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The influence of the structure of humic substances extracted from different soils and peats on their capacity to photosensitize 1-naphthol

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Abstract

This study compares the photosensitizing properties of a variety of humic substances (HS) extracted from soils (Kaldenkirchen, Bouzule, Scheyern and Belle fontainerendzine) and peats (W1, W9B and W9C). All the HS under consideration induced the photodegradation of 1-naphthol (2.10^{-6} M) at 365 nm. The results revealed that 1-naphthol is oxidized into naphthoquinones and hydroxynaphthoquinones. Generally, humic (HAs) and fulvic (FAs) acids of both W9B and W9C peat were the least effective. Significant correlations between the photosensitizing properties and the structural features of the examined humic substances were established. Thus,the pollutant phototransformation rate increased with the increase in N/C fraction, but decreased with the increase in O/C fraction, aromatic fraction or ash content. These results indicate that the aromatic part of the humic structure plays an important role in the inhibition of 1-naphthol oxidation suggesting they are, at leastpartly, responsibleforthe antioxidant properties of the HS.

Keywords: Humic substances structure, aromatic fraction, elemental content, photosensitizing capacity, 1-naphthol.

Introduction

Photochemical transformation is a possible path for abiotic degradation of organic pollutants present in soils and natural waters. Humic substances constitute the coloured moieties of dissolved organic matter, they absorb sunlight and can therefore act as sensitizers or precursors to produce reactive species with a high potential to transform organic molecules **[1]**. Solvated electrons and hydroxyl radicals$^{\cdot}$OH are produced when the HS are irradiated at wavelengths lower than 350 nm **[2]**, whereas singlet oxygen $^1O_2$ and reactive excited triplet states are produced at longer wavelengths.Experimental studies using substrates with a low energy triplet state or oxidizable substrates have provided unambiguous evidence that reactions initiated by reactive excited triplet states of HS are possible through hydrogen, electron or energy transfer processes. When the energy level of organic molecules' triplet states is lower than that of HS, the reactive excited states of HS can transfer their energy to the ground state of the organic molecules. Concrete examples of these reactions have been reported in the literature, such as the cis-trans photoisomerization of 1,3-pentadiene **[3]** and the E-Z isomerization of cinnamic esters photosensitized by HS **[4]**, to name but a few. It was also found that the reactive excited triplet states could abstract hydrogen atoms or electrons from oxidizable organic molecules. Aniline **[5]** and phenolic compounds are likely to be oxidized via this type of reaction **[6,7]**. From the kinetic study standpoint, it was proved that the transformation of many substances was accelerated by irradiation of HS in sunlight. Nevertheless, the authors found an inhibitory effect of HS on the degradation of a few of them. This inhibitory effect was observed when the direct photolysiswas faster than the one photo induced or photosensitized by humic substances **[8]** and is named a screen effect. However, the inhibitory effect of dissolved natural organic matter (DOM) on the oxidation rate of twenty-two different kind of organic pollutants was attributed to its antioxidant properties **[9]**. In the present work, we examined the ability of several types of HS of different geographical origins, extracted from four soils (Kaldenkirchen, Scheyern, Bouzule, Belle fontainerendzine) and three peats (W1, W9B and W9C) to photoinduce1-naphtholtransformation at 365 nm. The choice of 1-naphthol was based on its physicochemical properties, mainlyits aqueous solubility, its dissociation constant (p*K*a), which are 866 mg/l (25°C) and 9.34, respectively, and its oxidability. Finally, we attempted to correlate the photoinductive properties of the HS withtheir main structuralcharacteristics to get a better understanding of the complex mechanism of the HS action on organic compounds.

2. Materials and methods

2.1 Chemicals

1-Naphthol, 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, 1,2-naphthoquinone,5-hydroxy-1,4-naphthoquinone were purchased from Aldrich. Water was purified using a Milli-Q (Millipore) device. The methanol used was of the highest grade available. Solutions were buffered at pH 6.5 with phosphate buffers (3.1 $\times 10^{-3}$M).

