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Direct Fluorescence Monitoring of Coal Organic Matter Released in Seawater

C. Jaffrennou · L. Stephan · P. Giamarchi · J. Y. Cabon · L. Burel-Deschamps · F. Bautin

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Abstract Whenever immersed in seawater after a collier accident, a fossil fuel such as coal could become a source of pollution to the marine environment. To study the effect of such a contamination, four coal samples from different origins were used. A first analysis on those coals enabled us to determine the content of polycylic aromatic hydrocarbons. Seawater was then mixed with coal to study the organic matter released from coal into seawater. Fluorescence was used for its sensitivity to aromatic compounds, with the additional purpose of evaluating the relevance of using an immerse fluorescence probe to monitor water pollution. Excitation–emission matrices were recorded and the excitation–emission wavelength range corresponding to the highest fluorescence intensity was 230 nm/[370 nm; 420 nm]. The samples with coal happened to fluoresce more than the coal-free samples, the difference depending on the coal origin. The fluorescence intensity increased with coal mass, up to some limit. The particle size also influenced the fluorescence intensity, the finest particles releasing more fluorescing substances, due to their higher exchange surface. When seawater percolated through coal, the samples fluoresced highly at the beginning, and then the fluorescence intensity decreased and reached the seawater level. However, even with a 10 ns acquisition time shift, the fluorescence spectra were not specific enough to show the presence of PAHs in the samples, which were too diluted to be detected, whenever released from coal into seawater. The lifetimes of the seawater and of the coal samples were respectively 4.7 and 3.8 ns, indicating that the substances released from coal mainly consisted of short-lived fluorescing substances, such as natural humic or fulvic substances. Consequently, the presence of coal does not seem to be too detrimental to the marine environment, and a direct fluorescence probe could be used to monitor the seawater organic charge increase due to the immersion of coal in seawater.

Keywords Coal · Seawater · Polycyclic aromatic hydrocarbon · Humic acid · Laser-induced fluorescence

C. Jaffrennou (✉) · L. Stephan · P. Giamarchi · J. Y. Cabon · L. Burel-Deschamps
Chemistry Department, University of Brest, Brest, France
e-mail: cathy.jaffrennou@gmail.com

F. Bautin
Coal Department, Total Gas and Power France, Paris, France

Introduction

Coal is a sedimentary rock formed during two biochemical and thermophysical processes, respectively diagenesis and catagenesis, which first produce peat from dead plants, and then coal. Coal contains (in % weight) less than 50% of inorganic material and more than 50% of organic matter. The organic matrix can be classified into different macerals, depending on some physical, chemical and optical characteristics. Due to its natural origin, coal contains many different complex organic substances, such as humic acids, sulphur compounds and polycyclic aromatic hydrocarbons (PAHs) [1–8], which represent a different amount of the coal matrix according to the type of plants from which it was formed.

Over the past few decades, many studies have been published dealing with the issue of oil spills at sea and focusing on the impact of PAHs on the environment and on the marine fauna and flora. It has been shown that complex mixtures of aliphatic and aromatic hydrocarbons can be

leached, e.g. in case of rainfall percolating through an outdoor coal storage pile [9, 10], but accidental immersions of coal and their environmental impact in seawater have scarcely been studied.

In this work, we intend to study whether some organic pollutants can be released from coal into seawater in case of a collier accident, so as to assess to what extent the immersion of coal can be detrimental to the marine environment. Fluorescence spectroscopy is chosen for its fast and sensitive response to some organic compounds like humic acids and PAHs and also to assess the benefits and the accuracy of using an immersed probe based on direct fluorescence measurements for an in situ monitoring of the contamination levels in seawater. Four coals from different countries are used; they are first analyzed to determine their PAH contents and therefore a part of their potential toxicity. Then, they are mixed with seawater to study the organic fraction released, depending on different experimental parameters. Gas chromatography coupled with mass spectrometry detection (GCMS) is also used to separate and identify organic compounds (and particularly PAHs) after extraction and concentration protocols.

Materials and methods

Products

Four different commercial coals from the South African Republic (SAR), Indonesia (IND), Columbia (COL) and Venezuela (VEN) were used throughout the different experiments.

The seawater used was natural coastal seawater taken from Brest harbour, France, by the ocean discovery park Océanopolis. This seawater was treated by UV light and filtration at 0.45 μm before use; its pH was 8.0 and its salinity was 27 kg m^{-3}.

Three organic solvents were used: acetone, dichloromethane (Carlo Erba analytical grade) and hexane (Prolabo, HPLC grade). The silica gel used was from Merck (grade 60, 70–230 mesh, 60 Å).

Powdered humic acids, technical grade, from Aldrich were also used.

Classical fluorescence measurements

Classical fluorescence measurements were conducted on a Cary Eclipse Varian spectrophotometer and fluorescence spectra were registered on a computer (Scan software, Varian).

