

WEATHERING OF ORGANIC MATTER IN TIPS OF COAL MINES, PLZEŇ BASIN, CZECH REPUBLIC

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Summary

Weathering of Carboniferous organic matter was studied in spoil tips of coal mines in the Plzeň Basin, 1 to 112 years old. Weathering mechanisms were tested experimentally by low-temperature oxidation at 140°C. Weathering in the tips is manifested by gradual lowering of hydrogen index (HI)_{Rock Eval} and by an increase in the amount of polar compounds in organic matter pyrolysates relative to aliphatic and aromatic hydrocarbons. The total amount of pyrolysate decreases in the course of the weathering process. In contrast, the amount of extractable humic substances gradually increases with the length of weathering. The increasing amount of humic substances correlates with the increasing sorption capacity of the substrates deposited at tips. As a result of the highly acid environment in the spoil tips, humic substances are present in the H⁺ form. Therefore, these substances participate in the exchange reactions with cations (Ca²⁺, Mg²⁺, K⁺) in the evolving soil profile in the oldest spoil tips only, where gradual increase in pH occurs as a result of the completed pyrite oxidation.

It has been demonstrated experimentally that the oxidation of coal-type organic matter from the Plzeň Basin proceeds through at least three different stages. In the first stage, the O/C atomic ratio increases with the H/C ratio being almost constant. This indicates that oxygen is taken up with no water and carbon dioxide removal. During the second stage of oxidation, the H/C atomic ratio substantially decreases, the O/C ratio being almost constant. This is explained as due to decomposition of oxygenated species, with water and carbon oxides formation being temporarily the dominant chemical reaction. In the third stage, oxygen consumption and reaction product formation are in equilibrium, as evidenced by steady decrease in O/C and H/C atomic ratios in oxidized organic matter.

Introduction

In Czech Republic, millions tons of rocks are relocated and deposited in spoil banks, tips and quarry taluses every year. The deposited rocks frequently contain a high amount of the dispersed fossil organic matter which undergoes gradual weathering. During the weathering, the organic matter is partly mineralized, partly oxidized to form alkali-soluble products, i.e., humic acids. The products of organic matter weathering significantly modify the agrochemical properties of deposited rocks, especially their cation-exchange capacity (Stackhouse and Benson 1989; Livens 1991). Moreover, at least a part of soluble weathering products can be utilised as a source of carbon for the microbial growth or may act as stimulators of the plants growth (Krumbein 1983; Macurová *et al.*, 1996). Thus, the study of weathering of fossil organic matter can greatly contribute to our understanding of the changes that occur in the newly formed soil profile during the remediation of spoil banks and tips of mines.

It follows from the foregoing studies (see for example Nelson 1989; Kříbek 1996) that the rate of weathering of the organic matter depends on many variables. The most important are: (1) the time of exposition of rock toward the atmospheric oxygen, (2) local climatic and geomorphological condition, i. e., temperature, humidity and drainage, (3) petrography and mechanical properties

of rocks and, and, (4) type and thermal maturation of the organic matter. The objective of this study is to evaluate changes that occur in chemical composition of fossil organic matter of coal-type during weathering and to elucidate the role of fossil organic matter in agrochemical characteristics of deposited substrates.

Weathering of organic matter in coal mines tips

The organic matter from sediments dumped in tips of the Plzeň Basin has microscopic appearance of brown coal. The reflectance of vitrinite (R_r), measured on several samples, varies from 0.64 to 0.76%. The organic macerals are represented mostly by vitrinite, the macerals of the liptinite group (sporinite and cutinite) being less abundant. The fluorescence of liptinite is yellow or yellow-orange. Results of weathering of the fossil organic matter from tips 1 to 112 years old can be summarized as follows:

1. Weathering is petrographically manifested by formation of contraction cracks in vitrinite and by brighter colour and porous structure of liptinite (namely in megaspores). At a higher degree of oxidation, the formation of frequent contraction and oxidation cracks, breaking of vitrite and clarite bands, and secondary mineralization at cracks can be observed. Fusinite particles are sometimes bordered by oxidation rims with a higher reflectance.