2.2 Solutions preparation

The HS studied in the present work were extracted by the GSF-Institute of Ecological Chemistry group (Munich), from four soils; Scheyern (Sch), Belle fontainerendzine (BFR), Kaldenkirchen (Kal) and Bouzule (Bou), and three peats; W1, W9B and W9C.Successive extractions from soils, based on the IHSS protocol **[10,11]**, allowed to retrieve a single HA fraction and three fractions of fulvic acids which we named FA1, FA2 and FA3. From peats, the same protocol led to the recovery ofa single HA fraction and just a single FA fraction. The average mass of the extracted fractions increased according to the following order, FA1, FA2, FA3 and HA.Each fraction of the HS wasunderwent NMR, UV-Visible, IR and elementary analyses **[12-16]**. For the kinetic studies, solutions of HS were prepared just before irradiation by dissolving 1mg of each HS (FA or HA) into25 mL of Milli-Q water buffered at pH 6.5 with phosphate buffer (3.1×10^{-3}M). The solutions were stirred until complete solubilisation of HS was achieved. Then, we added 25 mL of the 1-naphthol solution to the HS solution. The resulting concentrations of 1-naphthol and HS were respectively 2×10^{-6} M and 25 mg.L^{-1}. The analytical studies (by products structures determination) were performed on solutions containing 1-naphtol (10^{-4} M) and HS (20 mg.L^{-1}).

2.3 Steady state irradiations

In both the analytical and kinetic studies, 20 ml of 1-naphthol-HS buffered solutions at pH 6.5 were irradiated in a cylindrical Pyrex reactor (14 mm internal diameter) placed along the axis of the irradiation device and left open to the air during the irradiation time. The device was equipped with three lamps (Philips HPW 125 W) emitting principally at 365 nm (85 % of the radiant energy). Although 1-naphtol does not absorb radiation at 365 nm, its direct photolysis was found very slow. This low disappearance rate is attributed to the minor presence of radiations of short wavelengths (313 nm) within the lamps emission spectrum.The reactor was refrigerated by water circulating inside a cooling jacket. Each experiment was repeated in triplicate.

2.4Analytical procedures

Aliquots of irradiated solutions were analysed using a Waters chromatograph equipped with a 996 photodiode array detector and a conventional C_{18} reverse phase (4.6 mm ×250 mm) column. The eluent was a methanol-water (0.1 % H_3PO_4) mixture (60:40 v/v). For the sample analysis containing humic substances we used a pre-column to protect the column by retaining macromolecules that were difficult to elute. 1-naphthol is a fluorescent molecule, the monitoring of its disappearance kinetics was performed using Merck HPLC equipped with Hitachi fluorescence detector of type F-1050.The excitation and emission wavelengths used were respectively 300 nm and 440 nm. UV-Visible spectra were recorded on a Cary 113 spectrophotometer (Varian).

3. Results and discussion

3.1 Phototransformation of 1-naphthol in the presence of humic substances

3.1.1 Byproducts identification

The analytical study was conducted on aerated solutions containing a mixture of 1-naphthol (10^{-4} M) and HS(20 mg.L^{-1}) extracted from four soils (Scheyern, Bouzule, Kaldenkirchen and Belle fontainerendzine) and three peats (W1, W9B and W9C). Careful examination of the obtained results showed a very pronounced influence of the different humic and fulvic acids used in the present work on the substrate degradation kinetics. In contrast, the same by products were detected whatever the photoinductor used. An illustrative chromatogram obtained from the typical case of W9C-FA peat is shown in figure 1.

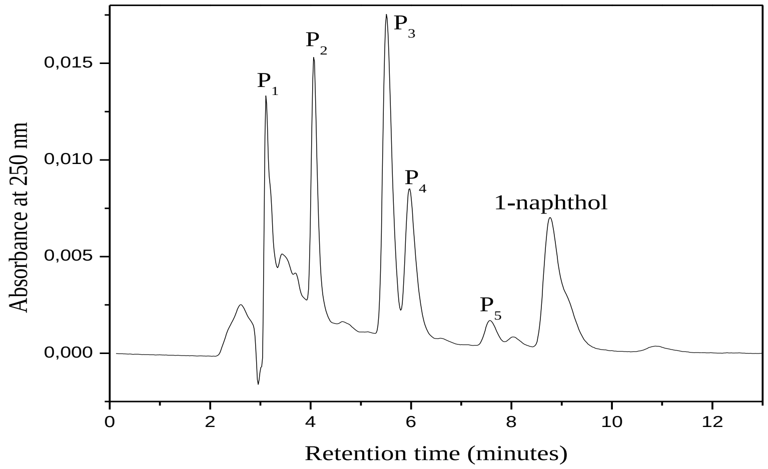
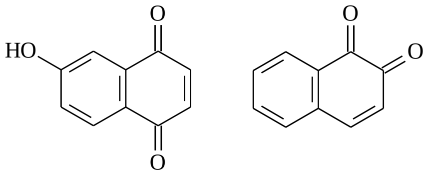
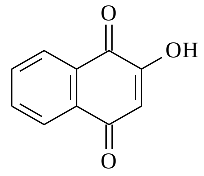


Figure 1:HPLC Chromatogram of an aerated solution of 1-naphthol (10^{-4} M) irradiated in the presence of W9C-FA peat (20 mg/L); 29 % conversion rate. Elution conditions: 40 % acidic water, 60 %MeOH.