The emission and excitation wavelengths could vary from 190 to 1,100 nm; the scanning rate ranged from 30 to 24,000 nm min^{-1}, according to the precision desired, and the detector gain could be changed too (up to 1,000 V), so as to optimize the fluorescence intensity detected, expressed in arbitrary units (a.u.). A 3D option provided access to Excitation–Emission Matrices (EEMs) in which the fluorescence intensity (*Z*-axis) was presented as a function of the excitation wavelength (*Y*-axis) and the emission wavelength (*X*-axis). Throughout all this study, a slit width of 5 nm was used for both the excitation and the emission.

Laser-induced fluorescence: experimental setup

For laser-induced fluorescence measurements, a lab set-up device was used [11, 12]. The light source was a Nd:YAG pump laser (Powerlite Precision 9010, Continuum Santa Clara, CA) pulsed at 10 Hz, coupled to an Optical Parametric Oscillator (OPO Sunlite EX, Continuum) and a frequency doubling extension unit (FX-1 UV, Continuum) which allowed continuous wavelength scanning from 225 to 1,750 nm. The available energy in the UV domain ranged from 2 mJ at 225 nm to 10 mJ per pulse at 275 nm. It could be lowered by positioning a divergent lens in the optical path. The beam diameter was 5 mm.

For liquid sample analysis, a quartz cuvette was set on the beam path and the fluorescence was collected perpendicularly from the excitation beam and focused with an f/8 cm lens. The energy received by the sample at any wavelength was lower than 2 mJ per pulse to avoid photobleaching. For the solid sample studies, prisms were used to make the beam come vertically through a pierced mirror onto a horizontal sample platform. The fluorescence was then collected vertically by the mirror and collimated to the f/8 cm lens.

The detection device included a spectrometer of 750-mm focal length (SpectraPro-750i, Acton Research Corporation, Acton, MA) equipped with a triple grating turret an an intensified CCD camera with a 512×512 array optimized for the UV-visible domain (ICCD-MAX Princeton instruments, Trenton, NJ). The resolution reached 0.2 nm $pixel^{-1}$ with a 150 g mm^{-1} grating. The camera was operated with a ST-133 controller (RS Princeton Instruments, Trenton, NJ) for data acquisition. Timing control was achieved with a DG 535 digital delay/pulse generator (Stanford Research System Inc, Sunnywale, CA).

The WINSPEC 32-bit Windows software package (Roper Scientific Inc, Trenton, NJ) provided acquisition, display and processing functions.

Gas-chromatography, mass spectrometry

The GCMS device used was a Varian Saturn 2100 T, with an ion trap detector. The chromatography columns were 30 m long, with a 0.25 mm inner diameter and a 0.25 μm film thickness; for the determination of PAHs, a BPX5

Table 1 Size repartition of the four coal samples (% weight)

Particle size range (mm)	Coal			
	Indonesia (IND)	Venezuela (VEN)	South African Republic (SAR)	Colombia (COL)
>25	8.6	23.1	24.2	61.8
10–25	26.5	24.8	20.9	13.8
2–10	48.6	29.0	32.1	15.0
1.6–2.0	8.6	2.7	3.8	2.3
1.0–1.6	6.9	4.7	6.6	4.5
0.5–1.0	0.7	5.7	7.1	2.1
0.25–0.50	0.1	4.1	3.3	0.4
0.10–0.25	0.0	4.8	1.9	0.1
0.063–0.100	0.0	0.9	0.1	0.0
0.050–0.063	0.0	0.2	0.0	0.0
<0.050	0.0	0.0	0.0	0.0

column was used, whereas a Cp-Sil 8 CB column was used for alkanes.

The temperature varied as follows: first of all, it was kept at 50°C for 2 min. The temperature then increased up to 320°C at 30°C min^{-1}. Last, the temperature was kept at 320°C for 7 min. The column flow was 1 mL of He per min. The injector was at 280°C, and a splitless mode was used.

Experimental results

First of all, the organic compositions of the four coal samples were determined in order to identify the pollutants contained in this fossil fuel. Then, coal and seawater were mixed to study the organic matter released.

Coal studies

The four coal samples were first sifted to determine they size fraction repartition (Table 1). Very few particles were smaller than 0.1 mm, and those bigger than 2 mm formed the greatest part of the samples (more than 60% (in % weight)).

The organic content of our samples was then determined: since coal is liable to mix with sediments when immersed into seawater, it was decided to analyze it following an AFNOR (French Standardization Agency) method preliminary norm draft [13] for the determination of PAHs in sediments. 20 g of coal were thus smashed, sifted through a 0.5 mm sieve, corresponding to the finest particles, that is to the highest exchange surface, and then sonicated in 50 mL acetone for 30 min at 40°C. Once filtered through fiberglass filters (to prevent the loss of PAHs by adsorption on the filter surface, which occurred when using polymer filters), the acetone solution was concentrated 2.5 times by evaporation and thereafter introduced at the top of a silica gel column. First, the aliphatic fraction was eluted by 25 mL hexane and the volume was adjusted to 50 mL with hexane. The aromatic fraction was eluted by 50 mL of an hexane 40%/dichloromethane 60% mixture. Gas chromatography, mass spectrometry analyses were then run to determine the hydrocarbon contents in coal. Both aliphatic hydrocarbons (alkanes) and PAHs were studied.

