composition and probably, the physico-chemical characteristics of NOM. Overall, the FEEM spectra supported the results of LC-OCD analyses regarding the breakdown and oxidation of humic substances in NOM in the presence of UV-visible light. Oxidation processes, including chlorination, ozonation and advanced oxidation processes application of both UV alone and UV/hydrogen peroxide are reported to breakdown humic substances, hence reduced humic like peaks/spectra (9, 26). Decreases in fluorescent intensity of humic materials when advanced oxidation processes are used have been attributed to the decrease in molecular weight since the hydroxyl radicals are postulated to attack high electron density regions within double bonds (9).

Fig. 9

3.3 Overall implications of advanced analytical assessments of NOM attenuation

The techniques, SUN simulation, LC-OCD and FEEM used for the assessment process of NOM in river water (for Eskom cooling in condenser tubes in power stations), gave important information on NOM fractions and how they change due to the influence of sunlight and the presence of an oxidant. Advanced treatment processes which apply to both solar radiation and solar radiation combined with hydrogen peroxide, showed reduced humic like peaks/spectra, especially for the latter. However, the changing intensities of solar radiation did not impact greatly on the humic substances. A similar study by Legrini et al in 1993, reported this observation: “that the humic substances in water remain relatively stable when irradiated with UV light” (27). Since humic acids and fulvic acids are structurally large molecules with many carboxylic and hydroxyl groups, it is therefore expected that they remain relatively stable in solution. In terms of denticity, Mg and Ca ions will prefer multi-dentate binding with the large molecules due to their chelate effect. Once Ca and Mg form stable complexes with these large molecules, precipitation of their carbonate salts is inhibited. This is because the complexation of the Ca and Mg by the organic matter reduces the total concentration of the metals and hence inhibits the formation of their carbonate salts that cause scaling. That way these cations (whose salts normally form scale in pipes carrying cooling water) are kept in solution, with reduced potential for scale formation.

The impact of solar radiation on the distribution of NOM fractions (including HS) must therefore be measured appropriately. With the advanced LC-OCD, it is possible to quantify various NOM fractions (discussed in **Section 3.1**). The FEEM technique on the other hand, offers capacity to explain the spectral maps and signatures formed by fluorescing groups shown in **Fig. 3.**

4.0 CONCLUSIONS

The LC-OCD technique was used to quantify the distribution of NOM fractions in water samples after irradiation with simulated sunlight alone as well as sunlight in the presence of an oxidizing agent such as H_2O_2. The DOC values and the NOM molecular weights were altered by light and more significantly by a combination of light and H_2O_2. Except under the influence of H_2O_2, the HS peak remained, relatively stable.

All irradiated sample aromaticity versus molecularity relationships could be explained on the HS-diagram. On the contrary only one ‘photo-oxidised’ sample data point (measured for 250 µL H_2O_2) could be shown on the HS-diagram. This implied that a combination of light and an oxidant (H_2O_2 in this study) is very effective in breaking down aromatic and unsaturated structures in the NOM matrix. This was confirmed by the decrease SUVA values.

Low molecular weight acids formed were found to increase with increase in hydrogen peroxide amounts. In this case, the low molecular weight neutrals showed a decreasing trend i.e. 2.32, 2.31 and 1.32 ppm for 250, 500 and 750 µL aliquots of H_2O_2 added.

The cooling water at Eskom undergoes continuous recycling processes which in turn concentrate the organic constituents. The type of NOM classified as the "humic-like" fraction was successfully identified and quantified using the FEEM spectral contours for raw and cooling water.

A decrease in spectral contour peak intensities was observed for the light-attenuated samples. No spectral contours in the HS region were formed for the samples illuminated by near natural sunlight intensity in the presence of hydrogen peroxide.

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Table 1:

Distribution of various NOM fractions in various raw, in samples exposed to light and samples exposed to both light and H_2O_2 (DOC = dissolved organic carbon and HS = humic substances)

	Concentration in ppb								
Sample	DOC	Biopolymers	HS	Dissolved organic nitrogen	SUVA	Molecular weight $(gmol^{-1})$	Building blocks	Low molecular weight neutrals	Low molecular weight acids
Raw water	9106.0	354	5597	321	4.11	523	1109	1382	nq
0.6 Sun	8832.0	304	5104	188	4.24	510	1013	1085	24.0
1.2 Sun	8838.0	287	5146	325	3.77	469	1095	918.0	Nq
2.0 Sun	8175.0	297	5021	300	3.74	408	1054	708.0	Nq
1.2 Sun + 250 µL H_2O_2	16813	139	5932	321	0.81	275	2266	2324	475
1.2 Sun + 500 µL H_2O_2	9946.0	145	4434	147	0.57	278	2253	2315	299
1.2 Sun + 750 µL H_2O_2	8832.0	55.0	3924	84	0.27	204	1653	1316	6.00

