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Fluorescence Characteristics of Triazine-Manufacturing Wastewater

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ABSTRACT

Samples taken at different points in the wastewater treatment process of a triazine-manufacturing plant were scanned by fluorescence spectroscopy, in the wavelength range of 200–900 nm. Reproducibly, the fluorescence spectra revealed one single major peak at excitation and emission wavelengths of 258 and 370 nm respectively. Aqueous solutions of purified active compounds, including Atrazine, Propazine, Simazine, Terbuthylazine, Metolachlor, and Benoxacor, were also scanned. No significant fluorescence was observed in these standard solutions at concentrations up to 100 mg/L. Selected plant samples as well as standard solutions of Atrazine, Metolachlor, and toluene were further analyzed using high-performance liquid chromatography with absorbance and fluorescence detections. Pure Atrazine was found to be light-absorbing but nonfluorescent while Metolachlor, with a benzene ring in its structure, was weakly fluorescent. The plant wastewater samples exhibited a single strong fluorescence peak, which also appeared as the dominant peak in the fluorescence chromatogram of Atrazine standard (due to impurity). The findings strongly suggested that the responsible fluorescent compound in the plant's wastewater was a byproduct of the synthesis processes. The fluorescent compound was found to be effectively removed by the carbon adsorption treatment (CAT) unit employed in the plant but not by the biological activated-sludge treatment process alone. The results indicated the feasibility of using online fluorescence measurements to effectively monitor the performance of the CAT unit.

Key words: fluorescence; triazine; carbon adsorption; activated sludge

INTRODUCTION

Triazines are used widely in agriculture as herbicides for pre- and postemergent control of leafy and grassy weeds in soybeans, corn, and other crops (Hogrefe *et al*., 1985; Frassanito *et al*., 1996; Liu *et al*., 2002; Wackett *et al*., 2002). Syngenta Crop Protection manufactures a variety of herbicides, including triazines (Atrazine, Propazine, Simazine, and Terbuthylazine), Metolachlor, and Benoxacor, at its plant at St. Gabriel, Louisiana (White *et al*., 1994; Sajjaphan *et al*. 2002). The wastewater treatment process in this plant consists primarily of a carbon adsorption treatment

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(CAT) unit and a subsequent aerobic biological activated-sludge (BAS) treatment. Although proven particularly useful in handling influent fluctuations, the CAT unit constitutes a major cost of the treatment process. It is economically beneficial if the CAT unit can be bypassed to the extent allowable by the treatment capacity of the BAS. Online monitoring of the influent and treated waters represents a promising approach to automatic control of the CAT bypass.

Various spectroscopic methods, including ultraviolet (UV)–visible (vis) (Ferree and Shannon, 2001; Langergraber *et al*., 2003), infrared (IR, mid or near) (Vaidyanathan *et al*., 2000; Mizaikoff, 2003), and fluorescence (monodimensional, two-dimensional or synchronous) (Ahmad and Reynolds, 1999; Lee and Ahn, 2004; Ju *et al*., 1995; Li *et al*., 2002; Farabegoli *et al*., 2003; Ju and Nallagatla, 2003), have been investigated for applications in noninvasive, nondestructive online monitoring of wastewaters and biological/bioprocessing systems. Among them, the fluorescence methods are much more sensitive than the other absorbance-based methods, and they are much less affected by the water/medium turbidity (Pons *et al*., 2004). Being more specific and selective, the online fluorescence technique is thus potentially the most effective way of monitoring the influent fluctuation. Technology is now available to develop robust and almost maintenance-free fluorometers for monitoring wastewater treatment plants (Ju *et al*., 1995; Li and Ju, 2002; Farabegoli *et al*., 2003; Ju and Nallagatla, 2003). As a first step, the fluorescence characteristics of the wastewater samples taken along the treatment process in the triazine manufacturing plant were examined in this study using bench-top scanning fluorometry and fluorescence detection coupled with high-performance liquid chromatography.

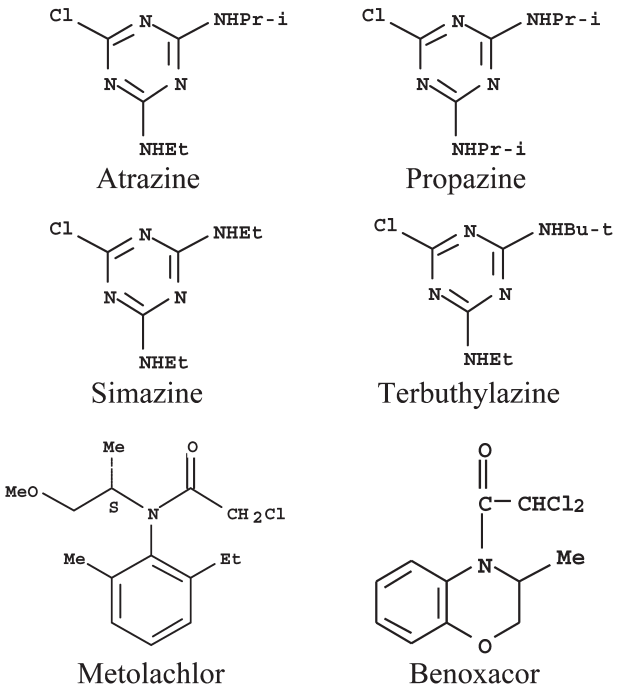

Figure 1. Chemical structures of Atrazine, Propazine, Simazine, Terbuthylazine, Metolachlor, and Benoxacor

