Water Science & Technology

Check for updates

IWA PUBLISHING

Identification of oil contamination in process water using fluorescence excitation emission matrix (FEEM) and parallel factor analysis (PARAFAC)

Heena Madhav [a],* and Adam Gilmore[b]

[a] Specialised Testing and Sustainable Energy Research Department, Eskom, RT&D, Johannesburg, South Africa
[b] HORIBA Instruments Inc., Fluorescence Division, Piscataway, NJ, USA
*Corresponding author. E-mail: heena.madhav@eskom.co.za

HM, 0000-0003-4611-5754

ABSTRACT

Fuel oil is widely used within Eskom, a power generation company in South Africa. Eskom's coal-fired power stations use up to 30,000 L of fuel oil per hour during a cold start-up, a consequence of which results in oil leaks to the dams. Oil contamination in water treatment plants causes irreversible membrane fouling, requiring costly replacement. This research work focused on the development of a rapid method for the identification of low concentrations of the water-soluble oil component fraction of crude fuel oil. For the developed method, known volumes of the water-soluble fraction of crude oil were spiked into various matrices of process water. FEEMs were collected using the patented HORIBA Aqualog spectrometer and data were modelled with PARAFAC. The results were well described with a four-component model, which included an oil component and three natural organic matter components, with a split-half validation match of 90%. The oil component was verified using linear regression of the PARAFAC component scores yielding an R^2 value of 0.98. From the scores, a qualitative pass/fail test was developed such that process water can be analysed and subjected to the model to indicate the presence of oil contamination beyond a damaging threshold.

Key words: BTEX, FEEM, fuel oil, naphthalene, PARAFAC

HIGHLIGHTS

- Development of model using FEEM and PARAFAC for identification of low concentration (ppb) of oil contamination in process water.
- PARAFAC Split-Half model for verification of the developed oil identification model was 90%.

GRAPHICAL ABSTRACT
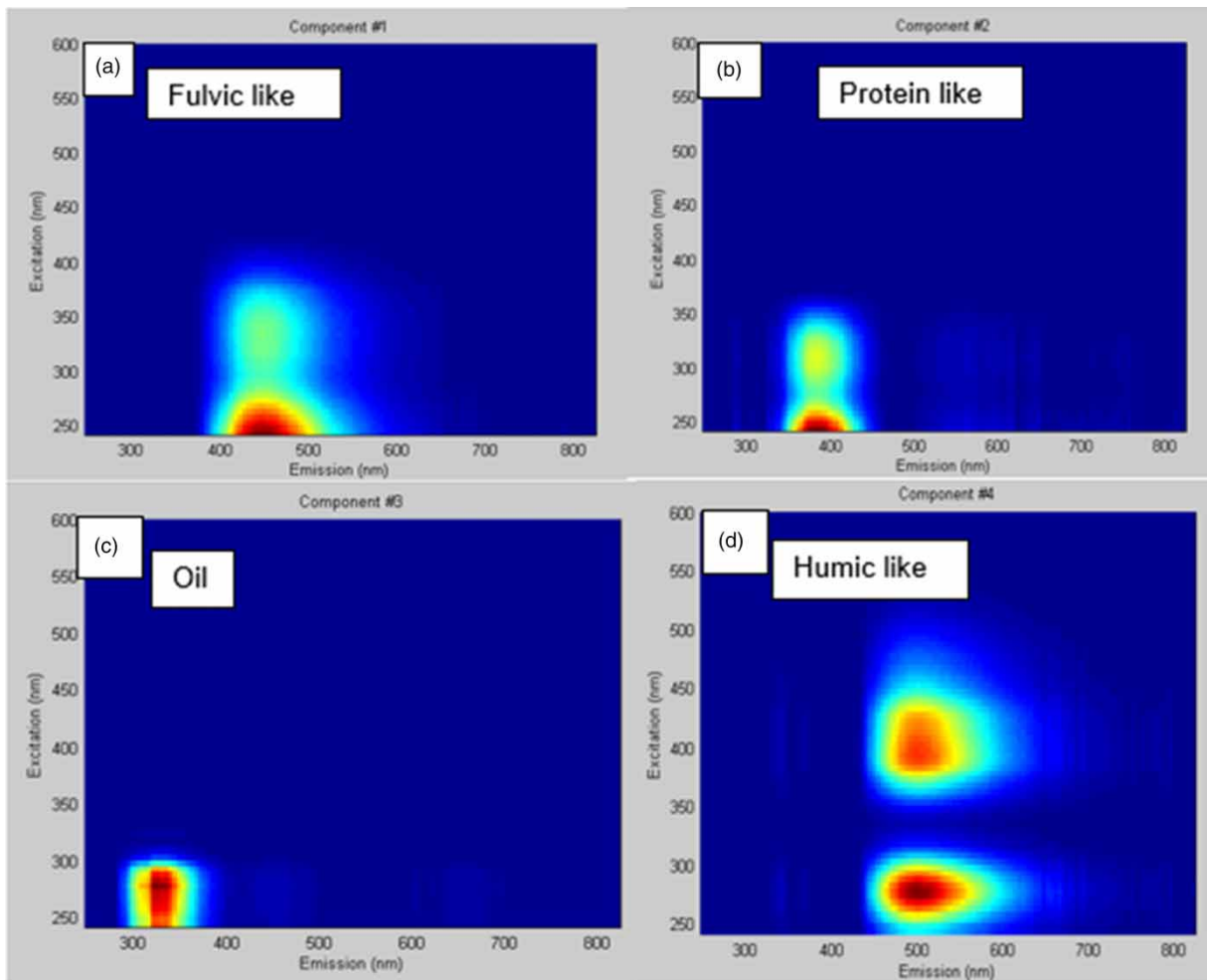
INTRODUCTION

Insulating and fuel oils are widely used within Eskom and are integral materials that are crucial to the generation, transmission, and distribution business. Fuel oil is mostly used in generation and is the fraction obtained from petroleum distillation, either as a distillate or a residue. Commercial fuel oils are usually blended with other petroleum fractions to produce the desired viscosity and flash point.