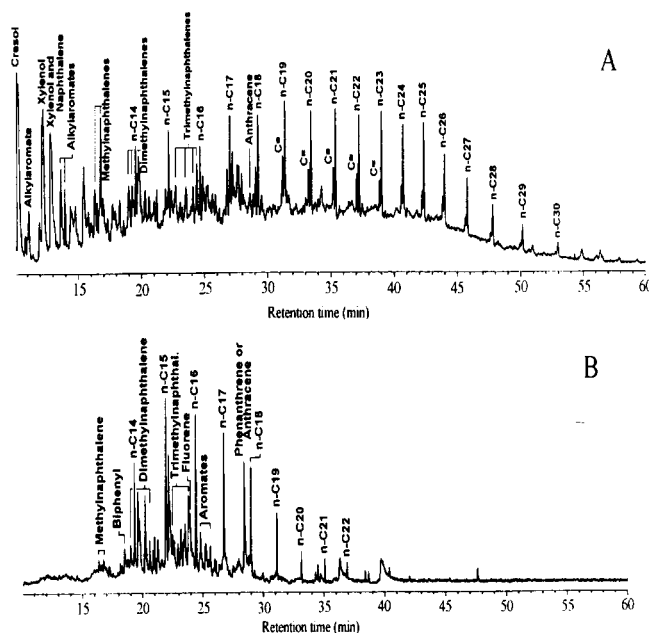


Fig. 1. Chromatograms of the pyrolysis products of fresh, coal-type organic matter (A), and weathered organic matter from rocks deposited 91 years at spoil tip of coal mine (Plzeň Coal Basin, Czech Republic).

2. Considerable decrease of the HI value (Rock Eval) from 270 - 290 mg HC/g C_{org} (fresh samples) to 130 - 120 mg HC/g C_{org} in old tip was observed. The T_{max} values remain unchanged during weathering.

3. Composition of extractable part of the organic matter changes significantly. The quantity of aliphatic hydrocarbons drops very quickly, the quantity of aromatic hydrocarbons decreased, comparatively to aliphatic hydrocarbons, in lower rate. The quantity of polars generally increase during weathering.

4. The quantity of the pyrolyzable portion of organic substance decreases during weathering. Moreover, spectra of pyrolysate of weathered organic materials show decreased quantities of aliphatic hydrocarbons and of low-molecular weight polars (phenols and creosols, Fig. 1).

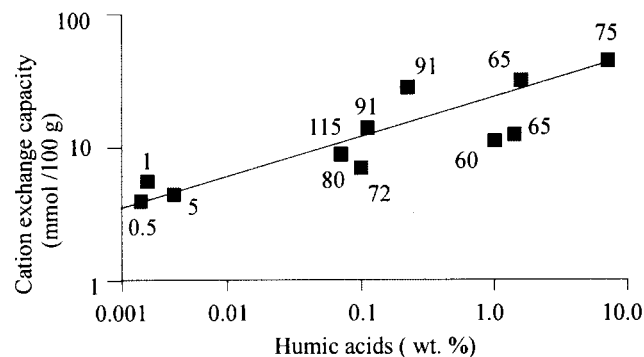


Figure. 2. Plot of cation exchange capacity vs. humic acid content in materials deposited in tips of Plzeň Coal Basin. Numbers in diagram denote the age of tips (in years).

5. The quantity of humic substances (humic and fulvic acids) increases during the long-term weathering. Relatively very small amount of fulvic acid is produced comparing with a humic acids.

6. As seen from the agrochemical point of view, the weathering of fossil organic substance affects namely the cation exchange capacity (CEC) of substrates discharged on tips (Fig. 2). It has been found that the sorption capacity of the deposited materials is in good correlation with an amount of humic acids produced and with an age of the tips. The CEC and exchangeable acidity values gradually increase over 75 to 91 years of deposition. As a result of the highly acid environment in the spoil tips, (3.1 to 4.9), however, humic substances are present in the H^+ form. These substances participate in the exchange reactions with other cations (Ca^{2+} , Mg^{2+} , K^+) in the evolving soil profile in the oldest spoil tips only, where gradual increase in pH to 6.5 occurs as a result of the completed pyrite oxidation.

7. In spite of the highly variable contents of C_{org} and N_{total} in the fresh samples, the C/N ratio gradually decreases from 90 - 100 (fresh samples) to 50 - 40 (tips 75 to 91 years old). The gradual decrease in C/N ratio is explained by loosening of rocks deposited in tips and thus faster development of microbial activity.