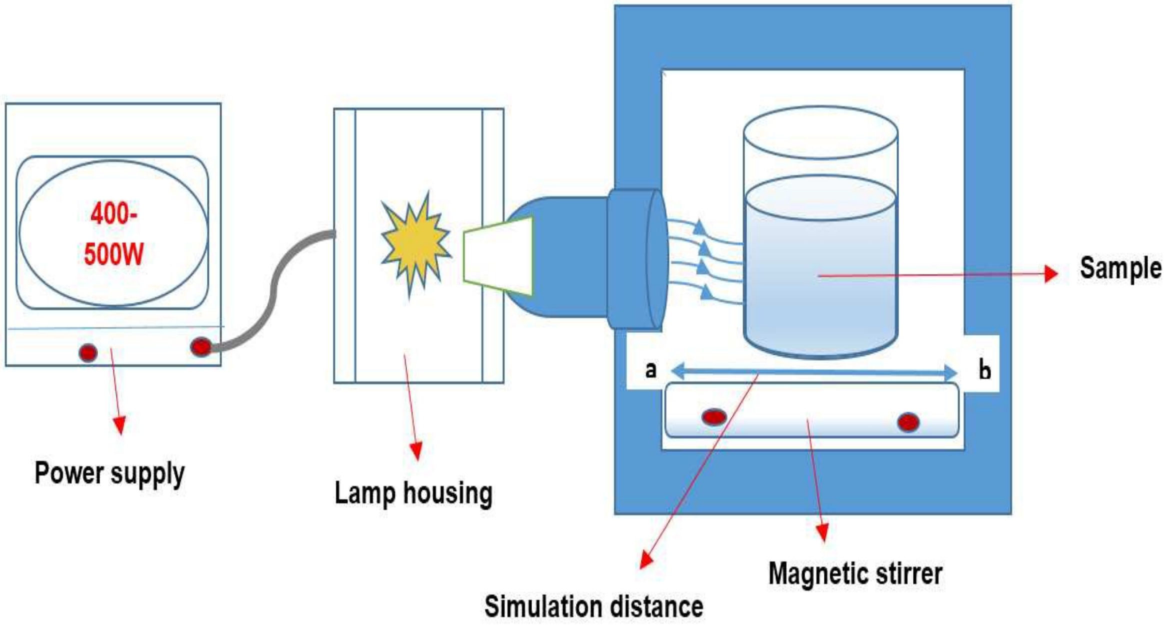


Fig. 1: A scheme showing the sun simulator

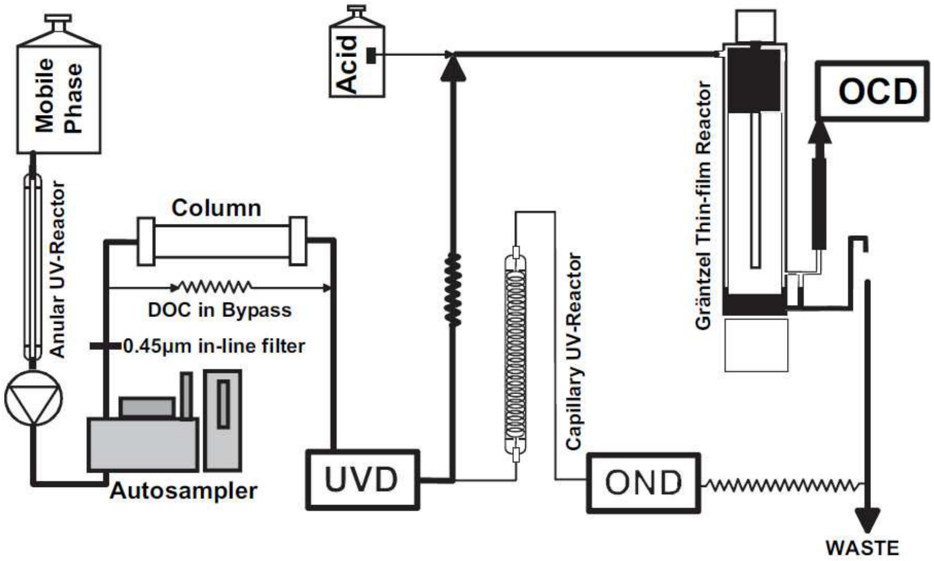


Fig. 2: Scheme of the liquid chromatographic LC-OCD system. The UVD detector for specific UV absorbance at λ-254 responses is the first detector (non-destructive) (Adopted from Huber et al., 2011)