Figure 1, presenting the C16 to C29 alkane concentrations in the four coals studied here, shows that the C17 concentrations are markedly higher than any other alkane, reaching 40 mg kg^{-1} for the Venezuelan coal and up to 50 mg kg^{-1} for the Indonesian coal. However, no alkane trace will be used as a fingerprint identifying the coal origin, since all four coals presented a similar alkane distribution.

For the aromatic fraction, it was decided to focus the study on sixteen particularly toxic PAHs listed by the United States Environmental Protection Agency and the European Union as priority pollutants [14, 15]. Seven PAHs were detected in the coal samples (Table 2): anthracene, benzo(a) anthracene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene. The highest amounts were found for

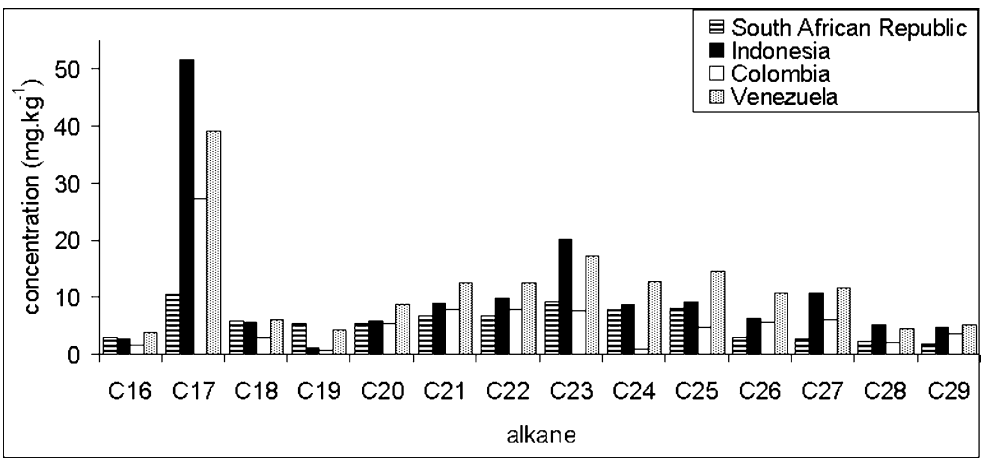

Fig. 1 Alkane concentrations in the SAR, IND, COL and VEN coals

Table 2 Polycyclic aromatic hydrocarbon compositions of the coal samples and of Zhao *et al.*'s coals

Polycyclic aromatic hydrocarbon (mg kg^{-1})	SAR	IND	COL	VEN	Zhao a	Zhao b	Zhao c
Fluorene	1.8						
Fluoranthene			2.0				
Phenanthrene		0.7	2.9	6.2	0.09	0.14	1.46
Pyrene	1.5		1.0		0.12		
Naphthalene	0.1					0.08	2.78
Anthracene	6.0				0.19	0.06	
Benzo(a)anthracene	24.8						
Acenaphthene							1.36
Benzo(b)fluoranthene						0.05	0.78
Total PAHs	34.2	0.7	5.9	6.2	0.40	0.33	6.38

phenanthrene in the Venezuelan coal (6.2 mg kg^{-1}) and for anthracene (6.0 mg kg^{-1}) and benzo(a)anthracene (24.8 mg kg^{-1}) in the SAR coal. Not all these 7 PAHs were found in the four samples but phenanthrene was almost always detected (IND, COL and VEN samples). Last, the SAR coal was the most concentrated sample with a benzo(a)pyrene content of 24.8 mg kg^{-1} and a total PAH content of 34 mg kg^{-1}. Those results are quite in accordance with those presented by Zhao *et al.* [8] in raw coals, where 6 PAHs (acenaphthene, anthracene, benzo(b)fluoranthene, naphthalene, phenanthrene, and pyrene) were detected, and in comparable amounts.

Since the finest coal particles (<2 mm) could remain in suspension in seawater after coal immersion, it was attempted to use laser-induced fluorescence on those solid particles in order to detect the PAHs. The study was in this case focused on the SAR coal which contains the highest amount of PAHs.

The lab-designed setup for solid sample fluorescence studies was used with an excitation wavelength of 250 nm, which appeared to be the optimal excitation wavelength, and the beam energy was set so as to avoid a plasma formation. The fluorescence spectra (Fig. 2) showed that a weak fluorescence could be detected with a maximum emission around 450 nm. Between 370 and 450 nm, it was found that this spectrum enclosed the theoretical spectrum corresponding to the sum of all the PAHs detected in the coal sample. However, this observation was valuable only for a part of the whole fluorescence; from 450 to 600 nm, the fluorescence detected must come from other fluorescent substances contained in the coal. Those substances could be humic or fulvic acids, for which the highest fluorescence intensity usually occurs for an emission wavelength between 430 and 530 nm.