Experimental oxidation of organic matter

Samples and methods

Samples were homogenised and demineralized with the mixture of HCl/HF acids, washed with distilled water to neutral reaction and dried at laboratory temperature. Five grams of isolated organic matter was carefully ground and passed through a 50 μm sieve and

heated to 140 °C in a ventilated oven for times increasing from 8 to 256 h (8, 16, 32, 64, 128, 256 h) in order to obtain a representative series of oxidates. The samples on Petri dishes in the 3 mm thick layer were mixed periodically every 24 hours. Changes in IR spectra and elemental composition of oxidates were studied using Perkin-Elmer 624 spectrometer equipped with Data Station Model 3600 and Carlo Erba 2630 elemental analyser. Details on experimental method are given in paper of Hilgard and Kříbek (1997).

IR spectral changes during experimental oxidation

The spectral changes caused by oxidation are most marked within the aliphatic $\nu(CH)$ (2930 cm^{-1}) and carbonyl ($1730 - 1670\text{ cm}^{-1}$) regions. During oxidation, the absorbance of a (CH) bands decreases and simultaneously the absorbance of products with carbonyl functionality increases. Oxidation of all samples expressed in terms of CO product formation and of C-H group consumption consists of two characteristic periods. After an initial rather quick decrease/increase within 0 - 100 hours, the reaction enters a period of very slow decline/incline in practically constant rate.

Changes in absorption intensity in the $1620 - 1590\text{ cm}^{-1}$ region (overlapping absorption of skeletal vibrations of aromatic cycles, carboxylate anions) in the course of oxidation are small, practically on the limits of experimental error.

The decrease of absorption of the $\sigma(CH_2)$ and $\sigma(CH_3)$ bands in the 1460 and 1380 cm^{-1} corresponds with a spectral manifestation of these species in the stretching vibration region.

The changes in absorbance of the $1100 - 1250\text{ cm}^{-1}$ region ("wide band", formed by the summary absorption of various types of alkoxy- or aryloxy-species) remains unchanged.

Bands in the region $840, 810, 760\text{ cm}^{-1}$ are assigned to the out of plane deformation vibrations of aromatic CH species. They are highly characteristic for elucidation of the substitution type of aromatic structure. During oxidation, their absorption intensity generally decreases. However, the decrease of the 840 and 810 cm^{-1} band is more significant than in case of the 760 cm^{-1} band. This is in agreement with a higher sensitivity of isolated (840 cm^{-1}) or two neighbouring (810 cm^{-1}) CH-species to oxidation reactions in comparison with the reactivity of three or four neighbouring ones (760 cm^{-1}). These results are in good agreement with conclusions of Anderson and Johnson (1986).

Relationship between the alkyl-species consumption and carbonyl- or alkoxy- functionality production

To gain a deeper insight into consumption of alkyl groups and formation of carbonyl group during oxidation, the evaluation of the relationship between the alkyl-species (absorbance of the band 2930 cm^{-1} indicating the summary changes in both methylene- and methyl-species) consumption and carbonyl- (absorbance of the band in region $1680 - 1730\text{ cm}^{-1}$) or alkoxy-functionality (absorbance of the "wide band" in $1100 - 1250\text{ cm}^{-1}$ region) species production was analysed in detail. It has been found that the correlation is nearly linear. These results suggest that the chemistry of oxidation reaction does not change fundamentally during the whole oxydation run (0 - 256 h). The linear and absolute parameter values of correlation are presented in Table 1. The value of parameters k_1 and k_2 (slope of the correlation line) characterize the summary stoichiometric relations between the aliphatic CH species consumption and the oxygenated products

(containing C=O or C-O species respectively) formation. The parameters $-k_1$ and $-k_2$ express the absorbance ratio between the carbonyl- ($-k_1$, band in the $1730 - 1670 \text{ cm}^{-1}$ region) or alkoxy-species ($-k_2$, band in the $1100 - 1250 \text{ cm}^{-1}$ region) formed and fixed in sample and this of consumed CH-species (2930 cm^{-1} band). Parameters q_1 and q_2 express the extrapolated quantity of the C=O and C-O structures respectively at the total consumption of all C-H structures.