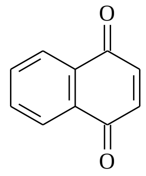
The four chromatographic peaks (P2, P3, P4, P5) shown in figure 1 correspond to the same by products as those observed in the direct photolysis of1-naphthol in pure water using a polychromatic light (290 -350 nm) **[17]**,as determined by their retention times and absorption spectra. These by products are: 1,2-naphthoquinone and 7-hydroxy-1,4-naphthoquinone which were eluted at the same time(P2), 2-hydroxy-1,4-naphthoquinone(P3), 1,4-naphthoquinone (P4) and 5-hydroxy-1,4-naphthoquinone (P5, trace amounts).P1 was observed only in the presence of HS and no attempt at its identification was made. The chemical structures of the four by products (P2 to P5) are presented below.



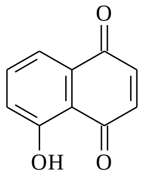
(P_2) : 7-hydroxy-1,4 naphthoquinone
1,2-naphthoquinone



(P_3) : 2-hydroxy-1,4-naphthoquinone



(P_4) :1,4-naphthoquinone



(P_5) :5-hydroxy-1,4-naphthoquinone

3.1.2 Kinetic Study

The analytical study clearly demonstrates the favourable impact of HS on 1-naphthol degradation. Another naturally arising question is how efficient in promoting 1-naphthol degradation is each of the HS fractions. It is also interesting to search for the existence of any significant correlation between the photoinductive properties and the structural characteristics of the studied HS. In consideration of the above, a kinetic study was performed on buffered solutions at pH 6.5 containing 25 mg.L^{-1}of HS and 1-naphthol at 2×10^{-6}M and irradiated at 365 nm. 1-naphthol disappearance was monitored using HPLC with fluorescencedetection.

3.1.2.1 Disappearance of 1-naphthol

The evolution of the concentration ratio C/C_0 of 1-naphthol, where $C_0$is the initial concentration, and C the concentration at t time, versus irradiation time (t) was determined for each HS fraction.1-naphthol phototransformation follows first-order kinetics for all the fractions. Fractions of HS extracted from Scheyern soil and W9B peat are shown as illustrative examples in Figures 2 and 3.

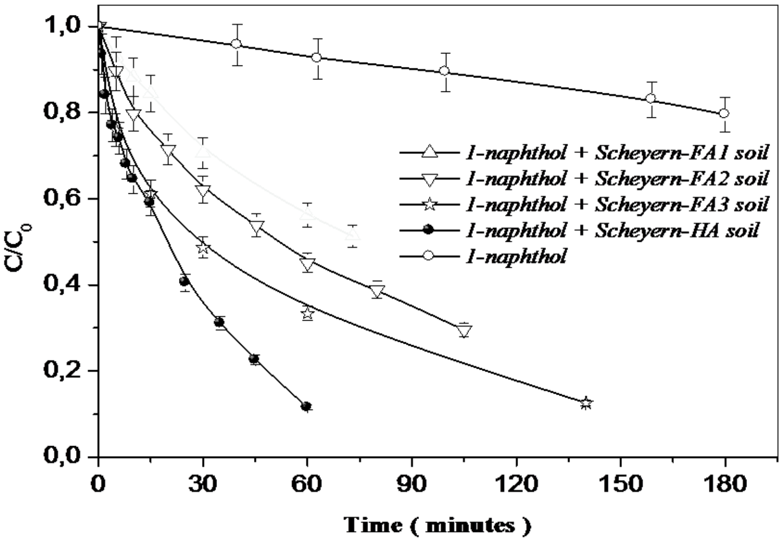


Figure 2: Disappearance kinetics of 1-naphthol (2×10^{-6} M) in the presence of four different fractions isolated from Scheyern soil (25 mg.L^{-1}).