In Generation, heavy fuel oil is used for starting-up pulverised coal plants by both igniting the coal and stabilising the combustion (Fuel Oil Generation Engineering Strategic Report 2022, document no.474-12478). Eskom's coal-fired power stations use up to 30,000 L of fuel oil per hour during a cold start-up. When a new unit is being brought out of mothball or is returned to service after an outage, frequent light-ups are often required until the unit can be put on load. These types of start-ups require huge volumes of fuel oil over a short time period (A. Lombard Eskom Fuel Oil Quality Assurance RES/RR/14/35684 2014).

Unfortunately, however, all Eskom power stations report oil leaks to the dams. In most cases, this is fuel oil, and usually occurs when the oil is off loaded to the tanks. In addition, oil from the turbine plant area sometimes contributes to oil contamination, i.e., when an oil spillage cannot be contained. Other oils such as lubricating, seal, hydraulic, and gear oil can also contaminate water. Oil contamination in water treatment plants in the generation division is problematic as it fouls ultrafiltration (UF) and reverse osmosis (RO) membranes, even at low concentrations (Sutrisna et al. 2022).

Oil-contaminated water, if released to the environment, will contravene legislation, hence identification of the source of the spill is important so that potential environmental and ecological impacts can be evaluated and mitigated. In the transmission and distribution areas, oil contamination is mainly from transformer oil.

Crude oils and petroleum products are complex mixtures of chemical compounds, and it is not feasible to analyse all these compounds. Although techniques such as gas chromatography-flame ionisation detection (GC-FID) and gas chromatography-mass spectroscopy (GC-MS) are used for oil fingerprinting, these techniques are complex and time-consuming (Christensen & Tomasi 2007).

The fluorescence excitation emission matrix (FEEM) instrument, however, has the potential to analyse/fingerprint oils within minutes, i.e., without any sample extraction, which would be required for GC-FID or GC-MS analysis. Researchers A. Gilmore and L. Chen explored the FEEM technique to identify (qualitatively and quantitatively) oils and develop a method for the analysis of benzene, toluene, xylene, and naphthalene. These researchers were successful at developing a method for the analysis of these compounds in surface water at very low (ppb) levels (Gilmore & Chen 2020).

Previous studies have addressed the detection of oil contamination using multi-dimensional fluorescence using FEEM and PARAFAC analysis including correlation with independent chromatographic methods. In 2018, F. Mirnaghi and fellow researchers worked on developing a rapid screening method (qualitative and semi-quantitative) for the fingerprinting of spilled petroleum products using FEEM, with the aim of it being a complementary technique as compared to conventional fingerprinting which utilises techniques such as GC-MS or GC-FID. The developed fingerprinting model (using PARAFAC) was based on the composition of polycyclic and heterocyclic aromatic hydrocarbons. Principal component analysis (PCA) was also utilised to distinguish the various classes of petroleum products from a variation of scores modelled. This model was validated using the GC-MS technique (Mirnaghi et al. 2018). In 2013, Z. Zhou and fellow researchers also utilised 3-D fluorescence spectroscopy and PARAFAC to characterise oil components of a crude oil spill in the Gulf of Mexico. Furthermore, the fate and transport of these oils were also studied by evaluating changes in the fluorescent component ratio (Zhou et al. 2013). In a study carried out by A.K. Driskill and fellow researchers, polyaromatic hydrocarbons (PAHs) were analysed using fluorescence spectroscopy together with PARAFAC to identify PAHs and their degradation compounds in Arctic waters. PAHs are highly lipophilic compounds that have two or more benzene rings which are fused together, with varying linear arrangements. As the molecular weight of these compounds increases, aqueous solubility decreases. Protein-like compounds also exhibit different emission maxima (i.e., 330/320 nm) when compared to the larger PAHs (four rings or more) that exhibit emission maxima at 420 nm (Driskill et al. 2018). Fluorescence techniques have also been used, particularly to monitor oil contamination during emergency responses and environmental assessments as indicated by Conmy, with BTEX concentrations used to estimate hydrocarbon concentrations (Conmy et al. 2022). Figure 1(a) and 1(b) show the chemical structures of BTEX and naphthalene compounds.

PARAFAC uses multivariate analysis, meaning that it uses data arranged in a three or higher-order array. Examples of three-way arrays that can be analysed with PARAFAC include FEEMs and chromatographic data, i.e., for example, gas chromatography-mass spectroscopy (GC-MS) (Murphy et al. 2013). PARAFAC has been used in a large number of publications for the effective characterisation of organic material derived from various environmental systems (Holbrook et al. 2006; García et al. 2020).

A method published by Murphy and fellow researchers was used in this study to obtain the PARAFAC model using FEEM data (Murphy et al. 2013) and the outcome from the PARAFAC model is then a set of components that are separated out from mathematically decomposing excitation emission matrix (EEM) spectra from a series of samples (data can range from various water sources to water within a treatment process), which can be used to interpret individual samples and the model was validated using split-half as described by Murphy.