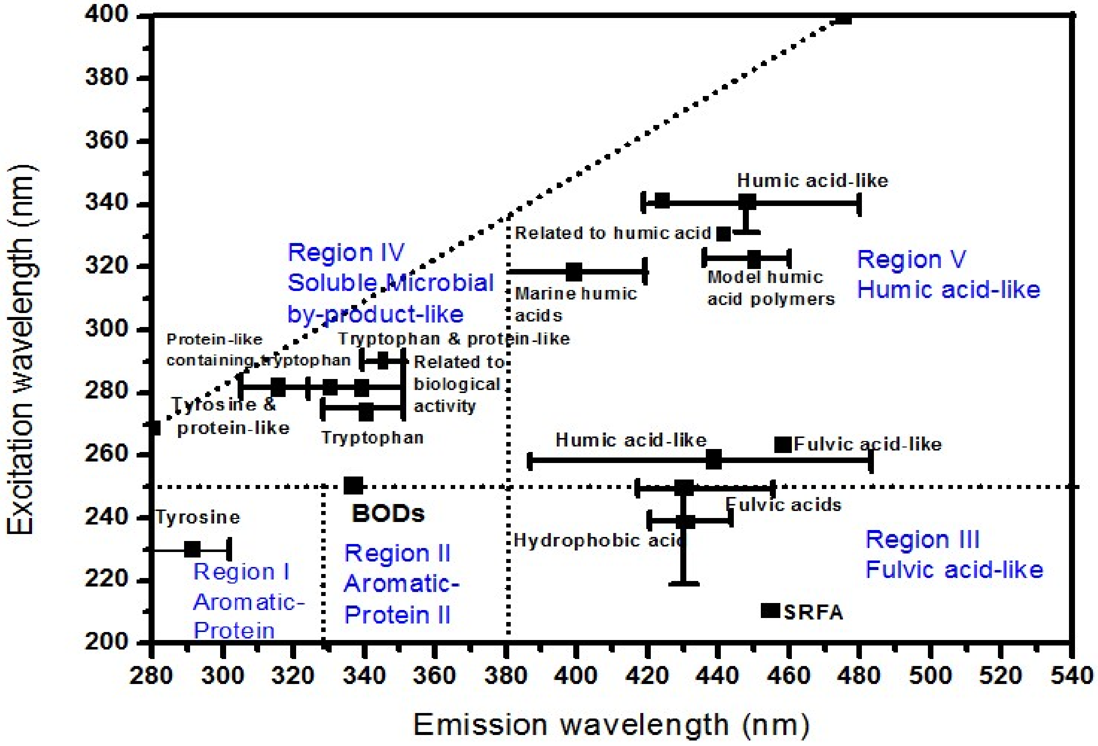


Fig. 3: FEEM spectral regions based on reported definite excitation (Ex) and emission (Em) wavelengths (I. Ex 250 nm, Em 350 nm; II. Ex 280 nm, Em 380 nm (soluble microbial by products); III. Ex 250 nm, Em 280 nm (humic acid-like organics); IV. Ex 300 nm, Em 400 nm and V. Ex 214 nm, Em 400 nm (fulvic acid-like molecules) (Nkambule et al., 2012).

