

## FIRE-INDUCED TRANSFORMATION OF SOIL ORGANIC MATTER FROM AN OAK FOREST: AN EXPERIMENTAL APPROACH TO THE EFFECTS OF FIRE ON HUMIC SUBSTANCES

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**This study is about the effects of forest fire on the organic matter from a Dystric Xerochrept under *Quercus rotundifolia*. In laboratory experiments carried out to simulate the effects of fire on isolated humic fractions, several physicochemical characteristics were described in the heated samples, as well as in humic substances extracted from samples of control and postfire soil areas.**

**The results obtained suggested that humic and fulvic acids underwent moderate structural modifications, but we found important changes in their colloidal properties, particularly regarding solubility.**

**The composition and properties of pyromorphic humus are discussed by using a tentative model for humus transformation on the basis of different fire-induced modifications of the soil organic fractions.**

Fire-induced changes of soil properties, as well as ecological consequences of forest fires, are considerable in most Mediterranean areas. The destruction of the vegetation is often responsible for an important erosion of the organic soil horizons, but even in burned forests on flat sites the effects of fire can lead to severe changes of the physical and chemical properties of the soil (De Bano et al. 1970; Savage et al. 1972; Viro 1974; Giovannini et al. 1987; Vega 1986; Giovannini and Lucchesi 1984).

The fire-induced changes can produce a varied evolution of the soil, depending on a series of factors, the study of which is of recognized importance for the correct application of controlled burnings in forest management (Ruiz del Castillo, 1983; De Bano et al. 1977; Vélez 1980; De Bano et al. 1976; Vega 1978; Gandullo 1979). With regard to the effects on the soil organic matter (Almendros et al. 1984b), fire can lead to

humus with specific characteristics ("pyromorphic humus").

The simulation experiments were designed to monitor the progressive changes in humus properties as a result of the presumably complex transformation paths during natural burnings (De Bano et al. 1970; Savage 1974; Scholl 1975; Lobo and Ibáñez 1985). After natural fires, it must be taken into account that the final composition of humus is simultaneously influenced by (1) the thermal diagenesis of soil organic matter, (2) the selective losses of humus substances, and (3) incompletely burned plant necromass falling to the ground and becoming incorporated into the soil. Such simulation experiments are also adequate to obtain a clue to the specific influence of each of the three phenomena listed above. Several changes in humus properties were recognized in previous studies after laboratory-controlled burnings of whole soil samples (Almendros et al. 1984b, 1987), but the transformations occurring in the course of that experimental design were too complex for us to understand the individual transformations of the different organic fractions in the soil. In the present study, we examine the behavior of humic substances isolated from a brown soil under evergreen oak, under laboratory conditions, and compare the characteristics of the final products with those of humic and fulvic acids extracted from the original soil after wild-fire.

### EXPERIMENTAL

#### *Soils studied*

Soil samples (Dystric Xerochrept) were collected from under a continental mediterranean forest of *Quercus rotundifolia* in Madrid (central Spain). The control soil area (C) lay at 25 m from the burned one (B). Burning was considered of high intensity, destroying the herbaceous and brush species, but leaving dead oaks without leaves.

Sampling was carried out approximately 15

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mo after the wildfire, by mixing five soil samples (from a depth of 10 cm) randomly collected from every site (50 m<sup>2</sup>), air-drying, and sieving them through a 2-mm screen. Several analytical characteristics of these soils are given in Table 1. The mechanical analysis was carried out following Kilmer and Alexander (1949), the cation exchange capacity was determined using the method of Mehlich (1948), total C was measured with a Carmhograph-12 analyzer, and the total N was determined by the Kjeldahl method (USDA 1972).

The *lipid fraction* was extracted with petroleum ether in a Soxhlet for 40 h. The *free organic matter* and the *inherited humin* were separated following Monnier et al. (1962) and Chouliaras et al. (1975), respectively. The extractable humic substances were then isolated from the dried residue by repeated treatments with 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and 0.1 M NaOH. The *humic acid* (HA) (the acid-insoluble fraction) was separated from the acid-soluble *fulvic acid* (FA) after precipitation with HCl to pH 1. The residual heavy fraction of soil was then treated with 1% Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and 1 M HCl-HF to set the *extractable humin free* (Merlet 1971), which was extracted with 0.1 M NaOH. The quantitative proportion (in C) of the above fractions as well as that of the residual C in the soil heavy fraction (*non-extractable humin*) was determined with the Carmhograph-12 carbon analyzer.