This research paper details novel work carried out to develop such a method for the identification and quantification of low (ppb) concentrations of oil in a real process water application using the FEEM technique. Samples obtained from sites within Eskom were also analysed using the developed method. Clearly, having a rapid test method for the detection of the presence of low-level oils is important as this routine test would enable oil-contaminated water to be detected early and could be attended to immediately.
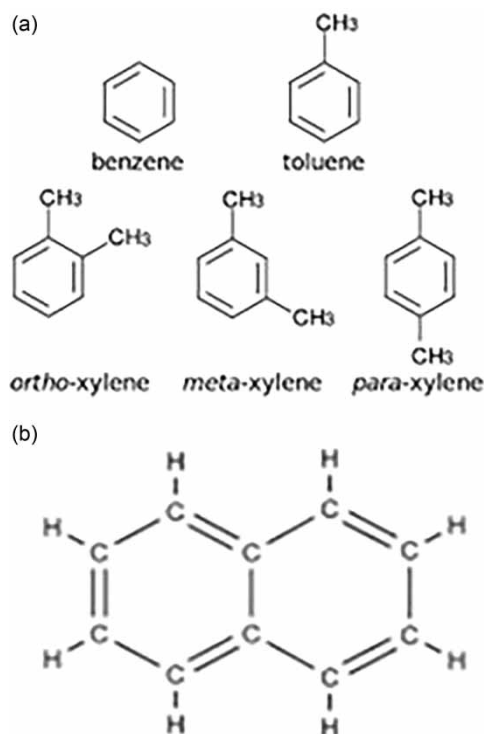
Figure 1 | (a) Chemical structures of BTEX compounds and (b) chemical structure of naphthalene.

MATERIALS AND METHODS

Liquid sample preparation

Sampling was carried out at two power stations, i.e., Station A and Station B. Samples obtained from Station A, included bulk cooling water (East), bulk cooling water (West), recovered mine water, recovered effluent water and clarified cooling water (CCW) which is also referred to as RO feed water and dirty dam samples for Power Station B. All samples were refrigerated at 4 °C for preservation and samples were analysed at room temperature. All reagents were of analytical grade and Millipore water (0.05 μS/cm) was used to prepare the standards.

For the dissolved organic carbon (DOC) analysis, the samples were first filtered through a 0.22 μm membrane filter before being analysed. Potassium hydrogen phthalate (99.5%, Associated Chemical Enterprises) was used to prepare the calibration standards. The potassium hydrogen phthalate (99.5%, AR grade) used for the quality control standard was obtained from Merck. Benzene, toluene, ethylbenzene and xylene (BTEX), and naphthalene standards were purchased from Chemetrix Export (Pty) Ltd.

The analytical techniques used for analyses included fluorescent excitation emission matrix (FEEM), GC-MS Purge and Trap and total organic carbon (TOC). FEEM data were interpreted using the parallel factor analysis (PARAFAC) modelling. In order to ensure that quality data were produced, the following controls were in place, i.e., use of clean cuvettes, analyses were carried out in a temperature-controlled room and samples were filtered to remove turbidity.

Samples obtained from Station A and Station B were analysed using FEEM and modelled using PARAFAC. The BTEX and naphthalene standards were also analysed using FEEM and modelled using PARAFAC. In addition, samples were also analysed using GC-MS Purge and Trap and TOC instruments.

Samples with different matrices were spiked with a prepared stock solution of demineralised water that was contaminated with crude fuel oil (Table 1). This stock solution was prepared by adding 20 drops of crude fuel oil to 500 mL of demineralised water and the mixture was shaken vigorously for 2 min. This solution was then left to equilibrate for 5 days before being used to spike samples.

Table 1 | Preparation of samples[a]

Sample	Volume of crude fuel oil added (mL)
1. Station A: Dirty water dam	5
2. Station A: Dirty water dam	10
3. Station A: Dirty water dam	30
4. Station A: Mine water recovery	5
5. Station A: Mine water recovery	10
6. Station A: Mine water recovery	30
7. Station A: Cooling Water East	5
8. Station A: Cooling Water East	10
9. Station A: Cooling Water East	30
10. Station A: Cooling Water West	5
11. Station A: Cooling Water West	10
12. Station A: Cooling Water West	30
13. Station A: Clarified cooling water 2 outlet (RO feed)	5
14. Station A: Clarified cooling water 2 outlet (RO feed)	10
15. Station A: Clarified cooling water 2 outlet (RO feed)	30
16. Station B: Dirty water dam (after oil clean-up)	5
17. Station B: Dirty water dam (after oil clean-up)	10
18. Station B: Dirty water dam (after oil clean-up)	30

[a]*Note*: All samples were made up to 100 mL.

To evaluate the accuracy and precision of the spiking process, a univariate model was utilised to independently evaluate the accuracy and precision using excitation and emission wavelengths of 300 nm and 325 nm, respectively.

INSTRUMENTATION

FEEM analysis

FEEM analyses were conducted using a patented Aqualog spectrometer (HORIBA Instruments Inc., Piscataway, NJ, USA) which rapidly and simultaneously collects absorbance and FEEM data and corrects for fluorescence inner-filter effects. The FEEM data were processed and interpreted using a patented and published method (Dellarole & Royer 2014; Gilmore 2019; ASTM International 2022). The background correction was carried out using Millipore water as a blank. The spectrometer used a xenon lamp with excitation and emission slits set to a 5 nm band pass.

A 1 cm quartz cuvette held the sample during analysis. To account for Rayleigh scattering, the response from a blank solution (Millipore water) was subtracted from the fluorescence spectra of the sample to be analysed. All spectra were then corrected by Rayleigh first- and second-order masking and inner-filter effect corrections. The PARAFAC mathematical model was used to separate the FEEM data into various components. The model scatter masking parameters were as follows: first-order Rayleigh scattering, 16 nm, second-order Rayleigh scattering, 32 nm, and Raman scattering, 16 nm.

All FEEMs were normalised using water Raman scattering units (RSU) as a function of the charged couple device (CCD) detector pixel binning, gain and integration time.