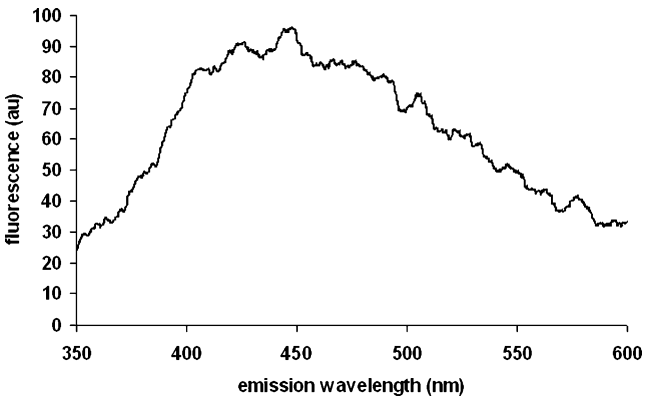

Fig. 2 LASER-induced fluorescence spectrum of the SAR coal – excitation wavelength=250 nm

Coal in seawater results

To simulate a coal immersion, coal and seawater were shaken for 24 h in glass flasks at ambient temperature (20°C) on an end-over-end mechanical shaker at a speed of 60 rpm. After shaking, the samples were centrifuged at 3,600 rpm (Jouan G4-12 centrifuge) in the same flask so as to avoid any contamination. The supernatant was then refrigerated for further analysis.

The first experiments were conducted to study the influence of the coal origin on the fluorescence intensities. Therefore, ten percent in mass of coal (particle size <2 mm-highest exchange surface) were introduced into seawater, according to a standard leaching protocol [16]. Figure 3

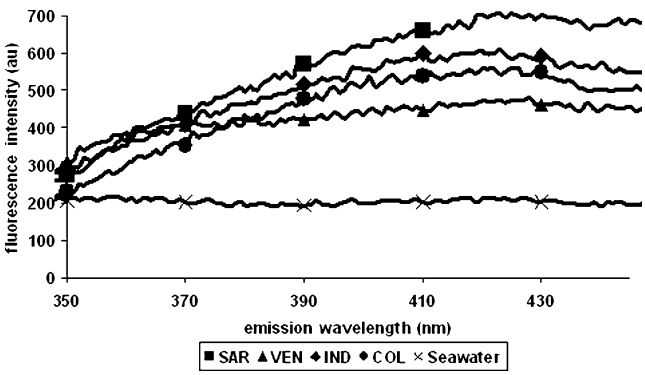

Fig. 3 Fluorescence emission spectra of seawater mixed with four different coals: Venezuela (VEN *filled triangles*), Colombia (COL *filled circles*), Indonesia (IND *filled diamonds*) and South African Republic (SAR *filled squares*) – particle size <2 mm. Excitation wavelength=230 nm; gain=1,000 V. Centrifuged samples