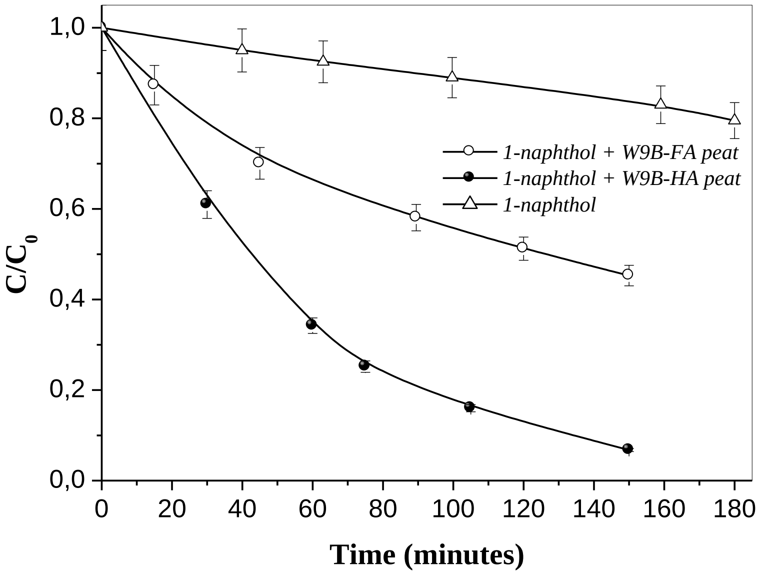


Figure 3: Disappearance kinetics of 1-naphthol (2×10^{-6} M) in the presence of the two fractions isolated from W9B peat (25 mg.L^{-1}).

We show in table 1 the apparent initial rates of 1-naphthol disappearance (R_0), and the half-life time of 1-naphthol ($t_{1/2}$) measured from the plotted graphs. The results are arranged so as to allow an easy comparison of the photoinductive capacity of HA and FA fractions originating from the same HS matter. Using $t_{1/2}$, histograms of figure 4 allow a straight forward photoinductive capacity comparison between the different HA fractions isolated from all the studied soils and peats on one hand (histogram a) and between all the different FA fractions on the other hand (histogram b).

From the histograms of figure 4, it clearly appears that the values of $t_{1/2}$ vary within large intervals for both HA and FA classes. Thus, within the HA class, Scheyern and Bouzule soils exhibit outstanding capacities with half-lives of 19 and 23 minutes respectively. Within the FA class, Bouzule-FA3 soil, W1-FA peat and Scheyern-FA3 soil are top ranking with half-lives of respectively 15, 30 and 30 minutes.

Taken as a whole, i.e. when we combine HA and FA classes, Bouzule-FA3 and Scheyern-HA exhibit the most remarkable capacities, while W1-HA and W9B-FA show the poorest capacities.

It also clearly appears that the photoinductive capacity depends greatly on the raw material (soil or peat), its geographical locality (Scheyern, Bouzule…) and the fraction (HA, FA1, FA2 and FA3):

(i) HS originating from soils (the mean initial rate, $\overline{R_0}$of which is around 7.5 $\times 10^{-10}$ $M.s^{-1}$) are 1.3 times more efficient than peat HS ($\overline{R_0} \approx 5.7 \times 10^{-10}$ $M.s^{-1}$); where $\overline{R_0}$ is calculated by considering all the humic and fulvic acid fractions;

(ii) The HS efficiency varies with the geographical origin in the following order (from highest to lowest): Scheyern ($\overline{R_0} \approx 9.9 \times 10^{-10}$ $M.s^{-1}$) ≈ W1 ($\overline{R_0} \approx 9.5 \times 10^{-10}$ $M.s^{-1}$) > Bouzule ($\overline{R_0} \approx 7.4 \times 10^{-10}$ $M.s^{-1}$) > Kaldenkirchen ($\overline{R_0} \approx 6.6 \times 10^{-10}$ $M.s^{-1}$)> Belle fontainerendzine ($\overline{R_0} \approx 5.8 \times 10^{-10}$ $M.s^{-1}$)> W9C ($\overline{R_0} \approx 4.2 \times 10^{-10}$ $M.s^{-1}$)> W9B ($\overline{R_0} \approx 3.4 \times 10^{-10}$ $M.s^{-1}$), noting that$\overline{R_0}$ is the arithmetic average of the initial rates of HAs and FAs originating from the same source;

(iii) When we compare the fractions belonging to the same HS group (table 1) we note, first, that the difference between these fractions is large in some cases, much smaller or moderate in other cases. Broadly speaking, in the case of HS extracted from soils, FA1 and FA2 show similar capacities while FA3 seems to be closer to HA. The latter fractions [$\overline{R_0}$(all FA3 fractions) $\approx 10.6\times10^{-10}$ $M.s^{-1}$ and $\overline{R_0}$(all HA fractions) $\approx 10\times10^{-10}$ $M.s^{-1}$] are *ca* twice more efficient than the former [$\overline{R_0}$(all FA1 fractions) $\approx 5.1\times10^{-10}$ $M.s^{-1}$ and $\overline{R_0}$(all FA2 fractions) $\approx 5.9\times10^{-10}$ $M.s^{-1}$].