The HAs were purified by 27 000-g-centrifugation at pH 12, reprecipitation, and demineralization with 1% HCl-HF (50%). The FAs were adsorbed with a column with insoluble polyvinylpyrrolidone (Divergan R, BASF), eluted with 0.1 M NaOH and purified by means of cation exchange chromatography, using Amberlite IR-120 (Lowe 1975). After lyophilization, the ash content of both kinds of substances was estimated to be lower than 2%. Gel filtration (Sephadex G-100) was carried out following Swift and Posner (1971), and spectroscopic parameters in

the visible range, by following Kononova (1966). The elementary composition was determined with a Hewlett-Packard CHN-185 analyzer, and the infrared spectra with a Perkin-Elmer 580B instrument.

Alkaline permanganate oxidation was carried out in conditions similar to those described by Matsuda and Schnitzer (1972) (2-h oxidation with 4% KMnO<sub>4</sub> at 90°C). The degradation products were extracted with ethyl acetate, methylated with diazomethane (Schnitzer 1974), and injected in a Hewlett-Packard 5730A (FID detector) gas chromatograph and a Hewlett-Packard 5992 GC-MS system equipped with OV-101 capillary columns (Almendros and González-Vila 1987). No attempt was made to calculate the yields of the degradation products in terms of the original sample; the gas chromatograms of the permanganate degradation products were considered fingerprints illustrating the different origin of the HAs (Almendros et al. 1989a). Nevertheless, calculations of the relative amounts of the different groups of degradation products were carried out for comparative purposes.

An incubation experiment was carried out to monitor the respiratory activity of the control soil and the soils after burning (Guckert et al. 1968). One hundred-gram samples of soil moistened to 50% of their WHC were incubated in 500-ml Erlenmeyer flasks with stopcocks at the input and at the output tubes. Three replicated runs of the control and burned soil samples were carried out at 27°C. The CO<sub>2</sub> evolution was estimated every day by connecting the flasks to the Carmhograph-12 gas analyzer. During the measurement, the input tube of the flask was connected to a soda-lime column (CO<sub>2</sub>-free air) followed by a gas-washing bottle with 10% NaOH (to prevent soil dryness in long experiments). The output tube of the flask was connected to a gas-washing bottle with H<sub>2</sub>SO<sub>4</sub> and then to the gas analyzer.

TABLE 1

Analytical characteristics of average soil samples (from a depth of 10 cm) of Dystric Xerochrept under evergreen oak taken from the control and the postfire areas

Sample	pH (in H <sub>2</sub> O)	Bases		Base saturation, %	Organic C	Total N	C/N	Soil color (Munsell)
		CEC	meq (100 g) <sup>-1</sup>					
C (control)	4.8	2.9	10.0	29.0	1.37	0.09	16	10YR 6/4
B (burned)	6.2	5.5	18.0	30.5	1.45	0.12	12	10YR 3/3

*Laboratory burnings*

Simulation experiments were performed based on the methods and results described by Savage (1974), Scholl (1975), De Bano et al. (1976), and Almendros et al. (1984b, 1987). The experiments were carried out in a Wösthoff furnace with a CO<sub>2</sub>-free air flow, connected to the Carmhograph-12 analyzer (to measure the CO<sub>2</sub> production). The isolated humic fractions (HA and FA) were ground to pass a 100- $\mu$ m screen and mixed with mineral substratum (the > 0.2-mm fraction of the original soil treated with hydrogen peroxide). Heating the humic substances without mineral substratum was found to be highly inadequate and nonrepresentative, producing very heterogeneous preparations (carbonized on the surface and rather unaltered at the core) with a poor reproducibility (influenced by the amount and form of the sample pile).

Ten replications were prepared by using 10-ml porcelain boats containing 5 g of soil and 100 mg of sample. After isothermal heating at 350°C during the periods indicated in Table 3, the sample boats were cooled by shifting them to the low-temperature zone of the furnace tube. Three of the above heated samples were used for triplicate determination of the amount of the residual fractions, another two for the estimation of the total C content, and the remainder for subsequent characterization of the transformed humic substances. They were labeled I, II, III, and IV, following the progressive oxidation times.

Previous experiments using different types of calcium or sodium humic salts, or humic samples associated with clay and mixed with wet soil, led to the same qualitative conclusions as in the experiment described above. In these experiments the quantitative recovery of humic substances from the mineral substratum was partial and nonrepresentative (often requiring addi-

tional alkali extractions and demineralizations, which probably altered the samples), whereas in the conditions used here, the qualitative separation of humic substances from the mineral particles was carried out physically (sieving through a 0.2-mm screen and flotation when necessary).