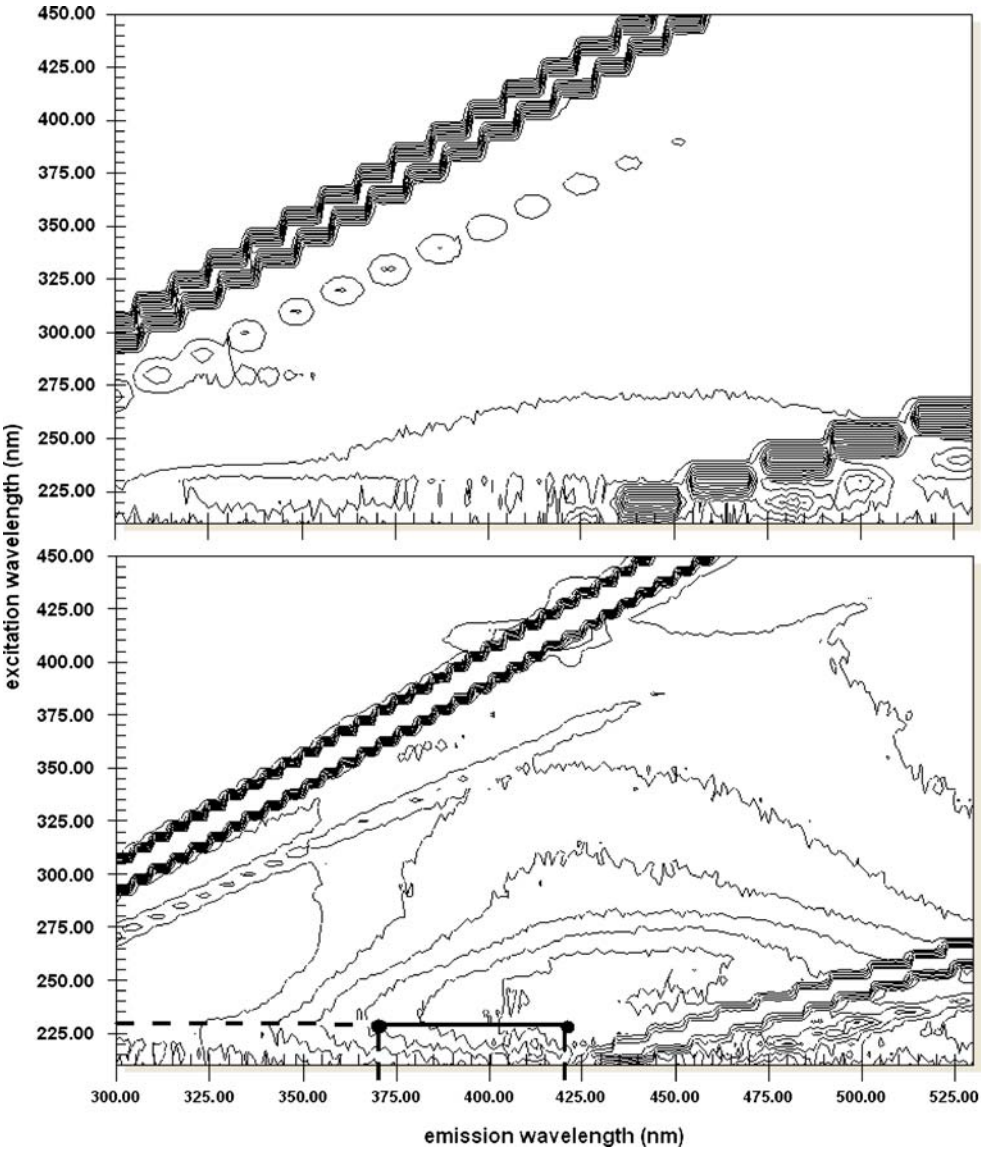

Fig. 4 Excitation–emission matrices of seawater (*up*) and of the SAR sample in seawater (*down*) – particle size <2 mm. Gain= 1,000 V. Centrifuged sample. (Excitation wavelength step size of 5 nm, slit width of 5 nm for both excitation and emission). The *thick black lines* were added to indicate the range of excitation and emission wavelengths corresponding to the highest fluorescence intensity

compares the fluorescence emission spectra obtained for seawater mixed with each coal for an excitation wavelength of 230 nm and an emission wavelength between 350 and 445 nm. In all cases, the addition of coal in seawater induced a significant increase of the fluorescence intensity beyond 350 nm. Compared to pure seawater, the fluorescence intensities were 200 a.u. higher for the VEN coal, 300 a.u. higher for the COL coal, 350 a.u. higher for the IND coal and 500 a.u. higher for the SAR coal. Since the SAR coal induced the highest fluorescence intensity and was the most concentrated in PAHs, which means that it is more liable to be detrimental to the environment than the other coals, it was decided to focus the study on this coal.

Figure 4 shows the EEMs (Excitation–Emission Matrices) of clean seawater and of an SAR coal–seawater mixture. Here again, the fluorescence intensity increases when clean seawater is contaminated by coal, the highest fluorescence intensity being obtained for an excitation wavelength of 230 nm and an emission wavelength between 370 and 420 nm.

Since it could be worth using an immersed probe based on direct fluorescence measurements for in situ monitoring, it has to be kept in mind that in this case the analyzed sample will be neither filtered nor centrifuged and the presence of suspended natural colloids or particles must be taken into account. Thus 10% of SAR coal (particle size <0.5 mm) were mixed with seawater for 30 min, coal suspensions were analyzed by fluorescence after 5 days decantation, and the samples were centrifuged for further fluorescence analysis. A comparison of the fluorescence spectra obtained from the centrifuged samples and from the coal suspensions showed that there exists hardly a difference between those samples. On the one hand, the excitation–emission wavelength couples (EEWC) are sim-