Table 1: Kinetic data measured experimentally for [HS] = 25 mg. L^{-1} and [1-naphthol] = 2×10^{-6} M, irradiation at 365 nm.

HS	A^{365}	$R_0(\times10^{-10} M.s^{-1})$	$R_0/I_a(\times10^{-5} M.E^{-1})$	R_0/OC ($\times10^{-10} M.s^{-1}/mgC.L^{-1}$)	$t_{1/2}$(min)
Sch-HA	0.20	16	8.6	1.3	19
Sch-FA1	0.09	3.4	3.6	0.30	75
Sch-FA2	0.13	6.3	4.8	0.54	51
Sch-FA3	0.11	14	12.4	1.27	30
Kal-HA	0.20	5.7	3	0.53	45
Kal-FA1	0.13	6.8	5.2	0.68	34
Kal-FA2	0.12	7	5.8	0.64	33
Kal-FA3	0.13	7	5.4	0.70	41
Bou-HA	0.20	8.3	4.4	0.70	23
Bou-FA1	0.08	5.2	6.2	0.46	44
Bou-FA2	0.11	5.2	4.6	0.50	44
Bou-FA3	0.107	10.8	9.8	0.93	15
BFR-HA	0.14	7.3	5.2	0.61	30
BFR-FA1	0.06	5	7.8	0.44	46
BFR-FA2	0.10	5	4.8	0.42	46
W1-HA	0.24	4	1.9	0.33	62
W1-FA	0.11	15	13.6	1.72	30
W9B-HA	0.23	4.2	2	0.35	42
W9B-FA	0.09	2.5	2.6	0.37	124
W9C-HA	0.20	5.8	3.2	0.46	42
W9C-FA	0.11	2.6	2.4	0.36	87

A^{365} is the absorbance at365 nm (only HS absorb, the optical path length was14 mm), $R_0$is the initial rate of 1-naphthol disappearance, I_0 is the incident photon flux ($5 \times 10^{-5} E.cm^{-2}.s^{-1}$), I_a is the photon flux absorbed by the solutions; $I_a = I_0 (1-10^{-A365})$; $t_{1/2}$ is the half-life; OC is the mass of organic carbon contained in the 25 $mg.L^{-1}$ of the HS.

Besides R_0, we computed two other parameters, i.e. R_0/I_a and R_0/OC. The three parameters offer different bases for comparing initial rates of HS disappearance: R_0 allows comparison merely on a mass basis (as all solutions contain the same HS concentration, i.e. 25 mg/L), R_0/I_a takes the absorption unit as the basis of comparison, while R_0/OC refers to the organic carbon mass unit. The three parameters may provide complementary perspectives and may help to give better insight into the source of the photoinductive properties of HS. The results for R_0/OC and R_0/I_a are gathered in table 1, together with R_0 and $t_{1/2}$. When the initial rate R_0 is divided by the absorbed light intensity, the efficiency of HAs is more affected than that of FAs, because of the higher specific absorbance of HAs at 365 nm. Therefore, when we adopt R_0/I_a as the comparison criterion, we note some important variations in the ranking. It appears that in most cases the three FAs fractions of a same soil are now more powerful photoinductors than their corresponding HA fraction. W1-FA peat and Scheyern-HA soil are still leaders in their respective classes (FAs and HAs) but W1-FA peat now appears much more efficient than Scheyern-HA soil. The ranking based on R_0 /OC is very similar to the R_0-based one. Slightly closer values of the capacities are noted, as approximately 80 % of them range from 0.3×10^{-10} to 0.7×10^{-10} M.s^{-1}/mg C.L^{-1}. At the upper end of the scale, we find the same two fractions as before, namely Scheyern-HA for the humic group and W1-FA for the fulvic group.