## RESULTS AND DISCUSSION

*Effects of fire on soil and humus*

Tables 1 and 2 show different analyses of the soil samples studied. The increase in the soil pH and in the amounts of most of the exchangeable cations can be an effect of forest fires (Viro 1974). The present case contrasted with the ecosystems where the lower fertility levels after fire can be due to leaching of basis and fly-ash phenomena (Smith and Bowes 1974; Athias-Binche and Saulnier 1986). Total C did not decrease in the sample from the burned area, suggesting that the incorporation of oak necromass was sufficient to compensate for the combustion of humus. This assumption agrees with the low autocombustibility of the fresh oak biomass; the high temperature generated during the burning of sclerophyllic brushwood was responsible for the death of the oaks and subsequent massive incorporation of unburned plant material to soil humus. The C/N ratio of sample B was comparatively lower, a phenomenon often cited in several types of postfire soils (Viro 1974; Vega 1976).

The amounts of the principal humus fractions are shown in Table 2. When compared with the control soil sample, the postfire sample presented an increased proportion of the less transformed humus fractions: free organic matter ( $\times 3$ ) and inherited humin ( $\times 2$ ), whereas the lipid proportion was lower in the postfire soil sample.

The results of determining the respiratory activity of the soil samples are shown in Fig. 1.

TABLE 2

*Distribution of soil C: Organic fractions in soil samples taken from the control and the postfire areas*

Sample	Free organic matter	Lipid	Humic acid (HA)	Fulvic acid (FA)	HA+FA	Humic fractions		
						Inherited humin	Extractable humin	Nonextractable humin
C (control) (1) <sup>a</sup>	0.18	0.10	0.16	0.25	0.41	0.06	0.05	0.54
(2) <sup>a</sup>	13.40	7.30	11.68	18.25	29.93	4.38	3.65	41.61
B (burned) (1) <sup>a</sup>	0.56	0.05	0.11	0.21	0.32	0.13	0.05	0.34
(2) <sup>a</sup>	38.20	3.45	7.59	14.48	22.07	8.97	3.45	23.45

<sup>a</sup> (1), g C in 100 g of soil; (2) g C in 100 g of soil C.

It was observed that during the first period (0 to 20 d) the activity in the postfire soil sample was much higher than in the control soil sample, a phenomenon that could be interpreted as caused by rapid microbial recolonization of the postfire soil, presumably enriched by the incorporation of readily biodegradable plant material and the increased amounts of exchangeable cations previously described. The differences tended to disappear during the second half of the experiment, and, after the 30th day, the activity in the control soil sample became higher than in that from the burned area, although the differences were small. The reduced activity of the postfire soil sample during the second half of the experiment could be due to microbial immobilization or the consumption of the nutrients and the easily biodegradable materials released in the soil after the fire. The above results for the oak forests contrasted with those

obtained in pine forest under similar geomorphological and climatic conditions (Almendros et al. 1984a). In the latter case the higher combustibility of the resinous plants, which were more or less totally destroyed during the forest fire, led to the accumulation of lipids and of heavily carbonized, hardly biodegradable organic matter in the soil, and the samples from the postfire site showed reduced biological activity.

#### *The effects of fire on humic and fulvic acids*

The yields and recoveries obtained in the laboratory experiment using mineral soil mixed with the humic fractions are given in Table 3. According to De Bano et al. (1977), the laboratory conditions can validly be compared with those occurring at different soil depths during fires of low, medium, or high intensity in Mediterranean areas. The maximum loss of weight

FIG. 1. Carbon dioxide production curves for samples of forest soil under evergreen oak. C = control soil; B = post-fire soil; MC = mineralization coefficient, defined as the percentage of total carbon released as CO<sub>2</sub> during the 63-d incubation period.

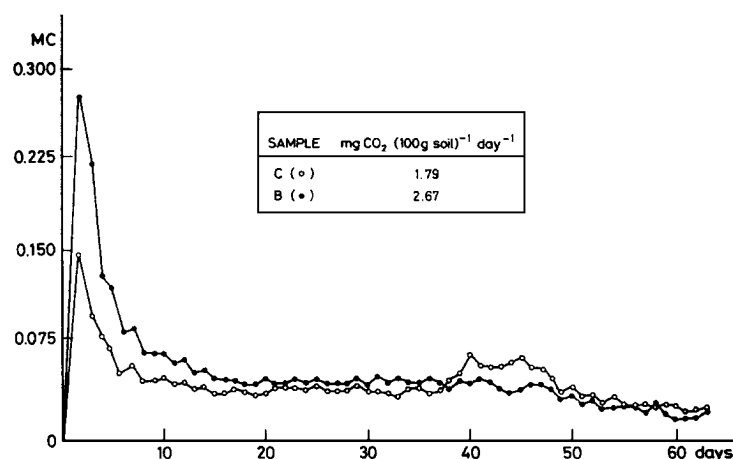


TABLE 3

*Experimental conditions and transformation extent of isolated humic fractions burned in the laboratory*