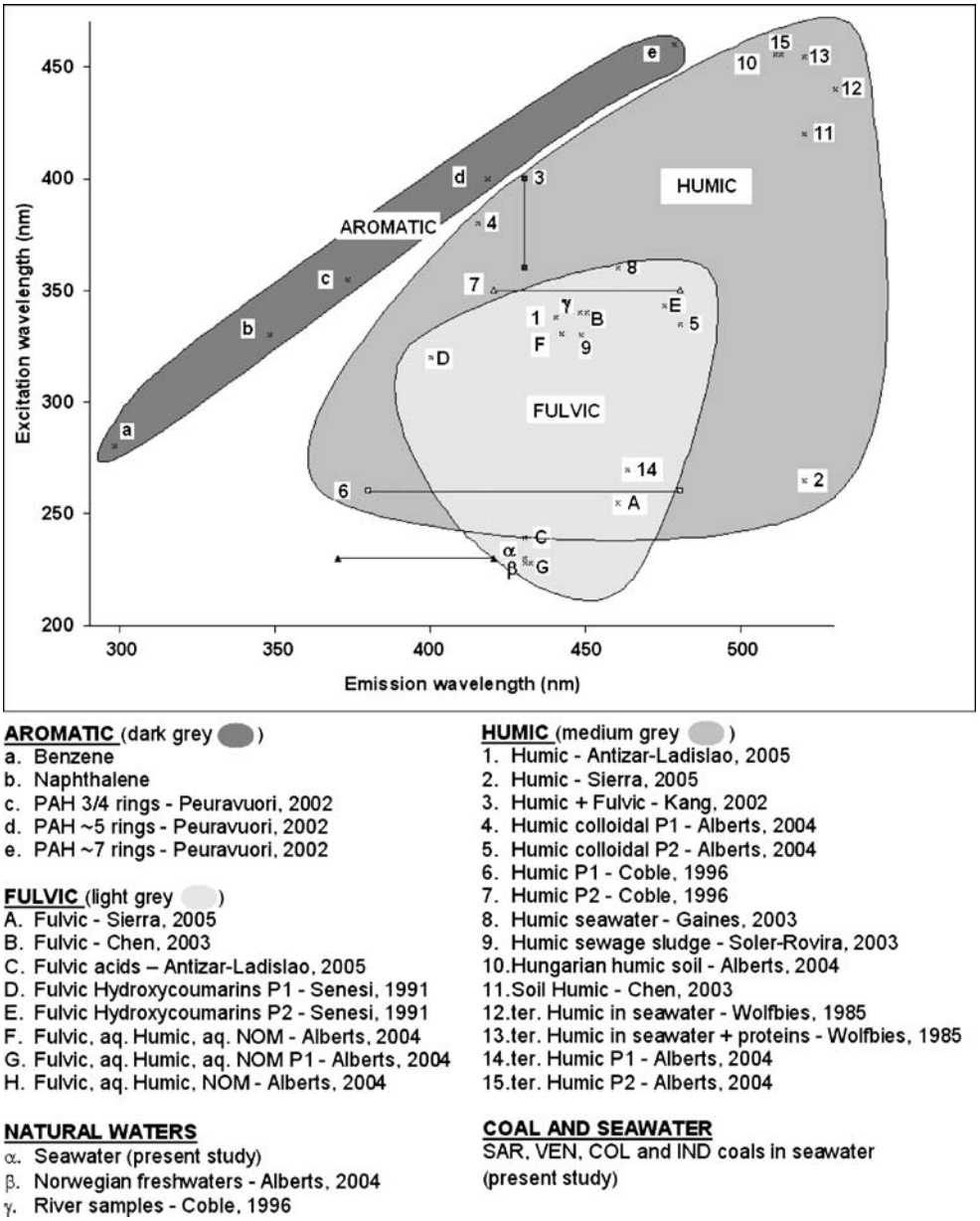

Fig. 5 Comparison of some excitation/emission wavelength couples (EEWCs) from different origins. *Horizontally*: emission wavelength; *vertically*: excitation wavelength. Lines represent the range of EEWC over which the related compounds fluoresce most (*down, left*: lowest excitation, lowest emission wavelengths; *up, right*: highest excitation, highest emission wavelengths). *Crosses* represent a unique EEWC. *Numbers* relate to humic substances; *capital letters* relate to fulvic substances; *small letters* relate to aromatic compounds; *Greek letters* are for natural waters. The EEWC relating to the coal and seawater mixes is indicated at the bottom of the graph (*filled triangles*)

ilar, and on the other hand, the fluorescence intensities are as high in both cases. This means that either the centrifugation is not efficient enough to get rid of all the particles, or the fluorescence of the decanted samples only stems from dissolved material. A work by Bayrakceken *et al.* [17] indicates that suspensions of powdered coals present the highest fluorescence intensity for an excitation wavelength of 230 nm and an emission wavelength between 360 and 400 nm, which matches our results.

The clean seawater fluorescence most probably came from natural organic matters such as humic or fulvic substances. Since the EEWCs of clean seawater and coal and seawater mixings are similar, it is possible that the fluorescence induced by the presence of coal mainly comes from compounds present in seawater, such as naturally occurring humic or fulvic acids. Other works [18–24] have shown that the EEWC giving the highest fluorescence intensity for fulvic or humic acids can vary, depending on the sample nature i.e.: 340/450 nm [25] and 255/460 nm [20] for fulvic acids; 265/520 nm for humic acids and 420/520 nm for of soil humic acids.

Figure 5, based on a bibliographic study, compares the different EEWCs obtained for various humic or fulvic sources to both the EEWCs of aromatic compounds and those obtained here. Each mark on this figure relates to an EEWC; the corresponding compounds and bibliographic references are indicated under the figure. Capital letters refer to fulvic matters, numbers to humic matters, small letters are for aromatic compounds and Greek letters are for natural water samples. This figure illustrates the fact that

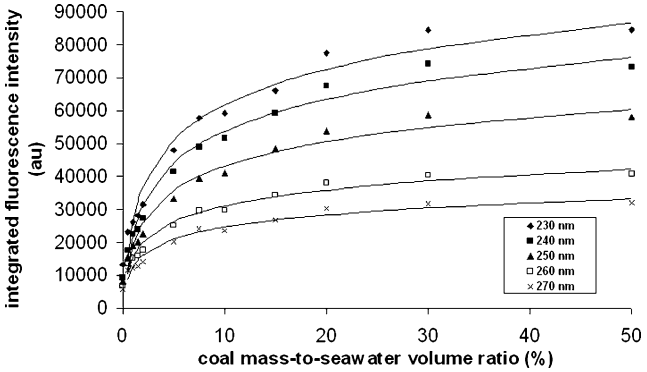

Fig. 6 Fluorescence intensity *versus* the coal mass (g)-to-seawater volume (mL) ratio for various excitation wavelengths. SAR coal; particle size <0.5 mm; gain=975 V. Centrifuged samples