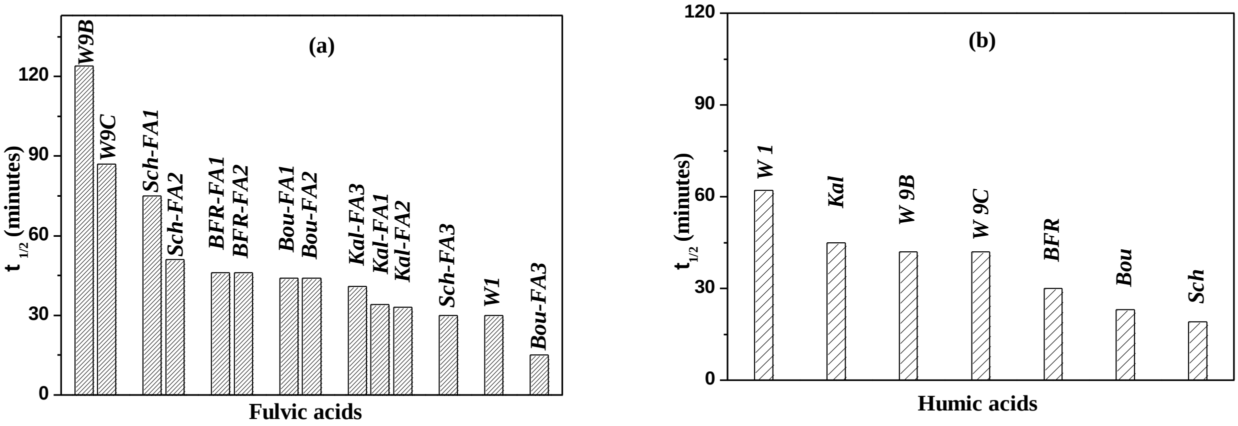


Figure 4: Comparison of the photoinductive capacity of the humic substances studied.
(a) fulvic acids, (b) humic acids

3.1.2.2 Photoinductive capacity and elemental content correlations

In an attempt to correlate the photoinductive capacity of HS to their elemental content, the carbon, nitrogen, oxygen and ash contents of each HS fraction are presented in table 2, as well as the relative aromatic content deduced from IR spectral determinations (table 3 and 4, *data provided by GSF-Munich*).

From table 2, we observe that the photoinductive capacity of HS is closely related to their (OC) content. Indeed, we note that a very small increase in the (OC) content may reduce significantly the half-life time for both FA and HA, the effect being more pronounced in the case of HA. This denotes the high impact of the carbon structure on the photoinductive capacity. Inversely, the half-life time globally increases as the ash content increases, which means that the latter has an adverse effect on capacity. This result confirms that the HS ability to photoinduce the reaction of 1-naphthol is due to their organic component and not to their mineral one. If we examine the impact of N/C and O/C mass ratios, we find that the half-life time of 1-naphthol tends to decrease when the (N/C) mass ratio increases or when the (O/C) mass ratio decreases. This suggests that nitrogen plays a positive role in favouring 1-naphthol disappearance, while oxygen is a disfavouring factor.

The last tested parameter is the aromatic content. From figure 5, it clearly appears that the half-life time increases when the aromatic fraction within the HS molecules increases (aromatic components in the region 1480-1620 cm^{-1}, table 3). This points to the adverse effect of the aromatic component on the HS photoinductive ability. This observation may be explained by the antioxidant properties of HS, as reported by Canonica et all **[9]**.

Table 2: *Elemental analysis of the studied HS*

	OC (%)	N/C	O/C	H/C	Ash (%)
Sch-FA1	44.76	0.043	0.694	1.249	7.0
Sch-FA2	46.61	0.058	0.656	1.181	4.0
Sch-FA3	44.09	0.111	0.671	1.336	5.6
Sch-HA	49.41	0.082	0.565	1.204	4.0
Bou-FA1	44.67	0.033	0.714	1.184	6.3
Bou-FA2	41.76	0.086	0.746	1.396	9.3
Bou-FA3	46.6	0.043	0.677	1.127	3.5
Bou-HA	47.74	0.088	0.519	1.251	4.9
W1-FA	34.79	0.049	0.744	1.186	7.8
W1-HA	47.87	0.063	0.591	1.178	5.8
W9B-FA	27.21	0.040	0.759	1.115	38
W9B-HA	48.22	0.053	0.611	1.221	3.5
W9C-FA	29.19	0.039	0.789	1.097	12
W9C-HA	49.06	0.060	0.594	1.225	2.5
BFR-FA1	45.3	0.032	0.622	1.295	11.2
BFR-FA2	47.13	0.058	0.664	1.204	4.1
BFR-HA	47.87	0.099	0.555	1.281	7.2
Kal-FA1	40.06	0.047	0.722	1.243	15.6
Kal-FA2	43.65	0.064	0.679	1.174	8.9
Kal-FA3	39.96	0.081	0.719	1.237	20.3
Kal-HA	43.27	0.078	0.633	1.367	14