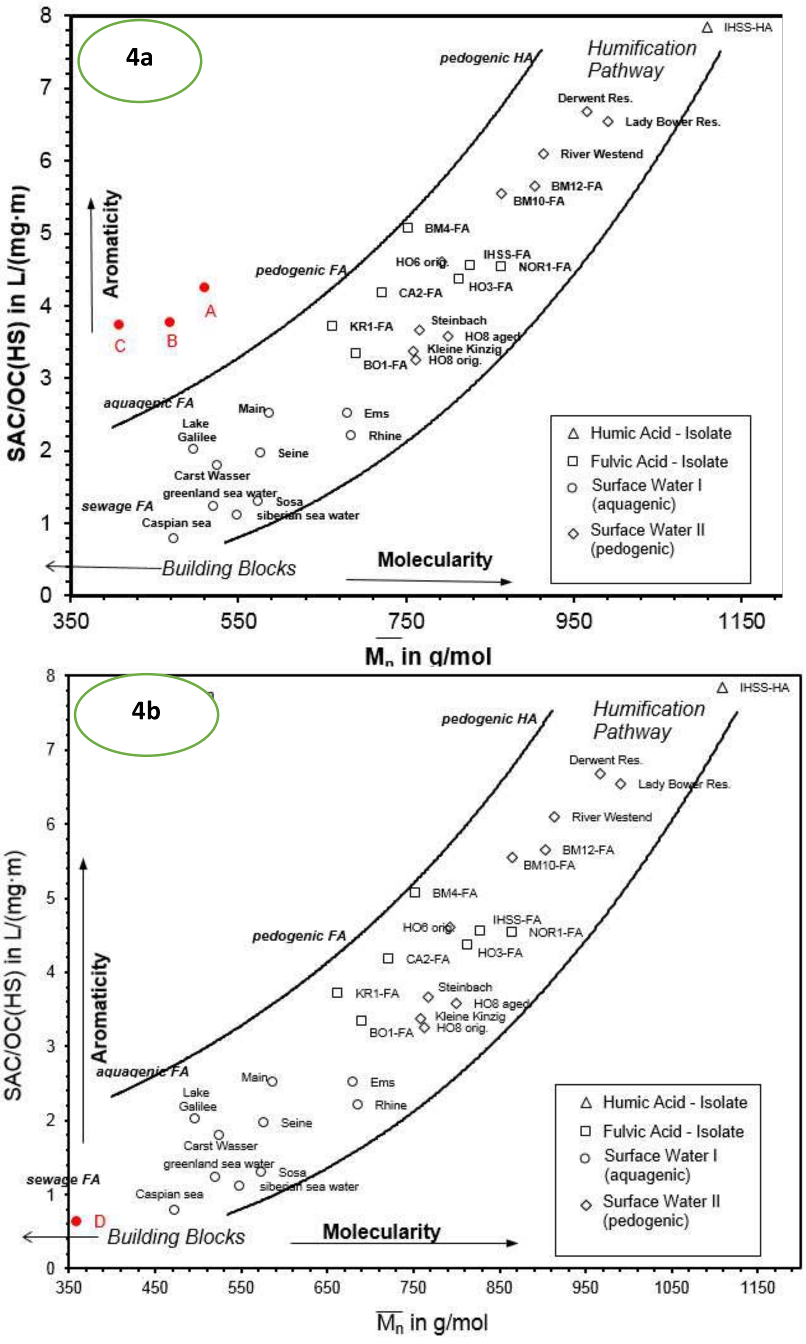


Fig. 4: The HS diagrams showing the aromatic character (x-axis) of HS fractions as a function of their molecularity (y-axis) as a plot of the Spectral Absorption Coefficient (SAC) to the organic carbon (OC) ratio (aromaticity) of each HS-fraction against its nominal molecular weight (M_n). **4a** shows three components: A raw water irradiated by 0.6-sun, B water irradiated by 1.2-sun and C irradiated by 2.0-sun. **4b** only shows element D, the raw water irradiated by 1.2-sun in the presence of 750 µL of H_2O_2.