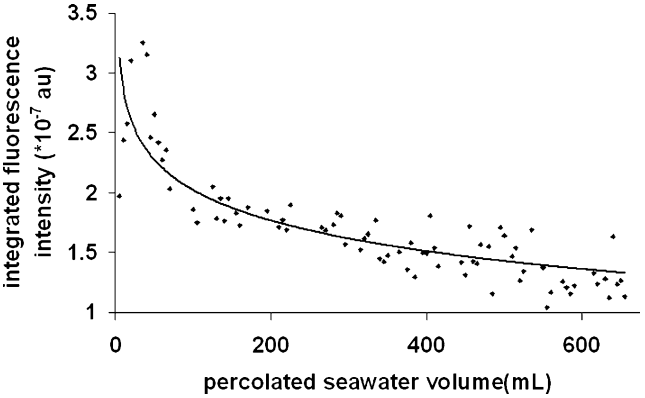

Fig. 7 LASER-induced fluorescence intensity during percolation through a column filled with 20 g of SAR coal (<0.5 mm) as a function of cumulated percolated seawater volume

the fluorescence from the fulvic matter occurs for an excitation wavelength between 250 and 350 nm, and an emission wavelength between 360 and 500 nm (see light grey area on Fig. 5). The fluorescence corresponding to the humic matter spreads over a larger area (see medium grey area on Fig. 5), with an excitation wavelength range from 250 to 470 nm and an emission wavelength range from 350 to 540 nm. Finally, the aromatic compounds fluorescence area, pointed out in dark grey, shows that the aromatics with 1 and 2 rings are separated from both the fulvic and the humic areas (excitation wavelengths from 280 to 330 nm; emission wavelengths from 300 to 350 nm), whereas the PAHs with three to five rings are closer to the humic area (excitation wavelengths from 360 to 460 nm; emission wavelengths from 370 to 480 nm).

Our results show first of all that the wavelength range 230 nm/[370 nm; 420 nm] is far from those corresponding to PAHs, suggesting that the coal-and-seawater samples do not contain many PAHs. The fluorescing substances released by coal into seawater show EEWCs close to fulvic acids and not that far from humic acids. This may be due to some particularity of the coal and seawater humic or fulvic substances, or to a mixing with other organic compounds.

Table 3 Influence of the particle size fraction on the fluorescence intensity

Particle size fraction (mm)	Venezuela coal VEN (a.u. $*10^{-6}$)	Particle size (mm)	South African Republic SAR (a.u. $*10^{-6}$)
0–1	5.38	0–0.5	16.7
		0.5–1	5.71
1–2	3.21	1–3	4.71
2–6	3.68	3–6	3.46
6–16	3.57	6–12	3.40
>16	3.58	12–25	4.10
		>25	4.82

Excitation wavelength 266 nm. Fluorescence integrated from 293 to 400 nm

If one considers that the detected fluorescence only comes from humic acids, a calibration enables to estimate the concentrations of humic acids corresponding to the fluorescence intensities. Thus, the fluorescence intensity of seawater (200 a.u.) corresponds to a humic acid concentration of about 1.3 mg L^{-1}, and the SAR, IND, COL and VEN coal samples fluorescence intensities (700, 550, 500 and 400 a.u., respectively) correspond to humic acid concentrations of 4.6, 3.4, 3.2 and 2.6 mg L^{-1}, respectively.

Influence of various factors on the organic matter released

The influence of different parameters such as the coal-mass-to-seawater-volume ratio and the coal particle size on the release of organic matter into seawater, and consequently on the fluorescence intensity, was also studied and the results are presented here.

The fluorescence variation versus the coal mass (0.25 g to 25 g) mixed with 50 mL seawater (coal-mass-to-seawater-volume ratio from 0.5 to 50%) was tested on the SAR coal (particle size <0.5 mm). Thus, the fluorescence emission was integrated between 320 and 440 nm for excitation wavelengths of 230, 240, 250, 260 and 270 nm. The fluorescence intensity increased logarithmically with increasing coal-mass-to-seawater-volume ratio, for the centrifuged samples (Fig. 6), and the same results were obtained for suspended samples.

Focusing on the linear part of those curves, it was possible to determine a detection limit using the following equation: $\mathrm{DL} = t_v \frac{s_r}{a_1} \sqrt{\frac{1}{n_0} + \frac{1}{n} + \frac{\bar{x}^2}{n.var(X)}}$, where t_v is Student's t, s_r is the residual standard deviation, a_1 is the slope of the linear regression line equation, n_0 is the number of repetitions, n is the number of points, $\bar{x}$ is the mean of the coal-mass-to-seawater-volume ratios and var(X) is the variance of the coal-mass-to-seawater-volume ratio. Using the experimental conditions depicted in this paper, a detection limit of x=0.36% was found. This means that

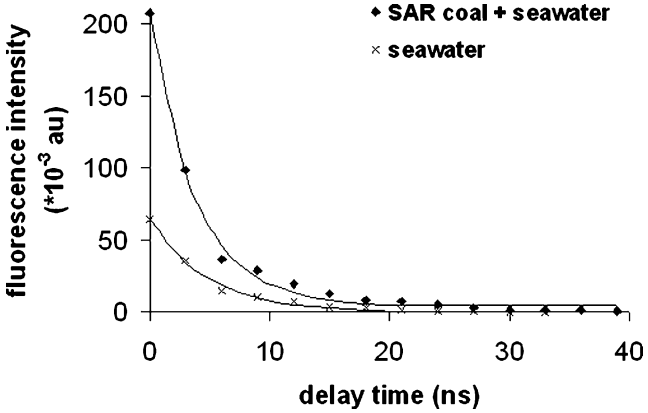

Fig. 8 Fluorescence intensity at 430 nm (excitation wavelength 250 nm) of seawater and of the centrifuged SAR–seawater mixture as a function of delay time (SAR coal <1 mm, 10%)

for a minimum of 3.6 kg of coal in 1 m^3 seawater, and after 5 days decantation, there can still be detected a significant fluorescence increase.