TOC/DOC analysis

The Sievers 900 TOC analyzer that was purchased from Chemetrix Export was used for the TOC and DOC analysis.

GC-MS PURGE and TRAP analysis

The GC instrument was a Chemetrix instrument, and the Teledyn Tekamr Atomx Purge and Trap instrument used was purchased from LabHouse.

Table 2 | Component scores from the Oil Model 15-03-2023.mat

Sample name	Volume (mL)	Sample	C1 fulvic -like	C2 protein -like	C3 oil	C4 humic- like	Pass/fail (oil component)
2023-02-14-13-25-18-B1S1T Mine Water RecoveryPEM.dat	0	1	0.53	0.33	0.12	0.21	Pass
2023-02-14-13-29-27-B1S2T DWD RecoveryPEM.dat	0	2	3.36	1.78	0.27	0.95	Pass
2023-02-14-13-32-54-B1S3T CW EastPEM.dat	0	3	14.42	6.41	0.98	5.06	Fail
2023-02-14-13-36-05-B1S4T CW WestPEM.dat	0	4	2.80	1.32	0.20	0.96	Pass
2023-02-14-13-43-26-B1S5 Clarifier CW Outlet, RO FeedPEM.dat	0	5	0.58	0.43	0.11	0.11	Pass
2023-02-14-13-47-16-B1S6K Dirty Water Dam (after oil contamination cleanedPEM.dat	0	6	0.40	0.56	0.16	0.14	Pass
2023-03-06-12-07-23-B1S1 T DWD Recovery + 5 mL crude oil stockPEM.dat	5	7	3.27	1.79	0.57	0.87	Fail
2023-03-06-12-10-31-B1S2T DWD Recovery + 10 mL crude oil stockPEM.dat	10	8	3.11	1.80	1.01	0.82	Fail
2023-03-06-12-12-59-B1S3T DWD Recovery + 30 mL crude oil stockPEM.dat	30	9	2.42	1.67	2.34	0.63	Fail
2023-03-06-12-15-32-B1S4T Mine Water Recovery + 5 mL crude oilstockPEM.dat	5	10	0.49	0.40	0.50	0.19	Fail
2023-03-06-12-17-56-B1S5T Mine Water Recovery +10 mL crude oil stockPEM.dat	10	11	0.50	0.46	0.88	0.19	Fail
2023-03-06-12-20-45-B1S6T Mine Water Recovery + 30 mL crude oil stockPEM.dat	30	12	0.43	0.73	2.68	0.15	Fail
2023-03-06-12-23-07-B1S7T CW East + 5 mL crude oil stockPEM.dat	5	13	14.85	7.08	1.00	4.86	Fail
2023-03-06-12-25-40-B1S8T CW East + 10 mL crude oil stockPEM.dat	10	14	13.92	6.75	1.37	4.56	Fail
2023-03-06-12-28-15-B1S9T CW East + 30 mL crude oil stockPEM.dat	30	15	10.93	5.49	2.70	3.56	Fail
2023-03-06-12-30-53-B1S10T CW West + 5 mL crude oil stockPEM.dat	5	16	2.56	1.30	0.55	0.86	Fail
2023-03-06-12-33-48-B1S11T CW West + 10 mL crude oil stockPEM.dat	10	17	2.57	1.40	1.01	0.84	Fail
2023-03-06-12-36-22-B1S12T CW West + 30 mL crude oil stockPEM.dat	30	18	2.05	1.45	2.46	0.65	Fail
2023-03-06-12-39-41-B1S13T RO Feed + 5 mL crude oil stockPEM.dat	5	19	0.57	0.48	0.44	0.09	Fail
2023-03-06-12-42-05-B1S14T RO Feed + 10 mL crude oil stockPEM.dat	10	20	0.57	0.51	0.69	0.08	Fail
2023-03-06-12-44-43-B1S15T RO Feed + 30 mL crude oil stockPEM.dat	30	21	0.59	0.69	2.10	0.04	Fail
2023-03-06-12-47-20-B1S16K Dirty Water Dam after clean-up + 5 mL crude oil stockPEM.dat	5	22	0.42	0.62	0.48	0.14	Fail
2023-03-06-12-49-46-B1S17K Dirty Water Dam after clean-up + 10 mL crude oil stockPEM.dat	10	23	0.43	0.67	0.84	0.12	Fail
2023-03-06-12-52-17-B1S18K Dirty Water Dam after clean-up + 30 mL crude oil stockPEM.dat	30	24	0.45	0.86	2.18	0.08	Fail
2023-03-06-12-56-17-B1S19 Crude oil StockPEM.dat	100	25	0.03	1.47	7.54	0.06	Fail

RESULTS AND DISCUSSION

PARAFAC model results

The data from FEEM was used to build a PARAFAC model, which resulted in a four component model (Table 2). The four components based on excitation and emission loadings were identified as follows: Component 1, fulvic-like; Component 2, protein-like, Component 3, oil; Component 4, humic-like. Component 3 was further verified as the oil peak using linear regression by the $R^2 = 0.98$ value for the scores as a function of oil spike volume (Table 3). Components 1, 2, and 4 by comparison showed very low R^2 values. The FEEM emission wavelengths and images of the four components are shown in Figures 2 and 3, respectively. The split half model for the PARAFAC model was 90% (Figure 4).

Furthermore, scores obtained for the oil component were used to build a pass/fail test for the identification of the presence of oil in various samples (Table 4). A fail result was an indication that the sample contained oil and a pass result was an indication that the sample contained, if any, a negligible concentration of oil. This test was then validated by testing the presence of oil in three known samples, i.e., a sample that was spiked with BTEX and naphthalene, a clean potable water sample and also clean Station A RO feed water. The results indicated that sample one, i.e., spiked sample, failed whereas the potable and RO feed water passed indicating that the latter two samples had sub-threshold concentrations of oil, if any (Table 4).