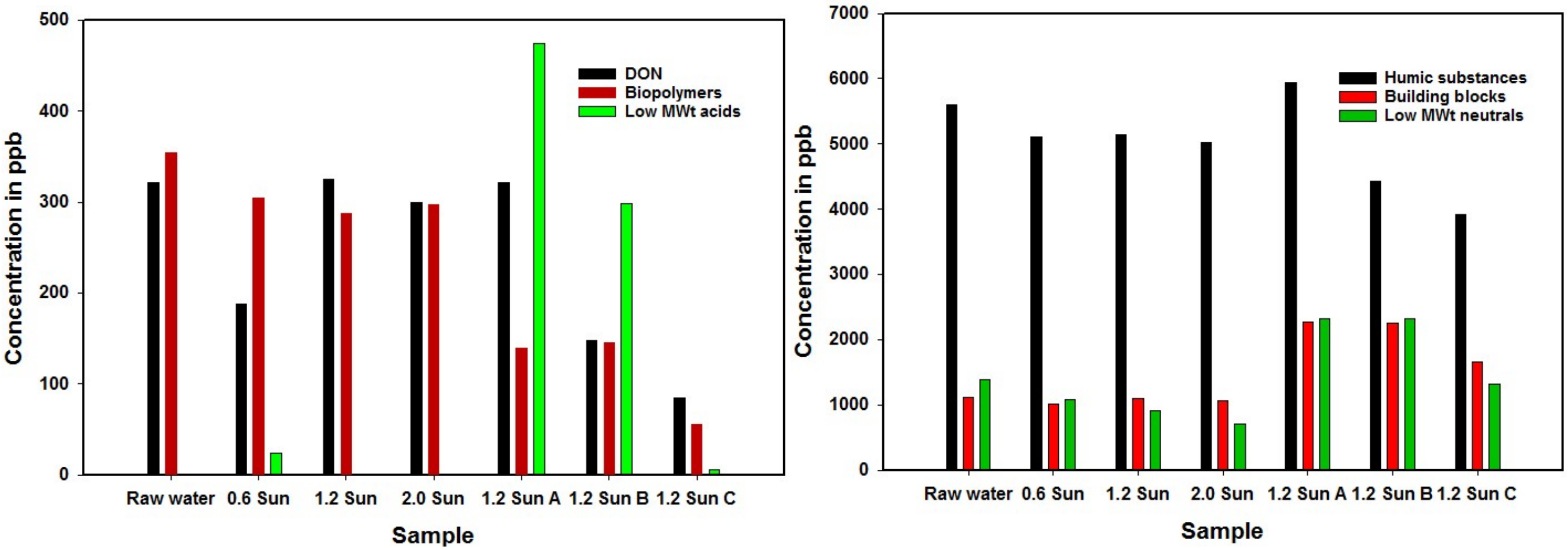


Fig. 5: The NOM fractions distribution after of exposition to sunlight. A, B and C represent increasing amounts of hydrogen peroxide i.e. 250, 500 and 750 µL, respectively.

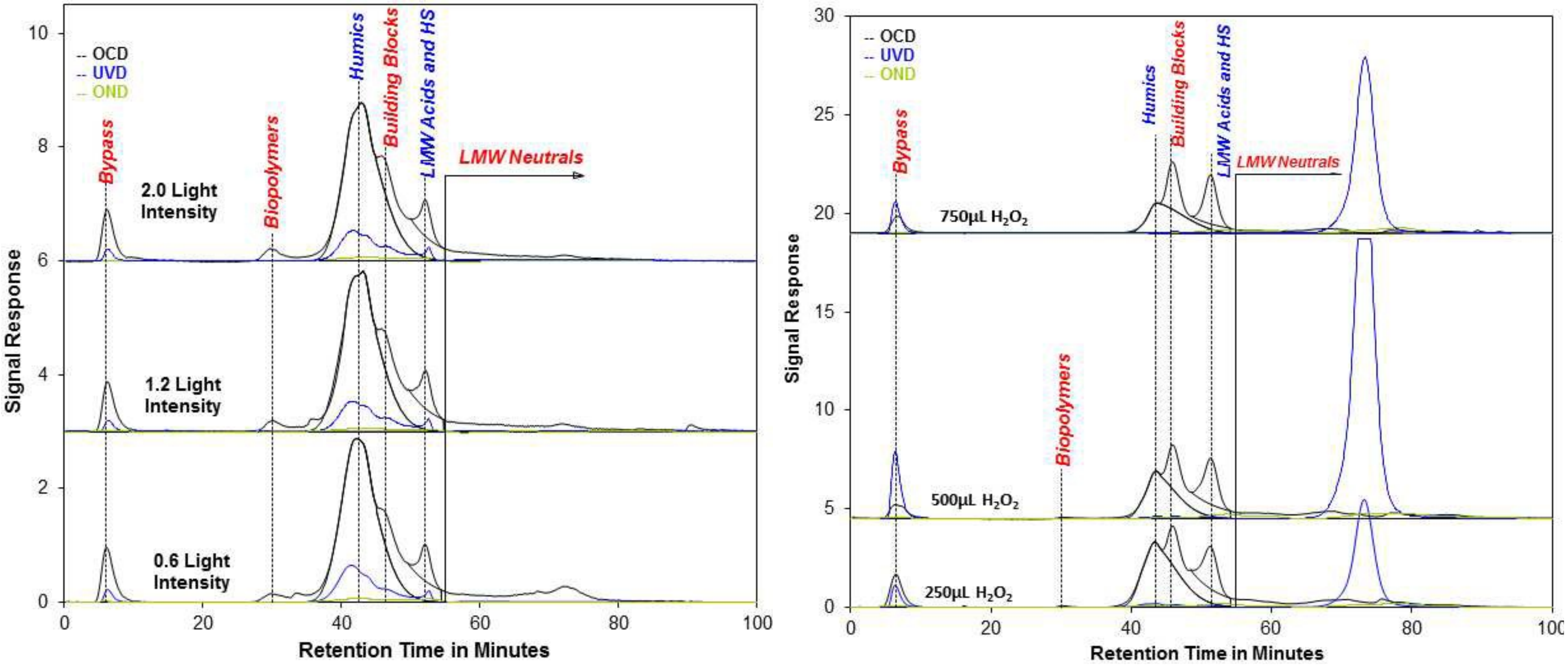
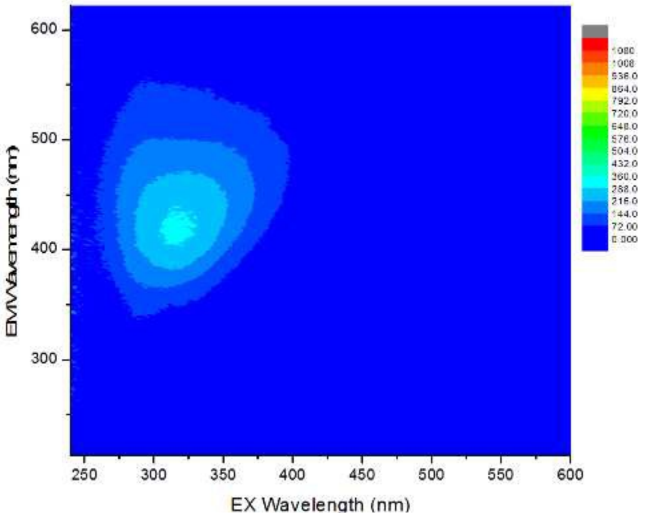
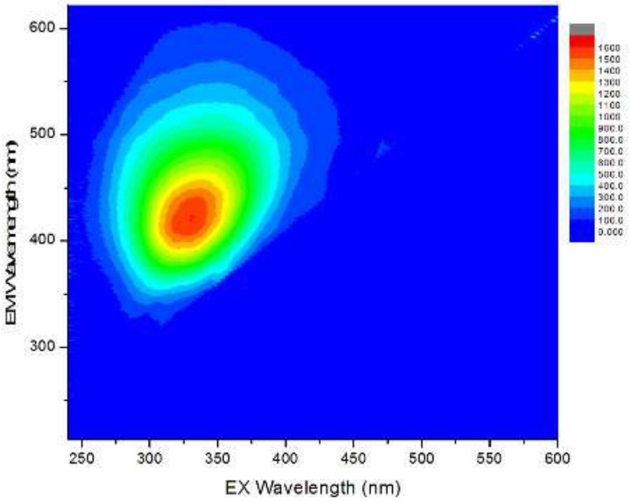