MATERIALS AND METHODS

Materials and chemicals

Purified standards of Atrazine, Propazine, Simazine, Terbuthylazine, Metolachlor, and Benoxacor (chemical structures summarized in Fig. 1) were obtained from Syngenta crop protection and scanned for their excitation and emission (fluorescence) spectra. Also provided by Syngenta were multiple batches of wastewater samples taken on different dates over a period of 9 months and shipped overnight on ice to our laboratory. In each batch, the samples were taken at several locations in the treatment process, including the influent to CAT, the effluent from CAT (which was the same as the influent to BAS), the mixed liquor in BAS bioreactor, and the effluent from the BAS clarifier. The properties of the influent-to-CAT samples used in this study varied considerably: pH—7.2 ± 0.3, total organic carbon (TOC)—279 ± 63 mg/L, total concentration of the aforementioned active compounds—41 ± 11 (mg/L), total Kjeldahl nitrogen (TKN)—87 ± 31 mg/L, toluene concentration—3.5 ± 3.4 mg/L, and ammonia-N concentration—37 ± 19 mg/L. (more detailed data for individual batches are given later in Results and Discussion, and summarized in Fig. 7.) The BAS mixed-liquor samples were centrifuged to collect the supernatants. Upon receiving, these pure compounds and samples were used to prepare test samples of serial dilutions and scanned using a luminescence spectrometer (Perkin-Elmer, Waltham, MA, LS50B). For the high-performance liquid chromatography (HPLC) analysis, some of the samples were dried by gentle surface air flow (after being passed through a 0.22-μm filter) and then redissolved in the mobile phase (80/20 mixture of acetonitrile (ACN)/water).

Fluorescence measurements

Using the luminescence spectrometer (Perkin-Elmer LS50B), three types of fluorescence measurements were performed in this study for different purposes. These were the prescan, the three-dimensional (3D) synchronous scan, and the fixed-wavelength measurement of fluorescence intensity. All fluorescence measurements were conducted at room temperature (22 ± 1°C) with standard Quartz fluorometer cuvettes of 1-cm pathlength (Starna Cells, Inc., Atascadero, CA). Both excitation and emission wavelengths were set with a fixed slit width (spectral bandpass) of 5 nm. The commercial spectrometer had the wavelength accuracy of ±1 nm and the wavelength reproducibility of ±0.5 nm. All

fluorescence measurements were made in duplicate or triplicate.

For initial samples, prescan was carried out over the entire wavelength range of the excitation and emission monochromators (200–900 nm), to identify the approximate ranges of excitation and emission peaks and the appropriate dilution factors for obtaining useful peak information (with intensities not too low or too high). For the equipment used, the maximum (saturation) intensity level was 1,000 (in the arbitrary unit set by the manufacturer).

With the appropriate dilution factors, the samples were next scanned under the 3D synchronous mode at constant wavelength differences between emission and excitation monochromators ($\Delta\lambda = \lambda_{em} - \lambda_{ex}$). The excitation wavelength was varied from 200 to 500 nm, while $\Delta\lambda$ was varied from 10 to 210 nm. The extensive 3D scans provided complete and accurate information on the excitation and emission peak(s) of the samples. As shown later, for the Syngenta plant samples, a single major peak was identified with excitation and emission wavelengths of 258 and 370 nm, respectively. With this information, the samples were then serially diluted with deionized water and measured for their fluorescence intensities at these excitation and emission wavelengths. As described later in the Results and Discussion section, the fluorescence intensities obtained for samples taken on different dates and at different locations of the wastewater treatment process were compared to indicate the removal efficiency of the fluorescent compound(s) by the CAT and BAS units. The duplicate or triplicate measurements made for each sample were found to give very consistent intensity readings, with standard deviations smaller than $\pm 2\%$. Accordingly, only the average intensities are reported in the Results and Discussion section.

High-performance liquid chromatography with absorbance and fluorescence detection

The analysis was conducted with an HPLC instrument (HP 1150, Hewlett–Packard) equipped with a diode array detector (DAD) and a fluorescence detector (HP 1100 series). The DAD detector was set at 254 ± 16 nm, with a reference wavelength of 360 ± 100 nm. The fluorescence detector was set with excitation and emission wavelengths of 255 nm and 370 nm, respectively. A Supelco C-18 column was used with a mixture of 80% acetonitrile (ACN) and 20% water as the mobile phase. The flow rate of mobile phase was 0.85 mL/min and the sample injection volume was 5 μL.

RESULTS AND DISCUSSION

Three-dimensional synchronous scans of pure compounds and wastewater samples

Purified standards of Atrazine, Propazine, Simazine, Terbuthylazine, Metolachlor, and Benoxacor were each dissolved in deionized water to make solutions of various concentrations, ranging from 1 to 100 mg/L. The chosen concentration range corresponded to that found in the plant wastewater. These aqueous solutions were scanned with the luminescence spectrometer under the 3D synchronous mode for potential fluorescent properties. Within the concentration range studied, none of these aqueous solutions of purified compounds exhibited fluorescence spectra of appreciable intensities. For example, as shown in Fig. 2, the 3D contour plot obtained for a 93-mg/L Atrazine solution was essentially blank (compared to that for an influent sample shown in Fig. 3). The nonfluorescent property of the triazines examined, that is, Atrazine, Propazine, Simazine, and Terbuthylazine, may be attributed to the fact that their unsaturated rings have only the strong light-absorbing C═N double bonds (Fig. 1), instead of the commonly fluorescent C═C bonds. Metolachlor and Benoxacor, however, have a typically fluorescent benzene ring in their structures. As described later (Fig. 8), when analyzed by HPLC with fluorescence detection, Metolachlor was indeed found to be weakly fluorescent while Atrazine was not. Benoxacor was not further examined because its concentration in the plant's wastewater during the study period was very low ($\leq$ approximately 1 mg/L).