DOC, BTEX and Naphthalene Results

The results of the samples analysed in this experiment are shown in Table 5. The general trend for DOC was consistent with the dilution of the water source with the spiked volumes of the crude oil stock, i.e., the concentration decreased for each

Table 3 | R^2 values of the four components

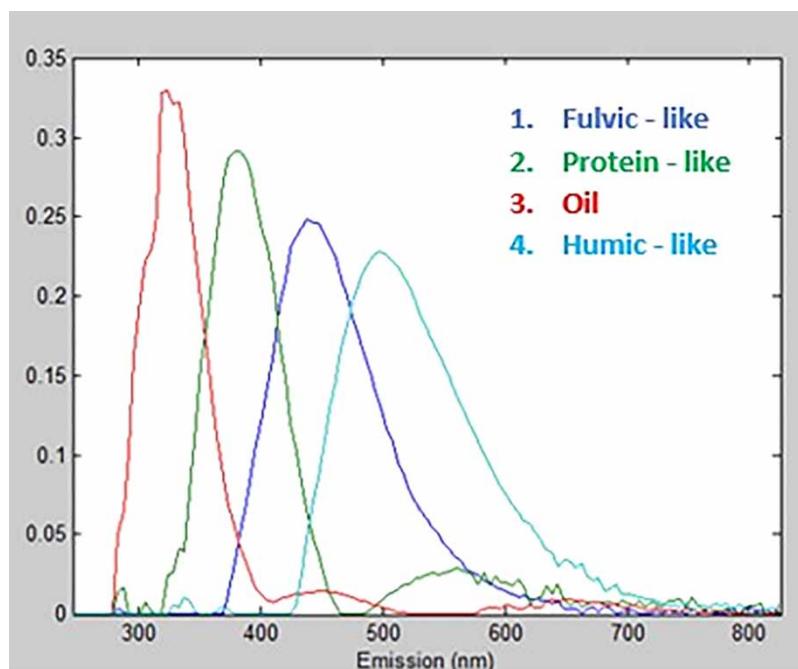| Components	R^2 (RSQ)
C1 – fulvic like	0.02611
C2 – protein like	0.001321
C3 – oil	0.9760
C4 – humic like	0.02498

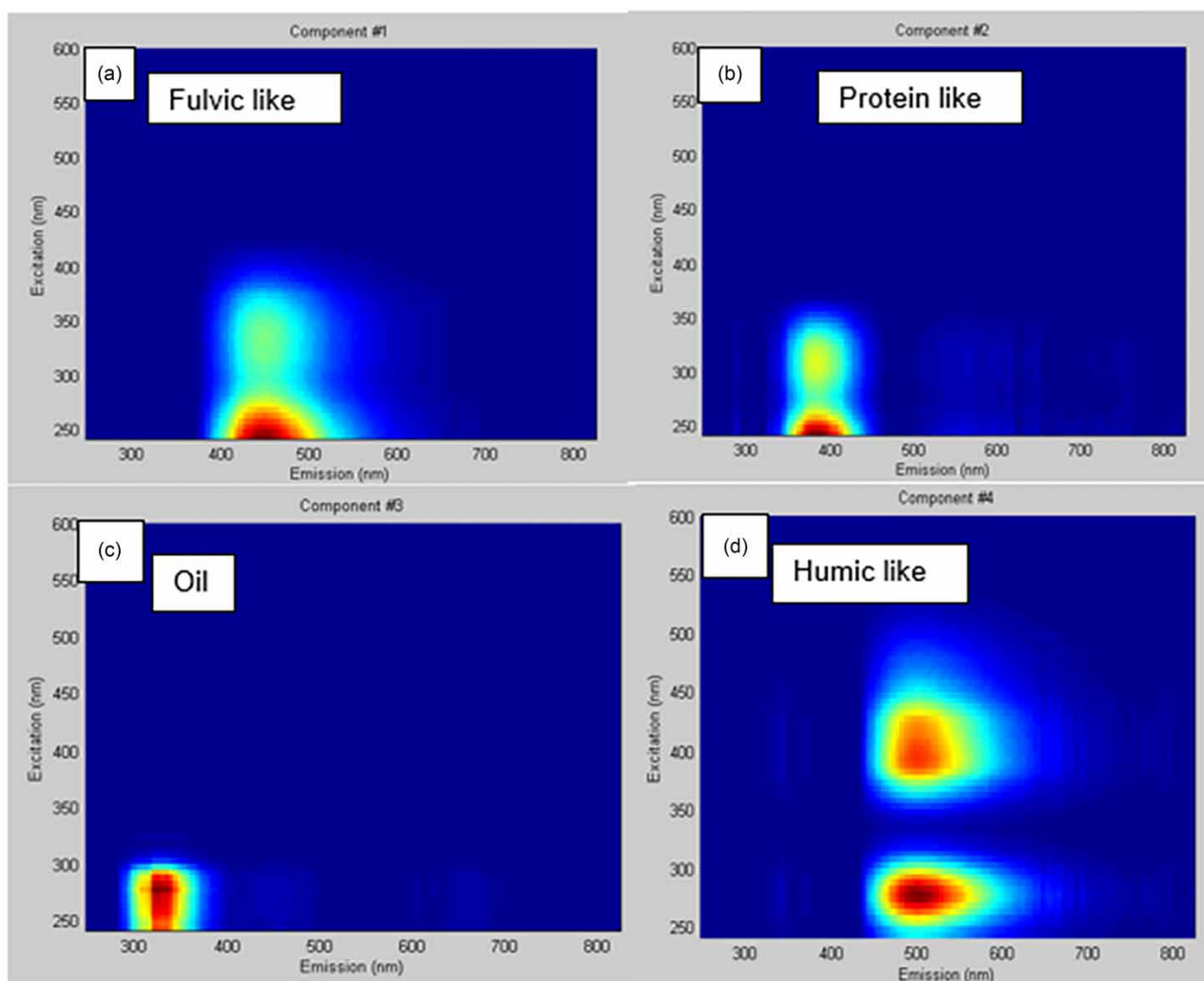**Figure 2** | Emission wavelengths of the four components.