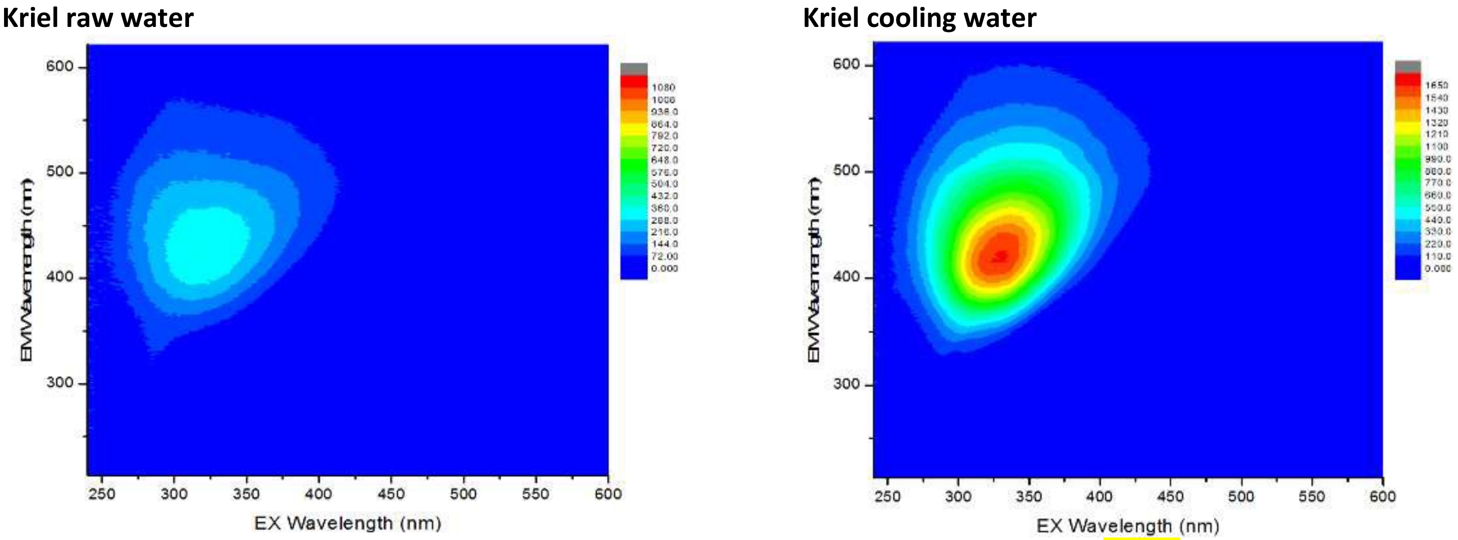
Fig. 6: Chromatograms water samples of exposed to light only and those exposed to light and hydrogen peroxide conditions