Sample reference	Oxidation time at 350°C, s	Weight loss	CO <sub>2</sub> production	Solubility	
				At pH = 1	At pH = 12
		g (100 g of initial sample) <sup>-1</sup>			
HA C (control)	0	0.0	0.00	0.0	100.0
HA I	60	10.1	0.81	0.3	50.2
HA II	90	23.7	3.91	0.2	5.5
HA III	120	32.0	33.60	0.2	0.3
HA IV	150	52.6	46.43	0.2	0.3
FA C (control)	0	0.0	0.00	100.0	100.0
FA I	60	15.6	1.46	68.7	84.4
FA II	90	29.3	3.26	39.9	70.5
FA III	120	64.2	27.80	0.90	2.6

observed was about 50% for the HA and more than 60% for the FA in phase IV. The mineralization of C was relatively important in the extreme conditions (up to phase III), whereas in the milder ones the losses of weight could be interpreted as dehydrations, volatilizations, and the release of pyrolytic products.

An important transformation observed in the heated HAs and FAs was the change in their solubility properties. After phase I, half the HA was transformed into an alkali-insoluble polymer, and that insolubility drastically increased in subsequent phases: the original polymers were transformed into a mixture of organic fractions with reduced solubility. This transformation was noteworthy in the FA case, which was first transformed into an acid-insoluble polymer (HA-like) and then into an alkali-insoluble substance (huminate-like). These results are expressed in Fig. 2 as percentages of the final weight after heating of humic substances.

In addition, after the alkaline permanganate oxidation of the humic substances, we found a variable amount of unoxidized residue. After examining these residues by IR spectroscopy and elementary analysis, we considered them to be a very heavily carbonized material, the relative proportion of which is also represented in Fig. 2.

Extrapolating the above results to field conditions requires a more complete knowledge of the original state of the humic fractions in the soil. This will probably affect the quantitative extent of such insolubilization processes. Although no definitive conclusions were to be drawn from the preliminary studies with humic salts indicated under Material and Methods, an apparent tendency to greater transformation in these cases could be attributed to the shifting of

the decomposition phases, described by Hoffmann and Schnitzer (1965) toward lower temperatures, as a result of the formation of organometallic derivatives.

The changes in the solubility of the humic polymers were explained through the elementary analysis of these substances (Table 4). When the atomic H/C and O/C ratios were represented in a Van Krevelen (1950) diagram (Fig. 3), we observed that fire induced an important decrease in the atomic H/C ratio, indicative of an increase in aromaticity, and a decrease in the atomic O/C ratio, revealing important losses of oxygen-containing functional groups, which could be main factors responsible for the progressive transformation in their colloidal properties. These changes (simultaneous dehydration and decarboxylation of humic substances) were observed both after natural and laboratory burnings and are in agreement with the behavior of humic substances during thermal treatments, summarized in Schnitzer and Khan (1972). The points represented in Fig. 3 are plotted on a contour diagram for the natural variability of atomic H/C and O/C ratios of 273 HAs from different types of soil, determined in this laboratory and used to establish a comparison with the composition of terrestrial humic acids (Almendros et al. 1985). In the present case it was evident that during the transformation paths the atomic ratios of FAs are included within the variability limits of the elementary composition of soil HAs (1 and 2), finally to reach—as the HA path—a composition different from that of the last-mentioned substances (Fig. 1).

It is probable that this irreversible dehydration and decarboxylation of the humus colloids may play an important role in the fire-induced water-repellency of soils after burning. The

FIG. 2. Transformation of humic acids (HA) and fulvic acids (FA) into mixtures of humiclike polymers at different phases of heating in laboratory-controlled conditions.