Figure 3 | (a–d) FEEM images of crude oil stock mixed with various sample matrices.

sample matrix as the volume of stock crude oil increased. One exception was for the sample matrix Station B Dirty Water Dam, whereby the DOC concentration increased with an increase in the concentration/volume of the crude stock oil. The reason for this could be that Station B Dirty Water Dam sample contained a background level of polyaromatic hydrocarbon (PAH) type compounds.

The results also indicated that the PAH compounds increased for all sample matrices, with the incremental increase of the crude stock oil, as was expected.

Samples were selectively spiked with oil as described in the previous results section. The model performance was evaluated based on the respective True Positive and True Negative Response ratios, TPR and TNR, and the False Positive and False Negative response ratios, FPR and FNR (Table 6). The response ratios were used to calculate the error (Err), probability (P), and F-statistic (F) for the model calibration and test set as defined earlier by Gilmore et al. 2022. Also reported are the Matthew's Correlation coefficients for the pass/fail model and test results.

Reproducibility of sample analysis

To document the reproducibility of the results, validation samples using the crude stock oil solution were prepared by adding 5, 10, and 30 mL aliquots into a Dirty Dam sample and made to 100 mL. Each of these samples, including the Dirty Dam sample was analysed six times (Table 7). The oil component score for each sample together with the mean and standard
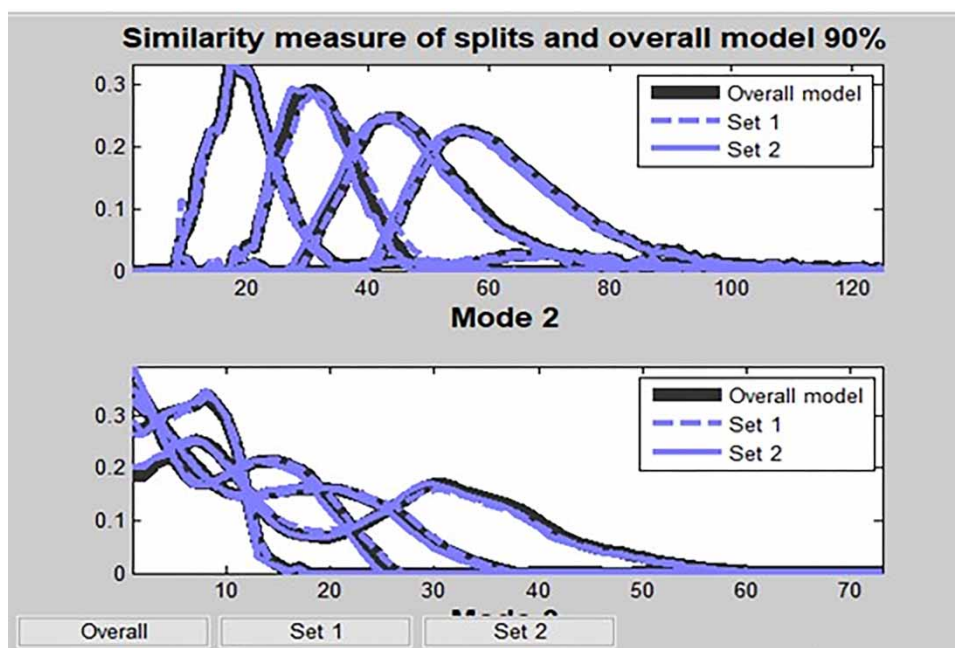
Figure 4 | Split-half model for the PARAFAC Oil Model 15-03-2022.mat.

Table 4 | Scores for test samples using oil model 15-03-2023.mat

Samples	C1 fulvic-like	C2 protein-like	C3 oil	C4 humic-like	Pass/fail
2022-12-12-15-31-06-B1S195 mL of 50 ppb BTEX-Naph and 35 mL of KDWD – 17PEM.dat	2.00	4.35	3.16	0.00	Fail
2022-08-22-14-53-07-B1S2 Potable Water Test 2PEM.dat	0.10	0.05	0.01	0.02	Pass
2022-09-02-10-12-35-B1S2T RO Feed (treated mine water) 2PEM.dat	0.08	0.05	0.02	0.02	Pass

deviation for each set of results are shown in Table 7. The detection limit for the unspiked samples was less than 11 ppb, whilst the lowest spiked sample was less than 33 ppb with a standard deviation of less than 1 ppb. The coefficient of variation was less than 3% for each spiked group of samples analysed.

The developed FEEM-PARAFAC model for the detection of low concentrations of oil in process water, although, a bench-top analysis technique, is a useful monitoring technique for process water, specifically when an oil spillage has occurred at the dams from which water is recovered at industrial sites for plant operation. Most often, oil spillages are cleaned as per environmental legislation; however, dissolved oil components remain in the water and upon recovery of this water for plant operation, dissolved oil components present in this recovered water tend to irreversibly foul membrane systems. Therefore, the rapid detection (reagent and solvent-free) method that has been developed in this study for the detection of low concentrations of oil in process water can assist plant operations by ensuring that water, free of dissolved oil is recovered to the plant, allowing for protection of downstream processes. According to the ASTM International method, limitations do, however, include naturally occurring fluorescing compounds, such as humic/fulvic acids and protein-like components, which could cause an interference as well as blank contamination and dirty glassware, which could also cause an interference (ASTM International 2022).