Lethabo raw water



Lethabo cooling water




Kriel raw water

Kriel cooling water

Fig. 7: FEEM spectral signatures obtained from raw and cooling water from Kriel and Lethabo Eskom power stations.

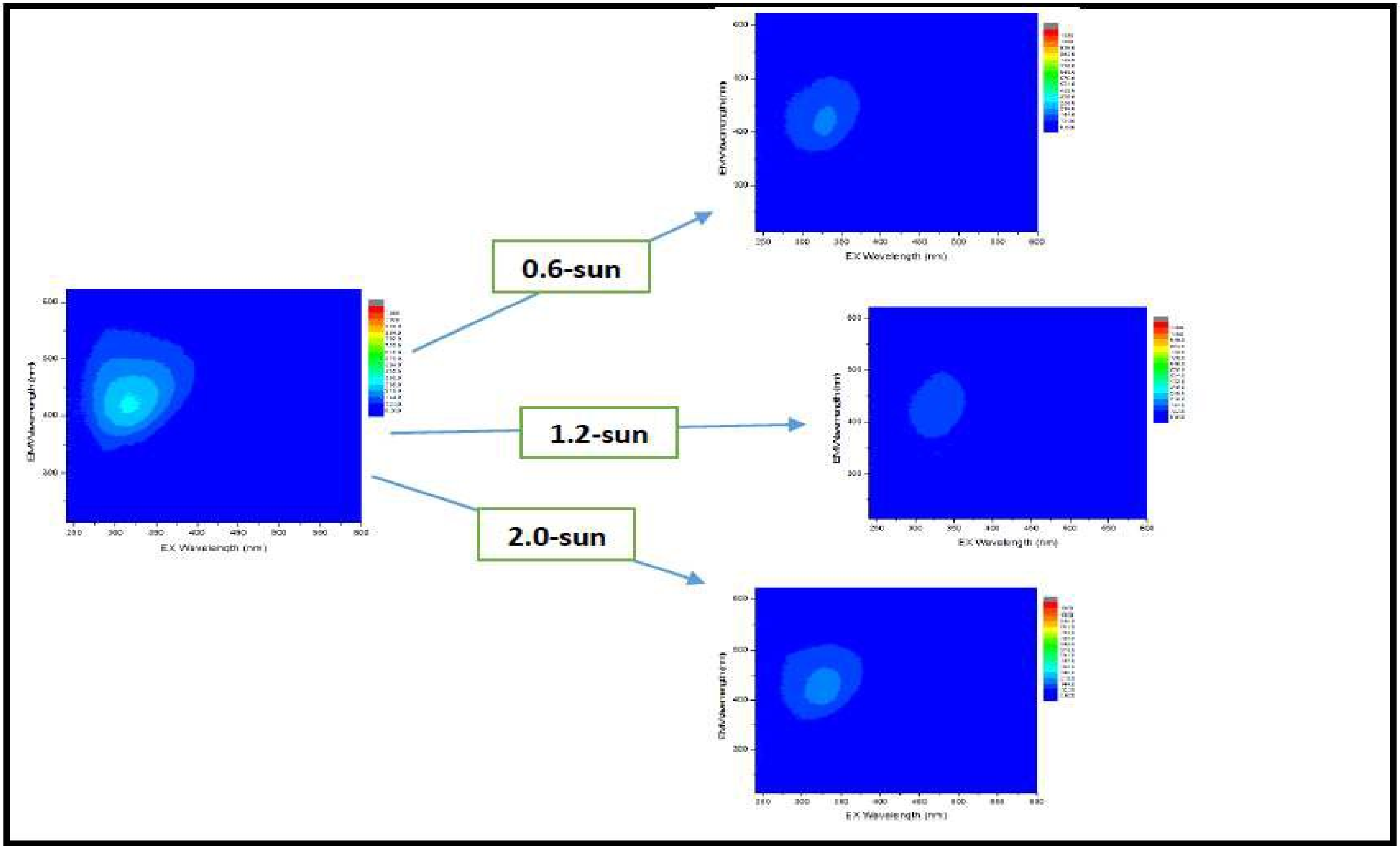


Fig. 8: Typical fluorescent EEM spectral signatures obtained of raw at Lethabo power station and after exposition to various intensities of sunlight for 4 hours i.e. 0.6-sun, 1.2-sun and 2.0-sun, respectively