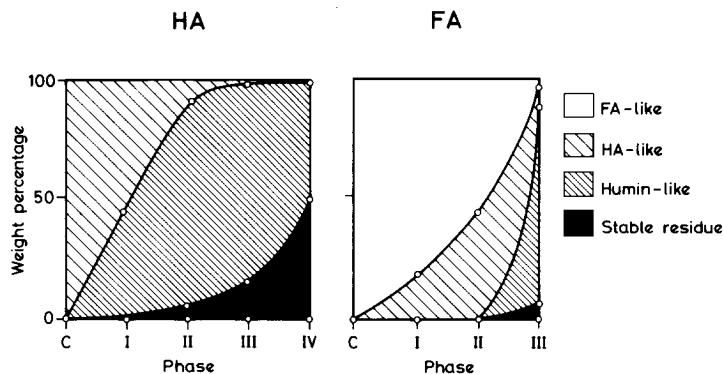


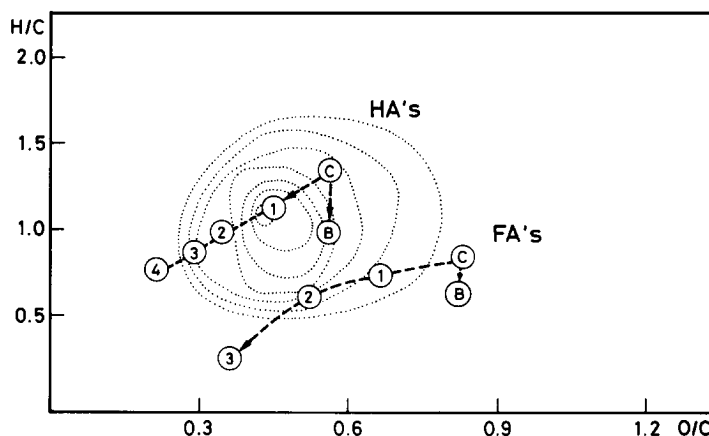
TABLE 4

Elementary composition of humic substances extracted from forest soil under evergreen oak taken from the control and the postfire areas and of humiclike substances obtained after laboratory-controlled burning of humic and fulvic acids from control soil

Sample	Ash-free percentages				C/N	Element balance <sup>a</sup>			
	%C	%H	%O	%N		Volatilized C	Volatilized H	Volatilized O	Volatilized N
HA C (control soil)	52.03	5.77	37.93	4.27	12.19				
HA B (burned soil)	52.77	4.65	38.70	3.88	13.60				
HA I	56.41	5.51	33.51	4.57	12.34	2.53	14.15	20.58	3.78
HA II	61.15	5.30	28.30	5.25	11.65	10.33	29.32	43.07	6.19
HA III	63.62	4.76	26.10	5.52	11.53	18.65	43.90	53.21	12.09
HA IV	69.51	4.54	20.12	5.83	11.92	36.68	62.70	74.86	35.28
FA C (control soil)	45.64	3.41	50.14	0.81	56.35				
FA B (burned soil)	46.44	2.68	50.70	0.18	258.00				
FA I	51.10	3.12	45.42	0.36	141.94	5.50	22.78	23.55	62.49
FA II	56.92	3.18	38.60	0.40	142.30	11.83	34.07	45.57	65.09
FA III	66.67	1.40	31.33	0.60	111.12	47.70	85.30	77.63	73.48

<sup>a</sup> Percentage of total element volatilized after heating.

FIG. 3. Graphical representation of the atomic H/C and O/C ratios of humic acids (HA) and fulvic acids (FA) from unaltered or burned humic samples. The data are plotted on a contour diagram of distribution and frequencies showing the natural variability for these parameters in soil humic acids. C: sample from control soil; B: sample from postfire soil; 1 to 4: different phases of humic and fulvic acids heated in laboratory-controlled conditions.



water drop penetration time (WDPT, Savage et al. 1972) of the soil sample C was estimated to be lower than 1 s, whereas this period was 32 s in sample B. This difference is noteworthy after considering that the free lipid fraction was much lower in sample B than in sample C (Table 2). Several studies (De Bano et al. 1970-1977; Savage et al. 1972) have shown that the fire-induced translocation and fixation of hydrophobic compounds are responsible for the formation of water-repellent soil horizons, but our results suggest that the changes in the surface properties of the humus substances may also greatly increase the hydrophobicity of soils after burning. In fact, it can easily be tested that the humus fractions (I to IV) became slowly wetttable after heating. The thermal loss of the oxygen-contain-

ing functional groups turns the surface of the humus macromolecules hydrophobic. The peripheral rearrangement of the resistant polymethylene constituents (Almendros et al. 1988) may contribute to this, as well as the fixation of additional lipid material to the humic acids discussed below.

Regarding the transformation of the nitrogen compounds, this element was observed to be very stable (Table 4): the C/N ratio was found to be surprisingly constant during the whole experiment in the case of the HAs, the relative losses of N and C being similar in the more extreme treatment (35%). This stability of N can partially explain the increase in the N content classically found in several postfire soils and could be partially attributed to the forma-

tion of very stable N forms during the thermal diagenesis of the HA-type polymers (Almendros et al. 1984a). However, the N compounds in the FA studied here did not present the above resistance to thermal effects. They were readily volatilized in laboratory conditions and also comparatively reduced in the sample from post-fire soil.

The comparison between the infrared spectra of the control and the fire affected HAs (Fig. 4) confirmed the above tendencies. A preferential decrease in the intensity of the bands produced by C-H aliphatic vibrations ( $2920$ ,  $1460$   $\text{cm}^{-1}$ ) was observed, whereas the bands affected by aromatic vibrations ( $1510$ ,  $1600$   $\text{cm}^{-1}$ ) remained constant. The broad band at  $2600$   $\text{cm}^{-1}$  (acidic groups) decreased in the heated samples and so did the intensity in the  $1000$   $\text{cm}^{-1}$  region, suggesting the destruction of polysaccharide material or methoxyl-containing structures.