The 3D synchronous fluorescence scanning was also carried out with some of the wastewater samples from the Syngenta plant. Contrary to the observations obtained with the aqueous solutions of purified standards, the wastewater samples were found to be clearly fluorescent. The fluorescence spectra were especially evident with the samples of CAT in-

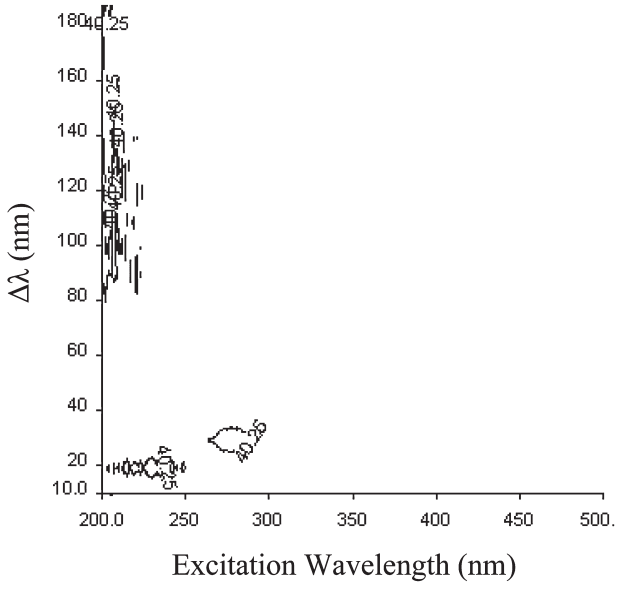

Figure 2. A contour plot of 3D fluorescence scans for Atrazine at 93 mg/L ($\Delta\lambda$ = Emission Wavelength − Excitation Wavelength).

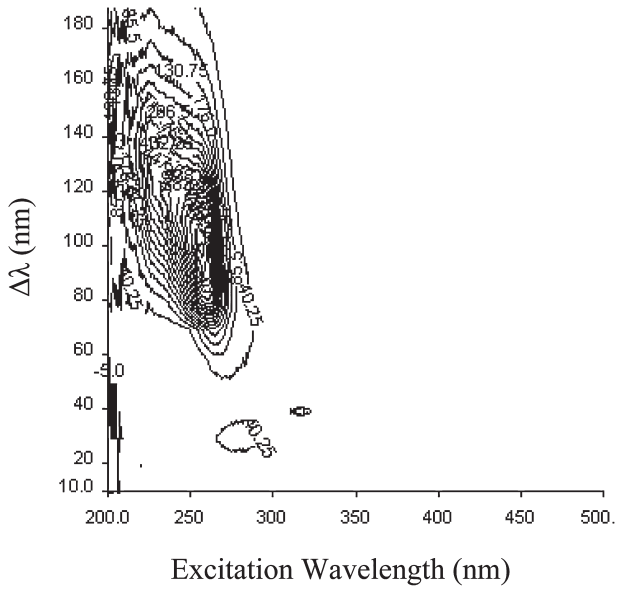

Figure 3. A contour plot of 3D fluorescence scans for 200-fold diluted CAT influent sample taken on 02/04/2004 ($\Delta\lambda$ = Emission Wavelength − Excitation Wavelength).

fluents. (The fluorescence intensities observed with the samples taken at different process points/locations in the plant were described in more details later.) For example, the 3D contour plot obtained for the CAT influent sample taken on February 4, 2004, is shown in Fig. 3. A primary fluorescence peak was clearly identified with an excitation maximum at 258 nm and an emission maximum at 370 nm. The fluorescence characteristics shown in Fig. 3 were consistently observed with all of the wastewater samples taken from the plant. Consequently, the fluorescence intensity of this peak was the primary target measured and compared for different samples in this study.

Fluorescence intensity vs. dilution factor

In dilute solutions, fluorescence intensity typically shows linear proportionality to the fluorophore concentration. At higher concentrations, the linearity no longer holds because the portion of sample nearest the surface of incident light absorbs so much light that little is available for the rest of the sample. At very high concentrations, the above "concentration quenching" effect can even cause the fluorescence intensity to decrease with increasing fluorophore concentration, if the measurement was not made at the surface detection mode that minimizes the depth of light penetration (Hercules, 1966). (The phenomenon of lower fluorescence intensities at higher fluorophore concentrations is avoided in online fluorometers by having the excitation and emission lights traveling in opposite directions (360° angle difference). With such an arrangement, the "concentration quenching" effect reduces the volume of sample excited and detected as the fluorophore concentration increases. As a result, the fluorescence intensity depicts a saturation profile, instead of the increase-then-decrease profile, with increasing fluorophore concentrations.) Therefore, proper dilution factor(s) needed to be identified for the samples used in this study, to ensure that the fluorescence intensities were obtained in the range of linear correlation and the comparison of intensities from different samples would not be misinterpret.

Accordingly, the fluorescence intensities at 258/370 nm were measured with a series of solutions prepared by diluting the original plant sample with deionized water. For example, the fluorescence intensities obtained with the serially diluted solutions of the CAT influent sample taken on May 19, 2003, are shown in Fig. 4. In Fig. 4A, the emission spectra at 280–480 nm (excitation at 258 nm) were compared for the original and the 50-, 100-, 200-, and 300-fold