This work was performed as a proof of concept for the basis of developing a fully documented method for the analysis of low (ppb) concentrations of dissolved oil in process water. The method used was based on referenced articles and considered quality checks, reproducibility of results as well as the analysis of process water for method validation.

Table 5 | Results for samples analysed for DOC, BTEX and naphthalene

Sample	DOC (ppm)	BTEX (ppb)	Naphthalene (ppb)	Total PAHs (ppb)
1. Station A: DWD recovery + 5 mL crude oil stock	28.4	10.5	22.3	32.8
2. Station A: DWD recovery + 10 mL crude oil stock	27.1	24.15	56.67	80.82
3. Station A: DWD recovery + 30 mL crude oil stock	23.5	81.36	189.93	271.29
4. Station A: Mine water recovery + 5 mL crude oil stock	13.2	16.22	37.4	53.62
5. Station A: Mine water recovery +10 mL crude oil stock	14.8	25.81	58.6	84.41
6. Station A: Mine water recovery + 30 mL crude oil stock	14.0	72.81	185.92	258.73
7. Station A: CW East + 5 mL crude oil stock	71.7	13.49	37.7	51.19
8. Station A: CW East + 10 mL crude oil stock	68.4	22.94	54.07	77.01
9. Station A: CW East + 30 mL crude oil stock	56.3	69.99	164.23	234.22
10. Station A: CW West + 5 mL crude oil stock	25.5	9.56	25.4	34.96
11. Station A: CW West + 10 mL crude oil stock	23.7	8.83	32.31	41.14
12. Station A: CW West + 30 mL crude oil stock	18.4	30.12	107.41	137.53
13. Station A: RO feed + 5 mL crude oil stock	12.1	4.11	18.74	22.85
14. Station A: RO feed + 10 mL crude oil stock	11.5	9.12	37.21	46.33
15. Station A: RO feed + 30 mL crude oil stock	10.1	47.41	126.84	174.25
16. Station B: Dirty water dam after clean-up + 5 mL crude oil stock	8.7	5.35	23.43	28.78
17. Station B: Dirty water dam after clean-up + 10 mL crude oil stock	9.8	20.36	53.10	73.46
18. Station B: Dirty water dam after clean-up + 30 mL crude oil stock	10.3	32.2	99.45	131.65
19. Station A: DWD recovery	24.0	ND	ND	ND
20. Sample A: Mine water recovery	10	ND	ND	ND
21. Station A: CW East	70.9	ND	ND	ND
22. Station A: CW West	17.2	ND	ND	ND
23. Station A: Clarifier CW outlet, RO feed	11.3	ND	ND	ND
24. Station B: Dirty water dam (after oil contamination cleaned)	9.7	ND	ND	ND
25. Crude oil stock	11.0	161.32	517.38	678.7

Table 6 | Confusion matrix evaluation of a four-component PARAFAC model for discrimination of oil contamination based on a threshold value of the component 3 score for the calibration and test set samples from the Eskom Dam reservoirs

Calibration	Model	Measured	TPR	TNR	FPR	FNR	Err	P	F1
Pass	5	5	1.00	1.00	0.00	0.00	0.00	1.00	1.00
Fail	19	19	1.00	1.00	0.00	0.00	0.00	1.00	1.00
Matthew's correlation	1.00								
Test									
Pass	2	2	1.00	1.00	0.00	0.00	0.00	1.00	1.00
Fail	1	1	1.00	1.00	0.00	0.00	0.00	1.00	1.00
Matthew's correlation	1.00								

CONCLUSIONS

This work shows that a PARAFAC model can be built using data generated from the FEEM instrument for the detection of low (ppb) concentrations of oil contamination in process water. Data (scores) from the model have been used to develop a

Table 7 | Reproducibility of sample analysis

Sample	(Oil component 3 Score)	Oil ppb[a]	Mean ppb (mean score)	Standard deviation ppb (standard deviation score)	% Coefficient of variation
Dirty dam (R0)	0.18	10.84	10.64 (0.18)	0.28 (0.005)	2.63
Dirty dam (R1)	0.18	10.84			
Dirty dam (R2)	0.17	10.24			
Dirty dam (R3)	0.17	10.24			
Dirty dam (R4)	0.18	10.84			
Dirty dam (R5)	0.18	10.84			
Dirty dam spiked with 5 mL crude fuel oil (R0)	0.56	33.73	32.93 (0.54)	0.67 (0.011)	2.03
Dirty dam spiked with 5 mL crude fuel oil (R1)	0.56	33.73			
Dirty dam spiked with 5 mL crude fuel oil (R2)	0.55	33.13			
Dirty dam spiked with 5 mL crude fuel oil (R3)	0.53	31.93			
Dirty dam spiked with 5 mL crude fuel oil (R4)	0.54	32.53			
Dirty dam spiked with 5 mL crude fuel oil (R5)	0.54	32.53			
Dirty dam spiked with 10 mL crude fuel oil (R0)	1.06	63.86	61.65 (1.02)	1.42 (0.024)	2.30
Dirty dam spiked with 10 mL crude fuel oil (R1)	1.05	63.25			
Dirty dam spiked with 10 mL crude fuel oil (R2)	1.02	61.45			
Dirty dam spiked with 10 mL crude fuel oil (R3)	1.01	60.84			
Dirty dam spiked with 10 mL crude fuel oil (R4)	1.00	60.24			
Dirty dam spiked with 10 mL crude fuel oil (R5)	1.00	60.24			
Dirty dam spiked with 30 mL crude fuel oil (R0)	3.10	186.75	178.31 (2.96)	5.29 (0.089)	2.97
Dirty dam spiked with 30 mL crude fuel oil (R1)	3.04	183.13			
Dirty dam spiked with 30 mL crude fuel oil (R2)	2.98	179.52			
Dirty dam spiked with 130 mL crude fuel oil (R3)	2.90	174.70			
Dirty dam spiked with 30 mL crude fuel oil (R4)	2.87	172.89			
Dirty dam spiked with 30 mL crude fuel oil (R5)	2.87	172.89			

[a]Calculated PAH concentration based on results from Table 4.

pass/fail result for the presence of low concentrations of oil contamination in water. Test samples were analysed using FEEM and data obtained were subjected to the pass/fail model test. Results obtained were indicative of the samples analysed and indicated the assay is 'fit-for-purpose' and warrants formal method documentation.