The gel permeation chromatography of the HA and FA extracted from the control and postfire soil samples suggested important changes in the molecular size distribution. The size of the excluded fraction was higher in the sample from the postfire area, both in the case of HA ( $\times 1.5$ ) and FA ( $\times 7$ ). In addition, the

specific extinction ( $E_{465 \text{ nm}} (100 \text{ ppm C})$ ) of the HA and FA was also higher in the postfire sample (HA-C = 0.6, HA-B = 1.2, FA-C = 0.8, FA-B = 1.1), whereas their  $E_{465}/E_{665}$  ratios were lower (HA-C = 5.8, HA-B = 5.4, FA-C = 10.7, FA-B = 8.2), which conforms to the molecular rearrangements of humic substances in pyromorphic humus (Almendros et al. 1984a, 1987).

#### Oxidative degradation of humic polymers

The results of the alkaline permanganate oxidation of humic substances are summarized in Fig. 7. The compounds identified (90 to 98%) were similar to those described by Schnitzer and Khan (1972), corresponding to  $\alpha,\omega$ -alkanoic diacids, alkanolic monoacids, aromatic (benzenecarboxylic and phenolic) acids, and alkanes.

Although the most prominent chromatographic peaks were essentially the same in the different samples (Fig. 5), there were very significant changes regarding the relative abundance of compounds (Fig. 7). In the case of the HAs, the relative abundance of the lowest-boiling-point alkanolic diacids tends to increase, suggesting thermal breakdowns in aliphatic or alicyclic structures. The size of the peaks corresponding to different benzenecarboxylic acids was comparatively higher, whereas the peaks of phenolic acids were more reduced in number and size. The same trends were observed in laboratory burnings (HA-IV), suggesting the expected selective thermal destruction of aliphatic and OH-containing structures. The variation of the HA benzenecarboxylic/phenolic ratio was important in these samples (HA-C = 3.1, HA-B = 146.3, HA-I = 3.2, HA-II = 16.4, HA-III = 24.2, HA-IV = 51.8). The changes in the fatty acid series are independently plotted in Fig. 6. Under laboratory conditions, the fatty acid patterns were found to be rather resistant to thermal effects, but a tendency to selective destruction of chains of a higher molecular weight ( $> 16\text{C}$ ) was observed. Myristic and palmitic acids tended to be the predominant acids under severe heating, suggesting thermal breakdown of long-chain fatty acids. Under natural conditions (HA-B versus HA-C) the pattern was different, and we found a significant proportion of even-numbered, high-molecular-weight fatty acids in the HAs, a circumstance that could correspond to an incorporation of fatty acids derived from epicuticular waxes of the burned plant residues (Simoneit and Mazurek 1982). This may par-

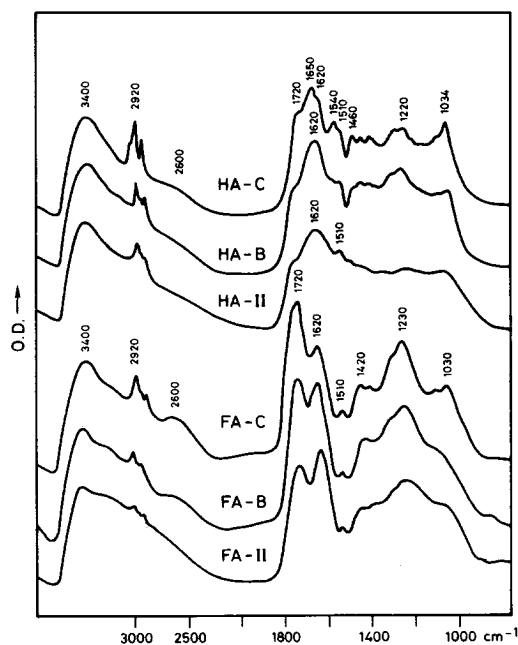


FIG. 4. Infrared spectra of humic acids (HA) and fulvic acids (FA) from control soil sample (C), postfire soil sample (B), and laboratory-burned soil humic fractions (II).