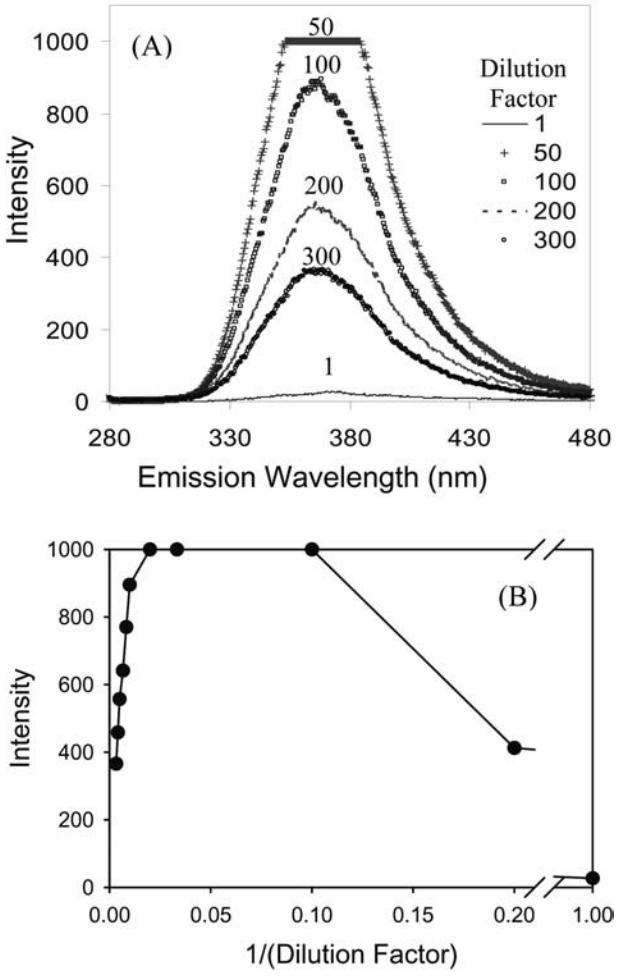

Figure 4. (**A**) Fluorescence emission spectrum at different dilution factors, and (**B**) change of fluorescence intensity with increasing fluorophore concentration, for CAT influent taken on 05/19/03 at fixed excitation wavelength of 258 nm.

diluted samples. The serial dilutions were shown not to shift the peak wavelength or the general spectral shape but to cause dramatic changes in the peak fluorescence intensities (at 370 nm). As summarized in Fig. 4B, with increasing sample strengths [plotted in 1/(dilution factor)], the peak fluorescence intensity increased initially but would start to decrease when the sample strength was higher than certain critical level, as expected from the concentration quenching effect. Nonetheless, the fluorescence intensity and the sample strength had a linear correlation in the dilute range. In general, the appropriate dilution factors for plant samples were found to be 200× for the CAT influents, 50× for the CAT effluents and the BAS effluents, and 20× for the BAS mixed-liquor supernatants, respectively.

Changes in fluorescence intensity along wastewater treatment process

For developing potential process monitoring and control strategies, it was important to know how the wastewater treatment process affected the fluorescence spectra and peak intensities of the wastewaters. The fluorescence spectra appeared to remain essentially unchanged (data not shown). Only the fluorescence intensities were affected, as described below.

The peak fluorescence intensities (at 258/370 nm) obtained for the plant samples taken at different points of the wastewater treatment process are summarized in Fig. 5 for four batches of samples (taken on 5/19/2003, 8/20/2003, 10/9/2003, and 2/4/2004, respectively). Proper dilution factors, as described earlier, were used in the measurements, and the intensities given in Fig. 5 had been adjusted for the dilution factors involved. While differing in absolute intensities, the results from the four batches of samples revealed the following typical trend: The fluorescence was very strong in the influent to CAT unit. The fluorescence was substantially lower in the effluent from CAT unit, especially in the samples taken on August 20, 2003. The finding indicated that the carbon adsorbed the fluorescent compound(s) effectively. In some batches of samples, particularly those taken on February 4, 2004, when the CAT unit was near its saturation capacity, the fluorescence remained significant in CAT effluent. The results supported the feasibility of using online fluorescence monitoring to follow the performance of the CAT unit and to schedule for carbon regeneration or replacement. On the other hand, the fluorescence intensities were not drastically different among CAT effluent (i.e., BAS influent), BAS mixed-liquor supernatant, and BAS effluent, suggesting that the fluorescent compound(s) was not appreciably degraded by the BAS treatment.

The fluorescence measurements were also made with the samples taken from a laboratory study that was conducted to evaluate the feasibility of directly treating fractions of the CAT influents by the BAS unit (i.e., partially bypassing the CAT unit). The laboratory bioreactor was operated under conditions similar to the BAS unit of the plant, that is, with hydraulic retention time (HRT) of 12 h and mixed liquor suspended solids (MLSS) of about 2 g/L. Batches of CAT influent and BAS influent samples were taken from the plant in relatively large volumes, kept refrigerated, mixed in chosen ratios, and used as the feed to the laboratory reactor. Many batches of these plant wastewater samples had been studied. The influent and effluent samples taken from the study with two particular batches were subjected to detailed fluorescence measurements. The compositions of these sam-

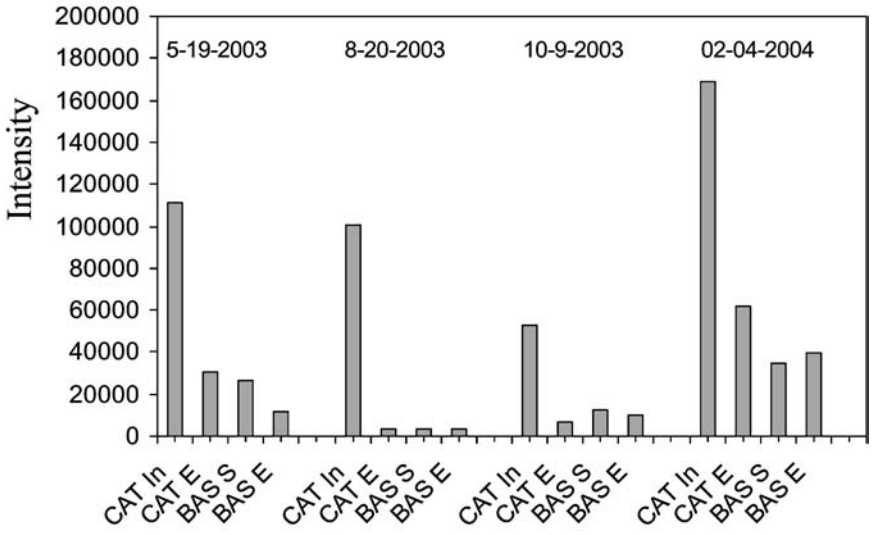

Figure 5. Fluorescence intensity (258/370 nm) of CAT influent (CAT In), CAT effluent (CAT E), BAS supernatant (BAS S), and BAS effluent (BAS E) samples taken on 5/19/03, 8/20/03, 10/9/03, and 02/04/04