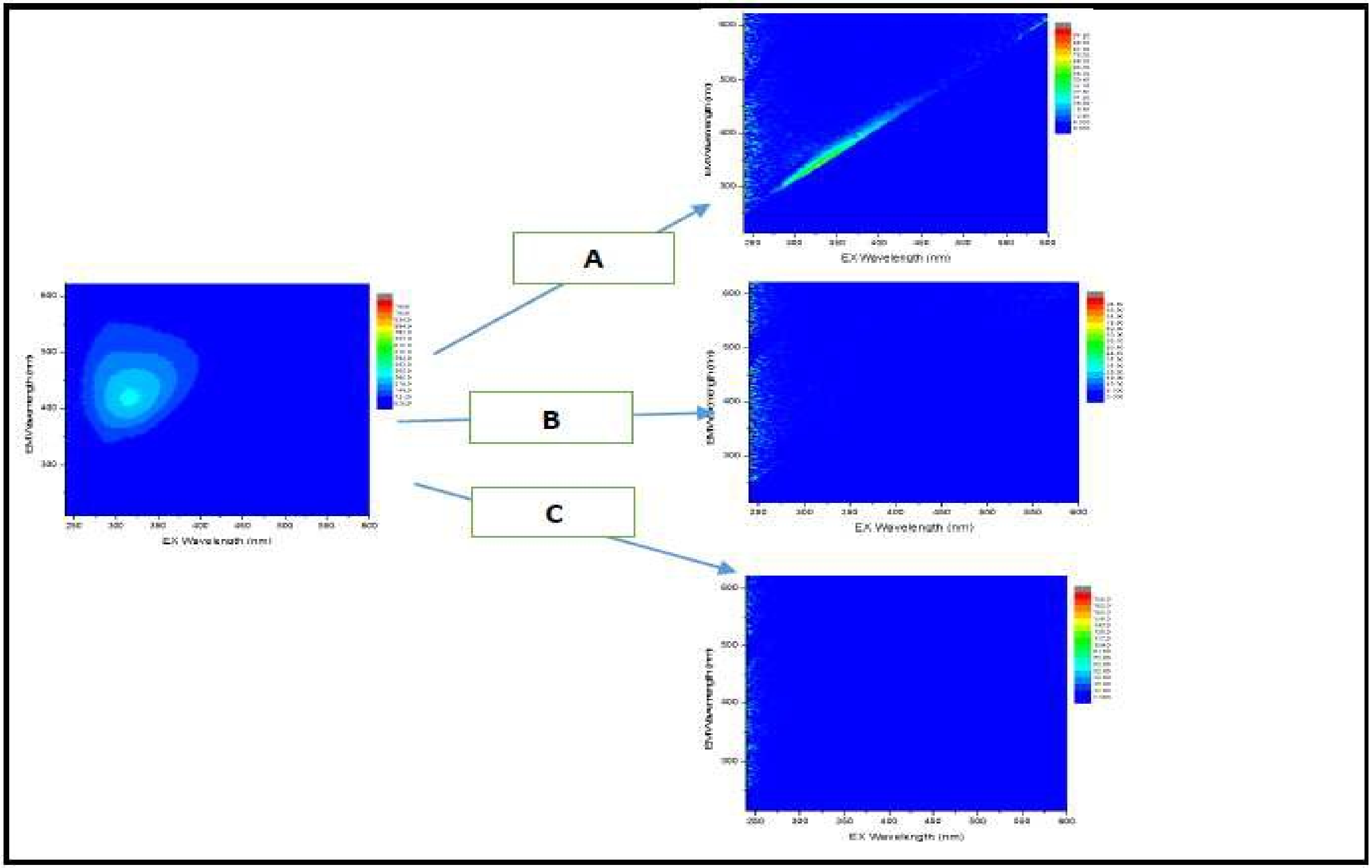


Fig. 9: Fluorescent EEM spectral signatures obtained from raw at Lethabo power station, after photo-irradiating with it at 1.2-sun with varying amounts for 4 hours of H_2O_2 (250, 500 and 750 µL)