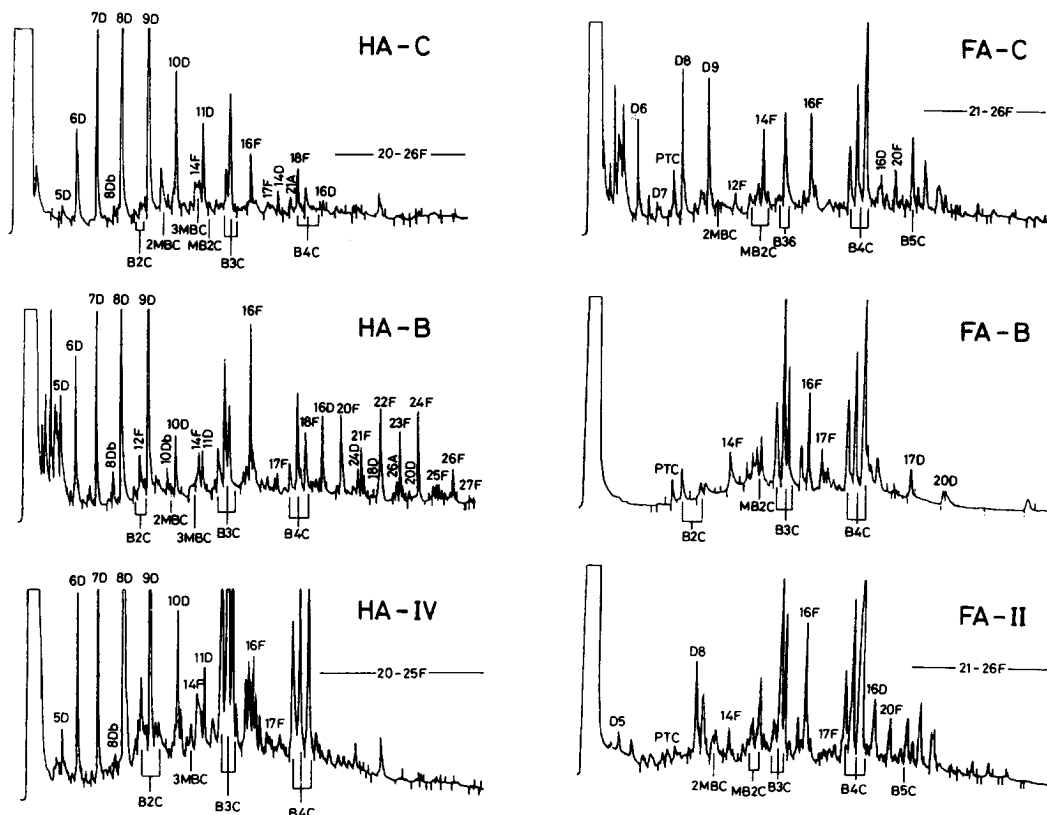
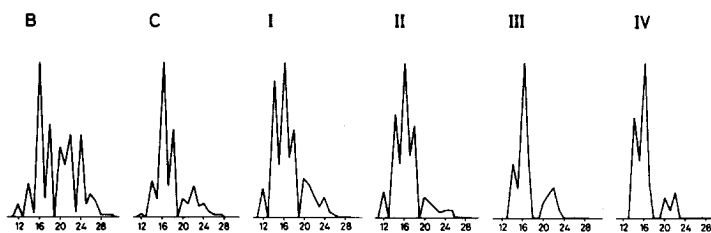


FIG. 5. Chromatographic patterns of degradation products from humic (left) and fulvic (right) acids of control soil, postfire soil (B) and laboratory-burned humic or fulvic acid (bottom). Abbreviations used: F = fatty acid methyl ester, D =  $\alpha,\omega$ -alkanoic diacid methyl ester, BnC = benzene-*n*-carboxylic acid *n*-methyl ester, M = methoxy, PTC = propane tricarboxylic acid trimethyl ester.

FIG. 6. Distribution diagrams (C number versus relative abundance) of fatty acids released after alkaline permanganate oxidation of humic acids from control soil (C), humic acids from postfire soil (B), and laboratory-burned humic acids (I to IV).



tially compensate for the thermal destruction of aliphatic structures in HAs (Almendros et al. 1987). The above phenomenon may be compared with the thermal "fixation" of hydrophobic substances in the soil, described by Savage (1974).

Similar trends were observed in the FAs. The peaks for  $\alpha,\omega$ -alkanoic diacids tend to be lower in number and in relative size, whereas the proportion of benzenecarboxylic acids was higher in the samples after burning. The variation in the relative proportion of the alkaline

permanganate degradation products is shown in Fig. 7.

CONCLUSIONS

The changes in the composition of humus after a Mediterranean oak forest had undergone intense burning are summarized in Fig. 8, showing a tentative model for the dynamics of organic matter in pyromorphic humus. According to this scheme, no generalized tendencies can be suggested for the fire-induced composition of hu-



FIG. 7. Comparative proportions of the major groups of degradation products obtained after alkaline permanganate oxidation of humic acids (HA) and fulvic acids (FA) from control soil (C), postfire soil (B), and laboratory-burned humic or fulvic acid (I to IV).