ples are given in Table 1. As indicated in Table 1, when used as the influent to the bioreactor, one batch of the plant wastewater caused partial inhibition to the biological treatment activity. The inhibition was corroborated by the lower TOC removal, incomplete nitrification, and poorer pesticide degradation attained in this batch, compared to those attained in the other batches. (More detailed results from the laboratory study, on the feasibility of CAT bypass, are to be published in a separate report.) The fluorescence examination was to evaluate if the inhibition could be identified from the fluorescence spectra and/or peak intensities.

The 3D fluorescence spectra for the 200-fold diluted influent and effluent samples from the two batches of study are shown in Fig. 6. (The serial dilution measurements, as described earlier, had been first carried out to ensure that the 200-fold dilution would bring the samples to the range of linear correlation between fluorescence intensity and sample concentration.) The samples from the two batches were found to have similar fluorescence characteristics (Fig. 6). The peak fluorescence intensity at 258/370 nm was lower in the inhibitory influent than that in the noninhibitory influent. In addition, the fluorescence intensity decreased slightly in the inhibited reactor (245 for influent and 198 for effluent) but remained constant (424/423) in the noninhibited reactor. While the mechanism causing the fluorescence decrease in the inhibited reactor requires further elucidation, the results confirmed that the fluorescent compound(s) was not responsible for the inhibition.

It is concluded accordingly that the fluorescent compound(s) was removed effectively by CAT but not by the BAS alone. For the potential bypass of CAT unit in the treatment process, this finding may or may not indicate problems depending on whether the fluorescent compound(s) has negative environmental effects if released without removal.

Table 1. Composition of influent and effluent samples collected in two laboratory experiments simulating the plant's BAS operation.[a]

	Inhibitory feed		*Noninhibitory feed*	
Composition[b]	*Influent*	*Effluent*	*Influent*	*Effluent*
TOC	273	157	240	90
Ammonia-N	77	10	49	<1
Atrazine	27	3.1	19.0	0.38
Simazine	10	0.16	0.5	<0.1
Propazine	2.7	0.8	1.5	0.16
Terbutylazine	N/A	N/A	1.1	0.24
Metolachlor	N/A	N/A	2.1	2.3

[a]Fluorescence characteristics of the corresponding samples are shown in Figure 6; [b]All concentrations are reported in mg/L (ppm); N/A, not analyzed.

Correlation between fluorescence intensity and water composition

The plant routinely analyzed the wastewater composition for concentrations of total organic carbon (TOC), ammonium, Propazine, Terbuthylazine, Atrazine, Simazine, Benoxacor, Metolachlor, benzene, toluene, chlorobenzene, ethylbenzene, and 1,3-, 1,4-, and 1,2-dichlorobenzenes (DCB). For all of the plant samples used in this study, the concentrations of benzene, chlorobenzene, ethylbenzene, and DCBs were all below 0.01 mg/L, which was the detection limit of the analytical procedures employed in the plant. These compounds were therefore not considered for potential correlations with the measured fluorescence at 258/370 nm. The fluorescence intensities of CAT influents (at 200-fold dilution) taken on different dates were plotted against each water composition parameter, totally 10 parameters, in Fig. 7. (The subsets in Fig. 7 contain different numbers of data points because some were below the analytical detection limits.) The fluorescence intensities of some CAT effluents and BAS effluents (at 200-fold dilution) are also included in Fig. 7 (indicated as the "open" symbols). The data points for TOC, TKN, ammonia, and Terbuthylazine scattered randomly, as shown in the four lower subsets on the right-hand side column of Fig. 7. This observation excluded possible correlation between the fluorescence intensity (at 258/370 nm) and their concentrations. On the other hand, it appeared that the fluorescence intensity increased with increasing concentrations of toluene, Metolachlor, Benoxacor, Atrazine and Propazine (as shown in the five subsets on the left column of Fig. 7), but decreased with increasing Simazine concentration.

Some arrowed lines are drawn in Fig. 7 to link the data points taken on the same date but at different locations/stages of the wastewater treatment process: the solid lines are for the samples taken from the plant while the dashed lines are for the samples taken from the laboratory reactor for the CAT bypass study, as described earlier. Linking these data points by arrowed lines helps to show the effects of the treatment process on the specific concentrations and the corresponding changes in the fluorescence intensity at 258/370 nm. For the plant samples, the fluorescence intensity clearly decreased with the decreasing specific concentrations (i.e., for Metolachlor, Atrazine, Propazine, and TOC). Similar corresponding decreases in the fluorescence intensity and the concentrations of Atrazine, Propazine and TOC were not seen for the samples taken from the laboratory reactor. (Note that the biological treatment in the laboratory reactor did not degrade Metolachlor.) The findings confirmed the earlier conclusion that the fluorophore(s) was removed by carbon adsorption but not by biological treatment, as the treatment process in the plant differed from that in the laboratory reactor primarily in the presence of the CAT unit. The findings also supported the notion that the fluorescence inten-