Table 3: IR data of HS extracted from soils

	Sch FA1	Sch FA2	Sch FA3	Sch HA	Bou FA1	Bou FA2	Bou FA3	Bou HA	BFR FA1	BFR FA2	BFR HA	Kal FA1	KaL FA2	Kal FA3	Kal HA
3010-3120	0.16	0.18	0.37	0.24	0.15	0.37	0.21	0.25	0.08	0.24	0.48	0.07	0.14	0.26	0.24
2830-3010	2.04	2.24	2.54	2.58	2,04	2.45	1.99	2.04	2.67	2.10	3.34	1.82	1.97	2.14	2.66
2380-2750	3.97	4.32	2.79	2.21	5,53	2.59	4.41	1.68	2.07	1.70	1.78	4.12	3.75	3.59	1.93
1760-1810	3.17	2.44	1.15	2.12	3,58	1.97	3.09	2.04	1.63	1.70	1.77	1,98	2.26	1.31	1.55
1700-1760	8.42	8.00	7.05	7.38	9,98	7.41	9.08	6.25	6.95	8.72	6.81	8.30	7.53	7.04	6.93
1620-1700	9.54	9.89	10.84	10.47	10,03	10.14	10.07	8.67	8.62	10.90	10.60	10.23	10.23	10.43	10.81
1565-1620	5.37	5.59	5.39	6.22	5,52	5.67	5.46	5.13	4.8	6.03	5.81	6.18	6.27	5.74	6.32
1525-1565	2.64	3.25	4.42	4.07	2.30	4.25	2.68	3.64	2.4	3.62	4.53	2.96	4.01	3.90	4.00
1480-1525	2.37	2.89	2.94	3.94	1.91	3.45	2.55	3.42	2.1	2.41	3.4	2.22	3.20	2.54	3.36
1445-1480	3.09	3.20	3.00	3.30	3.00	3.14	3.09	2.94	2.68	2.86	2.95	2.91	3.28	2.87	3.04
1400-1445	4.42	4.41	4.09	4.29	4.86	4.52	4.79	3.92	3.69	4.50	4.14	4.28	4.64	4.08	3.90
1350-1400	4.70	4.72	4.42	4.62	5.30	4.89	5.03	4.28	4.14	4.71	4.46	4.61	4.99	4.41	4.12
1315-1350	3.30	3.32	3.07	3.27	3.41	3.32	3.32	2.98	2.76	3.19	3.01	2.99	3.34	2.91	2.79
1260-1315	5.89	5.79	5.26	5.27	6.48	5.62	6.20	4.93	5.18	6.10	5.05	5.73	5.74	5.35	4.74
1190-1260	8.13	7.93	7.26	7.22	9.26	7.61	8.80	6.69	6.95	8.36	6.85	7.94	7.62	7.37	6.76
1140-1190	5.29	4.94	4.52	4.43	5.54	4.72	5.24	4.29	4.83	4.69	3.95	4.90	4.77	4.39	4.36
1110-1140	3.12	2.94	2.88	2.81	2.89	2.72	2.71	2.59	3.06	2.65	2.46	2.85	2.73	2.64	2.85
1060-1110	5.04	4.67	4.87	4.55	4.44	4.59	4.28	4.38	5.39	4.35	4.35	4.91	4.49	4.46	5.21
1000-1060	5.04	5.39	5.30	5.55	4.64	5.21	4.90	5.27	5.73	4.70	5.43	4.77	4.97	5.00	6.88

Table 4: IR data of peats

	W1 FA	W1 HA	W9B FA	W9B HA	W9C FA	W9C HA
3010-3120	0.27	0.31	0.26	0.24	0.22	0.39
2830-3010	1.69	2.37	1.83	2.02	1.64	2.62
2380-2750	5.72	3.85	5.18	4.49	5.38	4.06
1760-1810	4.30	3.58	4.09	4.00	4.29	3.26
1700-1760	14.40	10.33	12.30	10.42	12.99	10.32
1620-1700	14.25	13.85	12.99	13.92	14.25	14.37
1565-1620	7.72	8.82	7.31	8.94	8.14	8.77
1525-1565	3.60	5.64	10.58	5.59	3.85	5.35
1480-1525	1.89	4.88	2.03	4.96	2.45	4.54
1445-1480	3.19	4.07	3.11	4.19	3.38	3.96
1400-1445	5.62	5.85	5.21	5.81	5.71	5.55
1350-1400	5.51	6.16	5.11	6.03	5.62	5.80
1315-1350	3.49	4.08	3.33	4.08	3.67	3.97
1260-1315	7.30	6.66	6.71	6.59	7.30	6.67
1190-1260	11.14	8.64	9.92	8.43	10.44	8.95
1140-1190	6.13	5.15	5.57	4.95	5.70	5.01
1110-1140	2.83	2.78	2.89	2.87	2.97	3.10
1060-1110	4.18	4.45	4.28	4.26	4.54	4.63
1000-1060	4.44	5.05	4.54	4.96	4.70	5.75