The influence of the particle size was tested on the VEN and SAR coal samples by mixing and centrifuging 10% of a selected size fraction with seawater. The fluorescence intensity was integrated between 353 and 393 nm for an excitation wavelength of 266 nm, which corresponds to a tripled YAG wavelength, easy to obtain whenever an immersed probe is used. One can see in Table 3 that the finest particles induced the highest fluorescence intensity and probably the greatest organic matter release. This phenomenon must be due to the highest specific exchange surface offered by the smallest particles. Those fine particles are therefore more liable to be detrimental to the environment than the bigger ones.

In order to simulate an open environment, which is closer to the reality than a batch system, a glass column was used, in which 20 g of SAR coal (particle size <0.5 mm) were deposited. Seawater percolated through the coal at a speed of 100 mL h^{-1}, and 5 mL samples were collected every 3 min. The fluorescence intensity was integrated between 353 and 393 nm for an excitation wavelength of 266 nm. Figure 7 shows a fluorescence intensity decrease with increasing cumulated seawater volume. This means that, throughout the percolation process, the collected samples contained fewer and fewer organic fluorescing substances, and that there exists a limitation to the release of fluorescing compounds from coal into seawater.

Time resolved, laser-induced fluorescence

Laser-induced fluorescence enabled us to measure the fluorescence lifetimes of the seawater and the SAR–seawater mixture. The organic matter lifetime determination could indeed bring out some information about its nature. Therefore, an excitation wavelength of 250 nm was chosen so as to be closest to the 230 nm excitation wavelength mentioned above, and still have sufficient pulse energy (120 μJ) to excite molecules and be able to detect some fluorescence. For each measure, the opening time of the camera was set to 3 ns and a time delay of 3 ns was inserted between each successive measurement.

The fluorescence intensities decreased exponentially as shown in Fig. 8. A regression method using the following model equation was used to determine the lifetimes: $I_t = (I_0 - I_F) \cdot e^{-\frac{t}{\tau}} + I_F$, where I_t is the fluorescence intensity for a delay time of t (in ns), I_0 and I_F are the initial and final fluorescence intensities, respectively, t is the delay time (in ns) and τ is the sample fluorescence lifetime (in ns).The τ values are short in both cases: 4.7 and 3.8 ns for the seawater and the SAR–seawater mixture, respectively. Since both values are quite close, it shows again that the natural organic matter present in seawater could be of a nature comparable to the organic matter released from coal.

Since humic substances have a shorter lifetime than PAHs, the fluorescence spectra with a delay time of 10 ns after the laser pulse was recorded, so that the fluorescence intensity due to the presence of humic substances could become negligible compared to the fluorescence intensity of PAHs. However, the results did not allow isolating a specific PAH spectrum, owing to their very low concentrations (whenever present) compared to the humic substances. It can therefore be concluded that, despite the efficiency of laser-induced fluorescence in terms of detection limits for PAH, which is about 10 ng L^{-1} for benzo(a) pyrène [14], this method is not relevant to bring out the presence of PAHs in these samples.

To have a formal conclusion on the presence or absence of PAHs in seawater mixed with coal, an analysis by CGMS was conducted. 10 mL seawater were mixed with 10% SAR coal, shaken for 24 h, and eventually centrifuged. The supernatant was extracted by 1 mL hexane to concentrate the organic molecules 10 times. The results did not show the presence of any of the seven PAHs found in the coal, meaning that their concentration is below the detection limit of the method, estimated at 30 ng L^{-1}.

Conclusion

The results presented here focus on a specific type of contamination, namely dissolved organic pollution. They show that coal releases humic and fulvic matter after immersion in seawater, which can induce an important increase of the organic content, depending on the coal origin and the size of the coal particles.

However, although coal actually does contain PAHs, the potential release of such compounds into seawater is not that strong, and consequently their concentration appears

too low to be detectable. Therefore, it could not so far be asserted that the presence of coal in seawater is liable to pollute the environment through that specific way.

As the results show, although the fluorescence cannot allow identifying the type of compounds present in seawater even with time resolution, it can however be a measurement of the amount of organic matter in solution based on the fluorescence increase between the pure seawater and the coal-contaminated one. An immersed fluorescence probe could be used to directly monitor and follow a significant increase of the organic matter.

However, other impacts on the environment have still to be studied and assessed in future works. Water column darkening due to the presence of suspended particles may decrease the photosynthesis rate and thus prevent the phytoplankton and later zooplankton development. Coal particles could also be deposited on the seafloor and mix with sediments, which would induce a contamination of this milieu.

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