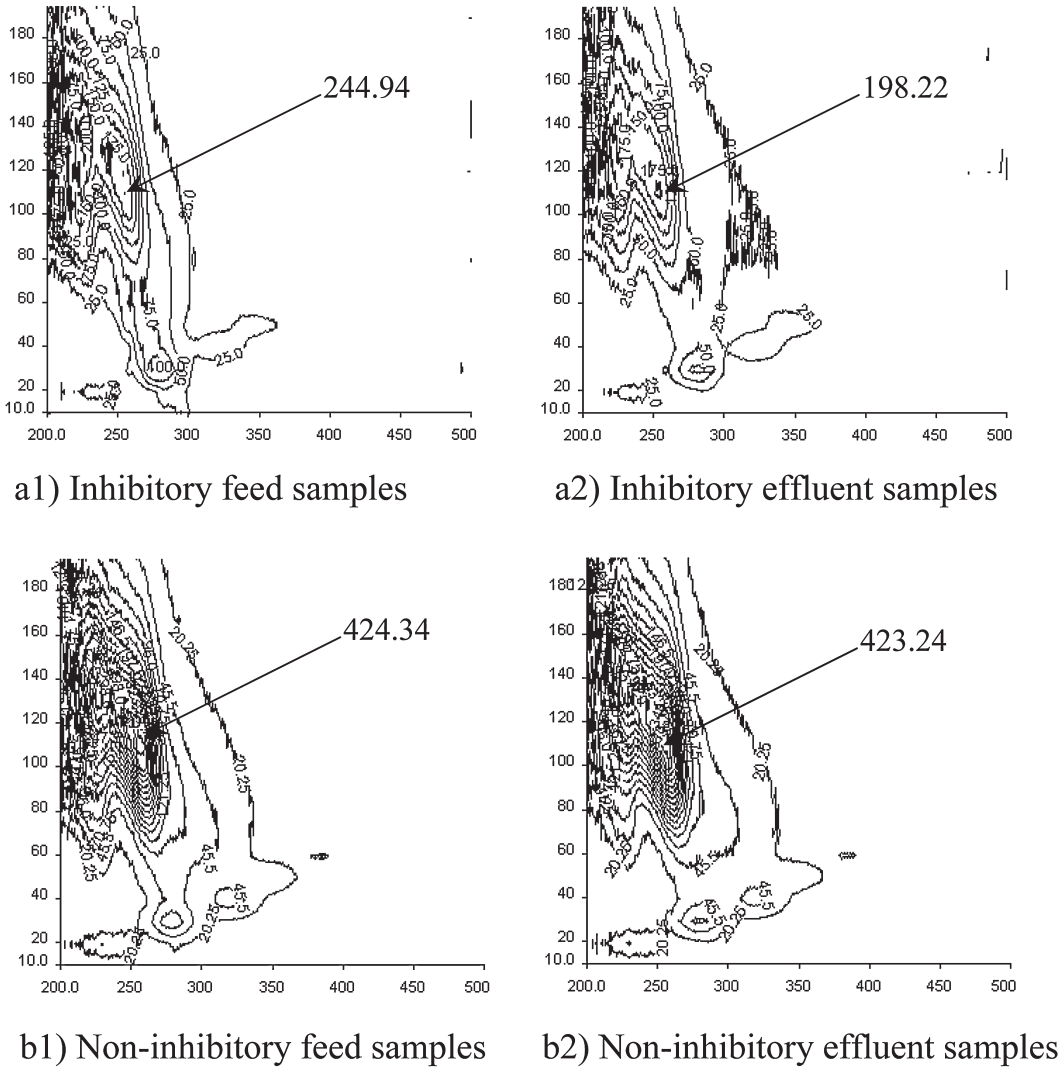

Figure 6. 3D contour plots for fluorescence of 200-fold diluted samples from the laboratory simulation study: (**a**) inhibitory feed and effluent samples, (**b**) noninhibitory feed and effluent samples. All figures are shown with Excitation Wavelength (nm) as the x-axis, and $\Delta\lambda$ (nm) (i.e., Emission Wavelength − Excitation Wavelength) as the y-axis.

sity did not correlate directly with Atrazine, Propazine, or TOC concentration; otherwise, corresponding decreases in fluorescence intensity would have been observed also with the samples from the laboratory reactor.

Elucidation of potential source of fluorophore using HPLC

To gain more insights into the possible cause(s) of the correlations revealed with the subsets in the left column of Fig. 7, HPLC with absorbance and fluorescence detections was carried out with the following samples: two plant wastewater samples (8/20/2003 CAT influent and 12/03/2003 BAS effluent), a sample of the fresh toluene used in the plant, Atrazine standard, and Metolachlor standard. The wastewater samples were prepared to have about 10 mg/L of total solutes in mobile phase. The toluene, Atrazine, and Metolachlor samples were analyzed at the concentration range of 5–100 mg/L. Selected results are shown in Fig. 8 and discussed in the following:

1. The 8/20/2003 CAT influent sample had a single dominant fluorescence peak at retention time (RT) of about 4.7 min and three absorbance peaks at RT of about 4.5, 4.6, and 5.7 min, respectively (Fig. 8A). The absorbance peak at RT ~4.6 min corresponded to the fluorescence peak at RT ~4.7 min due to the sequential flow through the two detectors. The absorbance peaks at RT ~4.5 and 5.7 min did not appear in the chromatogram for the