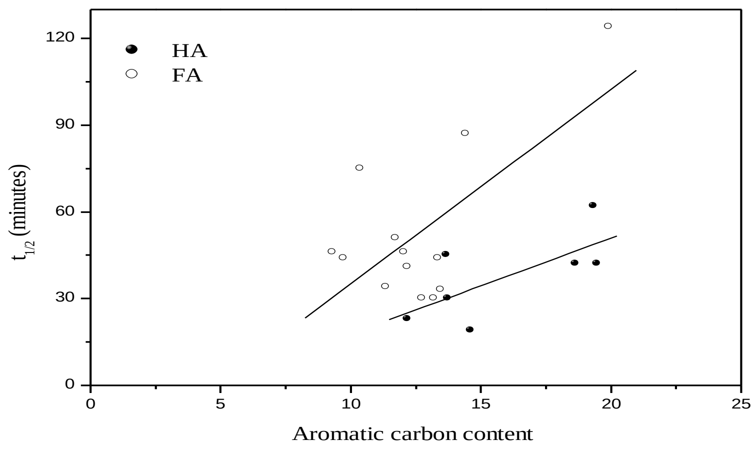
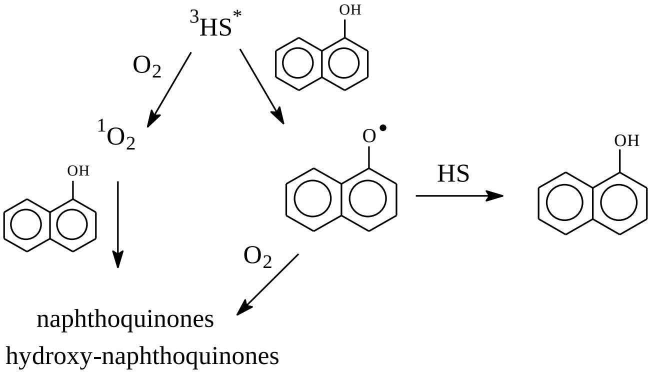


Figure 5: Half-life time of 1-naphthol disappearance versus aromatic carbon content (deduced from IR representative bands in the region 1480 – 1620 cm^{-1}).

It is generally admitted that HS excited triplet states are the reactive species involved in the HS photosensitized oxidation of phenolic compounds at 365 nm **[6,7]**. This occurs through H abstraction or singlet oxygen production. Assuming the same mechanism takes place in the present case, the triplet states would most probably abstract a hydrogen atom from 1-naphthol to yield a naphthoxyl radical. The oxidation of the freshly formed radical by dissolved oxygen gives rise to the experimentally observed naphthoquinones and hydroxy-naphthoquinones. However, according to Canonica et all **[9]**, a part of those radicals may be reduced back by HS to their parent compounds, which explains the antioxidant properties of HS. Then, applying this mechanistic scheme to1-naphthol, naphthoxyl radicals would be reduced by HS to regenerate 1-naphthol. Our results show that it is the aromatic part of the humic structure which plays the major role in the HS antioxidant properties, as it greatly contributes to the raise of the inhibition of the HS photosensitized oxidation of 1-naphthol.

We should also note that the excited triplet states could react concomitantly with dissolved molecular oxygen by energy transfer, leading to the formation of singlet oxygen. The latter could oxidize 1-naphthol to produce the same by products. Scheme 1 summarizes the main steps involved in the photosensitized oxidation of 1-naphtol:



Scheme 1

Conclusion

We confirmed that allhumic substances examined in this studyare able to phototransform1-naphtol, but with a greatly variable photosensitizing capacity. The latter depends on the geographical area from which the raw material was collected, the nature of the raw material(peat or soil) from which they were extracted and the fraction (HA, FA1, FA2, FA3)isolated from a given HS. We further established that the photoinductive capacity is correlated to the structural features of the humic substances. Thus, the capacity increases in a substantial way with the OC content and to a lesser extent with the nitrogen content. It is adversely affected by an increase in oxygen, ash or aromatic content, although for different reasons.

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