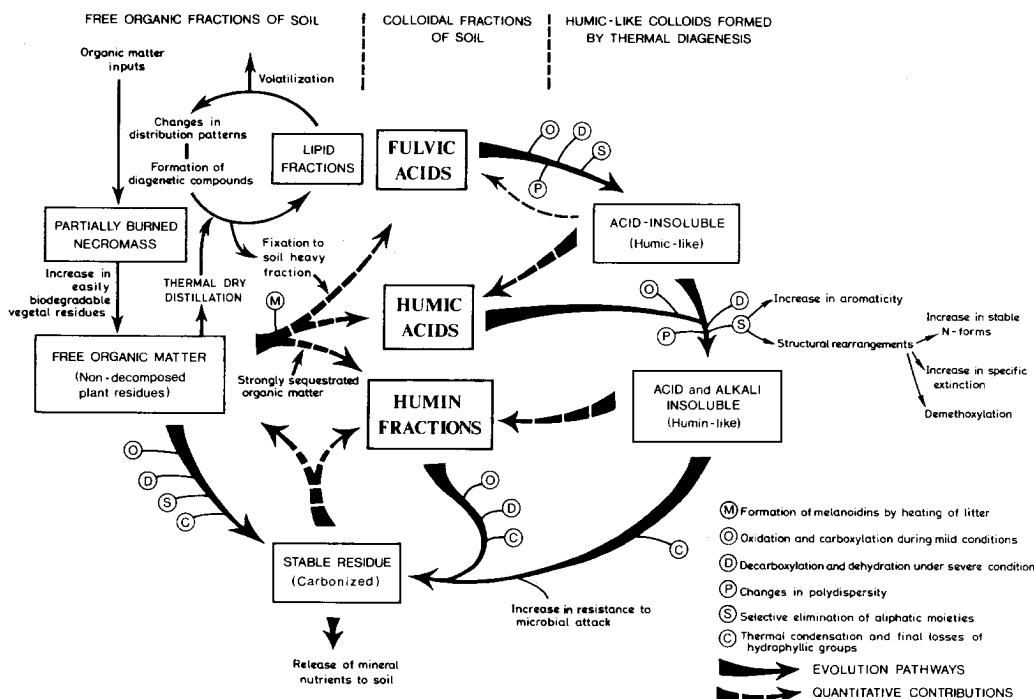
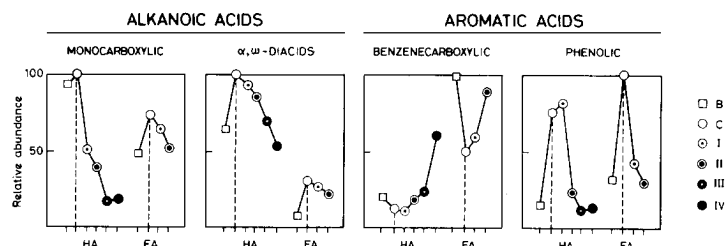


FIG. 8. Hypothetical changes occurring in soil humus during forest fire.

mus, because the processes for the incorporation and denaturalization of humic fractions greatly depend on the soil geochemistry, as well as on such external factors as the type of vegetation, the morphology of soil epipedon, etc.

The oxygen-containing functional groups of the humic polymers were found to be particularly labile to thermal treatment. In natural fires, an important amount of HA can be transformed into alkali-insoluble substances, quantitatively contributing (in terms of solubility) to the soil humin fraction. But, simultaneously, the FA fraction can, to an important extent, be transformed into acid-insoluble polymers, compensating for this quantitative reduction in the HA fraction. Moreover, incompletely burned plant necromass (containing an important pro-

portion of alkali-soluble lignin materials, as well as newly formed brown products from dehydration of carbohydrates, which are in part similar to humic substances (Almendros et al. 1989b)) may represent an additional contribution to the amount of extractable humiclike fractions in soils from burned areas.

In contrast with the low thermal stability of the peripheral functional groups, skeletal structures of the humic substances were rather resistant to the effects of fire in the most intense laboratory burnings. The selective destruction of aliphatic humic units may, to some extent, be compensated for by a "peripheral" incorporation of some lipid compounds in HAs presumably derived from thermal distillation of the necromass in the soil. These evolution pathways of

the humus substances could significantly contribute to the formation of water-repellent soils as a result of the passage of the fire.

The chemical characteristics of humic substances in fire-affected soils pointed to increased stability against chemical and biological degradation, but that stability of humus under a sclerophyllic evergreen forest can also be compensated for by the massive incorporation of lignocellulosic material that contributes to recovering the microbial activity of the soil after the fire.

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