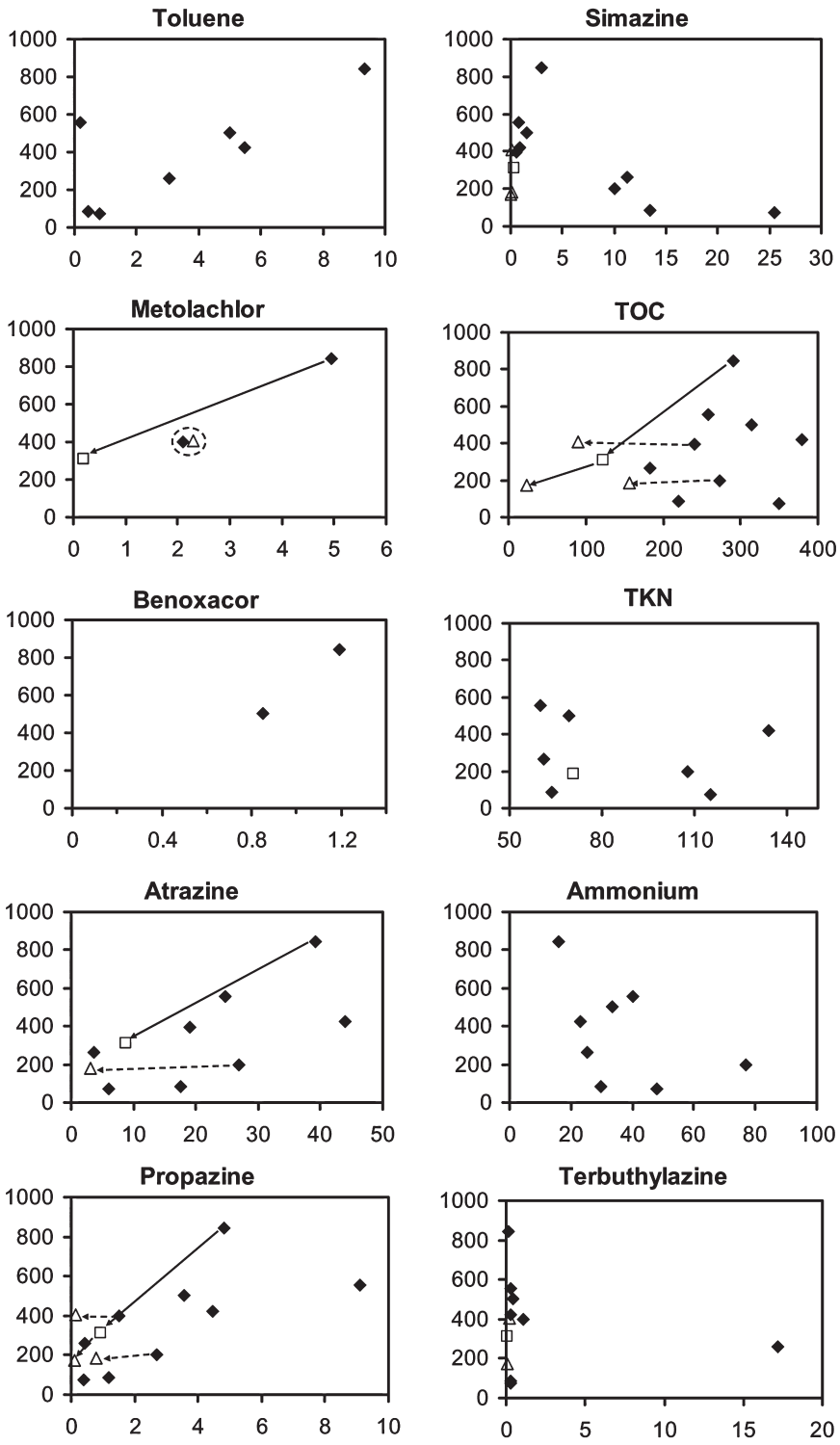

Figure 7. Correlation between fluorescence intensity and water composition (left column: toluene, Metolachlor, Benoxacor, Atrazine, and Propazine; right column: Simazine, TOC, TKN, ammonia-N and Terbuthylazine): ◆—CAT influents, □—CAT effluents, and △—BAS effluents.