RECOMMENDATIONS

The recommendation is that since a quantitative method for the determination of low (ppb) concentrations of oil contamination in water, specifically recovered water, has been developed, monitoring of this water must become a standard practice at water treatment plants at the various sites at Eskom. This would be a control that would mitigate the risk of membrane fouling and premature replacement of membranes.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

ASTM International 2022 *D8431-22 – Standard Test Method for Detection of Water-Soluble Petroleum Oils by A-TEEM Optical Spectroscopy and Multivariate Analysis. i, 1–14.* https://doi.org/10.1520/D8431-22.1.

Christensen, J. H. & Tomasi, G. 2007 A multivariate approach to oil hydrocarbon fingerprinting and spill source identification. In: *Oil Spill Environmental Forensics*, pp. 293–325. https://doi.org/10.1016/B978-012369523-9.50013-6.

Conmy, R. N., Hall, A., Sundaravadivelu, D., Schaeffer, B. A. & Murray, A. R. 2022 Fluorescence-estimated oil concentration (foil) in the deepwater horizon subsea oil plume. *Marine Pollution Bulletin* **180**, 113808. https://doi.org/10.1016/j.marpolbul.2022.113808.

Dellarole, M. & Royer, C. A. 2014 Fluorescence spectroscopy and microscopy. In: *Methods in Molecular Biology*, Vol. 1076. Available from: http://link.springer.com/10.1007/978-1-62703-649-8_4%5Cn. http://link.springer.com/10.1007/978-1-62703-649-8.

Driskill, A. K., Alvey, J., Dotson, A. D. & Tomco, P. L. 2018 Monitoring polycyclic aromatic hydrocarbon (PAH) attenuation in Arctic waters using fluorescence spectroscopy. *Cold Regions Science and Technology* **145**, 76–85. https://doi.org/10.1016/j.coldregions.2017.09.014.

Eskom 2022 *Fuel Oil Generation Engineering Strategic Report, Document no.474-12478.*

García, P. E., García, R. D., Soto Cárdenas, C., Gerea, M., Reissig, M., Pérez, G. L., De Stefano, L. G., Gianello, D., Queimaliños, C. & Diéguez, M. C. 2020 Fluorescence components of natural dissolved organic matter (DOM) from aquatic systems of an Andean Patagonian catchment: Applying different data restriction criteria for PARAFAC modelling. *Spectrochimica Acta – Part.*

Gilmore, A. M. 2019 Patent No. US10168310B2.

Gilmore, A. M. & Chen, L. 2020 Improving aromatic water-contaminant detection with machine-learning classification and regression for simultaneous Absorbance-Transmission Excitation Emission Matrix (A-TEEM) spectroscopy. February, 55. https://doi.org/10.1117/12.2556434.

Gilmore, A. M., Sui, Q., Blair, B. & Pan, B. S. 2022 Accurate varietal classification and quantification of key quality compounds of grape extracts using the absorbance-transmittance fluorescence excitation emission matrix (A-TEEM) method and machine learning. *Oeno One* **56** (4), 107–115. https://doi.org/10.20870/oeno-one.2022.56.4.5561.

Holbrook, R. D., Yen, J. H. & Grizzard, T. J. 2006 Characterizing natural organic material from the Occoquan Watershed (Northern Virginia, US) using fluorescence spectroscopy and PARAFAC. *Science of the Total Environment* **361** (1–3), 249–266. https://doi.org/10.1016/j.scitotenv.2005.11.020.

Lombard, A. 2014 Eskom Fuel Oil Quality Assurance, RES/RR/14/35684.

Mirnaghi, F. S., Soucy, N., Hollebone, B. P. & Brown, C. E. 2018 Rapid fingerprinting of spilled petroleum products using fluorescence spectroscopy coupled with parallel factor and principal component analysis. *Chemosphere* **208**, 185–195. https://doi.org/10.1016/j.chemosphere.2018.05.111.

Murphy, K. R., Stedmon, C. A., Graeber, D. & Bro, R. 2013 Fluorescence spectroscopy and multi-way techniques. PARAFAC. *Analytical Methods* **5** (23), 6557–6566. https://doi.org/10.1039/c3ay41160e.

Sutrisna, P. D., Kurnia, K. A., Siagian, U. W. R., Ismadji, S. & Wenten, I. G. 2022 Membrane fouling and fouling mitigation in oil–water separation: A review. *Journal of Environmental Chemical Engineering* **10** (3), 107532. https://doi.org/10.1016/j.jece.2022.107532.

Zhou, Z., Guo, L., Shiller, A. M., Lohrenz, S. E., Asper, V. L. & Osburn, C. L. 2013 Characterization of oil components from the Deepwater Horizon oil spill in the Gulf of Mexico using fluorescence EEM and PARAFAC techniques. *Marine Chemistry* **148**, 10–21. https://doi.org/10.1016/j.marchem.2012.10.003.