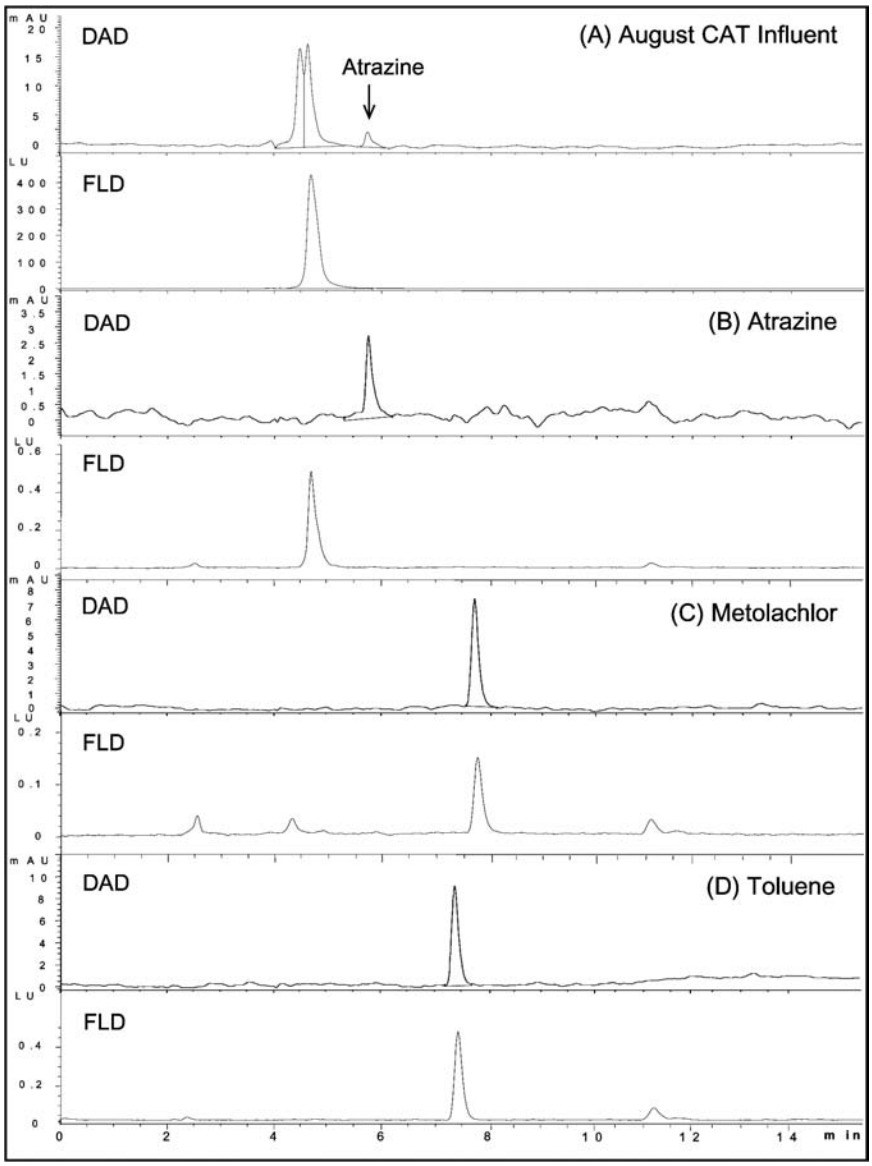

Figure 8. HPLC chromatograms by absorbance (DAD) and fluorescence (FLD) detections for (**A**) plant CAT influent sample taken on 8/20/03, with total solute concentration adjusted to about 10 mg/L; (**B**) 8 mg/L of Atrazine standard; (**C**) 100 mg/L of Metolachlor standard; and (**D**) 100 mg/L of toluene used in the plant as extraction solvent.

12/03/2003 BAS effluent sample but the fluorescent compound persisted at much lower absorbance and fluorescence intensities (3.5 mAU and 150 LU, respectively, chromatogram not shown). The absorbance peak at RT ~5.7 min is attributed to Atrazine, which has the light-absorbing but nonfluorescent C═N bonds. The same absorbance peak appeared in the chromatogram for Atrazine standard (Fig. 8B).

2. Besides the single absorbance peak, the Atrazine standard (at 8 mg/L) showed three fluorescence peaks at RT ~2.5, 4.7, and 13.1 min, respectively (Fig. 8B). The predominant fluorescence peak appeared at the same RT (~4.7 min) as that in the chromatograms of plant samples (Fig. 8A).
3. The Metolachlor standard showed a single absorbance peak at RT ~7.7 min with a corresponding dominant fluorescence peak. The fluorescence intensity was, however, only about 0.1 LU (an arbitrary luminescence unit) for 100 mg/L of Metolachlor, compared to the fluorescence intensity of about 400 LU for 10 mg/L of CAT influent (Fig. 8A). Metolachlor, with a benzene ring in its structure, was therefore very weakly fluorescent (thus, undetectable in the 3D fluorescence scan) and could not be the compound responsible for the strong fluorescence

observed with the plant wastewater. In addition to the primary fluorescence peak from Metolachlor, three small peaks of similar fluorescence intensities were seen at RTs of about 2.5, 4.3, and 13.1 min. Note that the peaks at RT ~2.5 and 13.1 min appeared also in the chromatograms of Altrazine and toluene standards from the plant but the peak at RT ~4.3 min did not match well with the dominant peaks in the fluorescence chromatograms of the plant wastewater sample (Fig. 8A) and Atrazine standard (Fig. 8B).

4. The toluene sample from the plant gave a single absorbance peak, and a corresponding fluorescence peak, at RT ~7.4 min.

The observations in Fig. 8 suggested that the fluorescence of the plant wastewater came predominantly from a single compound that was not toluene or any of the active compounds investigated (Atrazine, Propazine, Simazine, Terbuthylazine, Metolachlor, and Benoxacor). It was also not an impurity introduced with the toluene used in large quantities as the primary extraction solvent in the plant. The fluorescent compound was most likely a byproduct of the synthesis processes for some of these active compounds, particularly evident for Atrazine by the findings that the compound was the predominant fluorescent impurity present in the purified Atrazine standard (Fig. 8B) and that the wastewater fluorescence intensity showed a generally increasing trend with increasing Atrazine concentration (Fig. 7). As the fluorescent byproduct would be extracted into toluene, it is plausible to find in Fig. 7 the rather good correlation between the wastewater fluorescence intensity and the toluene concentration.

CONCLUSIONS

The plant wastewaters showed reproducible fluorescence characteristics, having one single major peak at excitation/emission wavelengths of 258/370 nm. The fluorescence intensity appeared to increase with increasing toluene, Atrazine, and Propazine concentrations in the wastewater but decrease with increasing Simazine concentration. The fluorescence intensity had no apparent correlation with Terbuthylazine, TOC, TKN, or ammonium concentration. The HPLC analysis suggested that the wastewater had a single dominant fluorescent compound, which was not toluene or any of the active compounds investigated (Atrazine, Propazine, Simazine, Terbuthylazine, Metolachlor, and Benoxacor). The fluorescent compound was most likely a byproduct of the synthesis processes for some of these active compounds, particularly evident for Atrazine. The wastewater fluorescence was strong in all CAT influent samples. The responsible fluorescent compound could be removed effectively by CAT but not by the BAS alone. The fluorescent compound also did not cause apparent inhibition to the biological activity of BAS treatment. The feasibility of using online fluorescence to monitor the performance of CAT unit was clearly indicated.

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AUTHOR DISCLOSURE STATEMENT

All authors declare that no competing financial interests exist.

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