Table 1. The linear (k_1, k_2) and absolute (q_1, q_2) parameter of linear correlation between the alkyl band (2930 cm^{-1}) consumption and C=O species ($1730 - 1670 \text{ cm}^{-1}$) or C-O species ($1100 - 1260 \text{ cm}^{-1}$) formation during oxidation of organic matter from the Plzeň Coal Basin.

$A(\text{C=O}) = k_1 \cdot A(\text{CH}) + q_1$	$-k_1 = 2.23$	$q_1 = 0.10$
$A(\text{C=O}) = k_2 \cdot A(\text{CH}) + q_2$	$-k_2 = 0.03$	$q_2 = 0.08$

Changes in elemental composition during experimental oxidation

Changes in the H, C, N and O content in the course of oxidation (recalculated for ash free substrate) are presented in Table 2. The changes in H/C to O/C atomic ratios are depicted in Figure 3. For comparison, the changes in the H/C and O/C ratios in the course of experimental oxidation of aliphatic (algae-type), hydrogen-rich organic matter and aromatic (coal-type) organic matter from the Miocene Coal Basin of Sokolov (Czech Republic) are plotted in the same figure. Slopes of possible reactions proceeding during experimental oxidation (oxygen consumption, decarboxylation, decarbonylation, dehydration, splitting-off hydrogen or hydrocarbon fragments) are presented on in Figure 4.

Table 2. Changes in the H, C, N and O contents of samples during oxidation (recalculated for ash free substrate).

Oxidation time (h)	H (%)	C (%)	N (%)	O (%)
0	5.18	72.77	1.71	20.34
8	5.36	70.18	1.73	22.73
16	5.4	70.34	1.67	22.59
32	4.62	72.16	1.63	21.59
64	4.35	70.08	1.66	23.90
128	4.35	69.02	1.66	24.83
256	4.07	66.65	1.68	27.45

As shown in Figure 3, predominantly aliphatic (algae-type) organic matter from the Sokolov Basin (Tertiary) displays a monotonous decrease of H/C and increase of O/C atomic ratios. This indicates that during the whole 256 hours of oxidation the mutual proportions of proceeding chemical reactions do not change substantially. The direction of this curve indicates that oxygen consumption and splitting of hydrocarbon fragments dominate the oxidation process. The oxidation of both samples of coal-type organic matter, i.e., organic matter from the Plzeň Coal Basin (Carboniferous) and from Sokolov Coal Basin (Tertiary), substantially differ from the aliphatic sample. Significant change in the direction of the diagram curve show that the oxidation proceeds through at least three different stages. In the first stage the O/C atomic ratio increases with constant or moderately increasing H/C atomic ratio. Such direction in the diagram

indicates that oxygen is taken up without water and carbon oxides being removed or more exactly, oxygen consumption by the

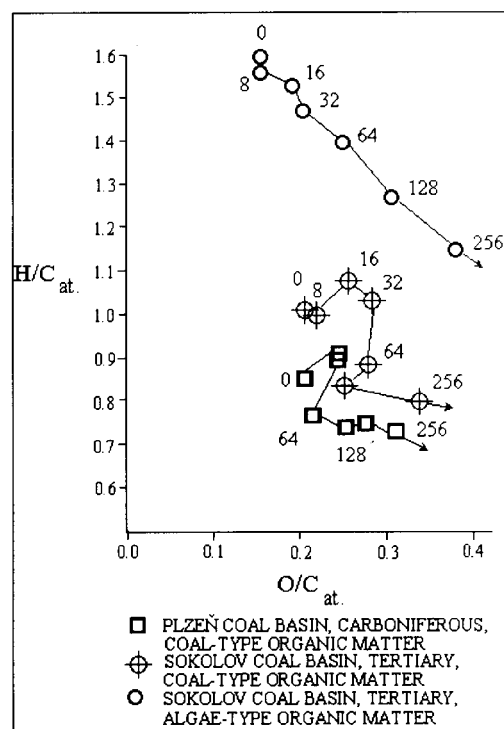


Figure 3. The plot of H/C vs. O/C atomic ratio changes during the experimental oxidation of organic matter from the Plzeň Coal Basin. Changes for aliphatic (algae-type) and aromatic (coal-type) organic matter from the Sokolov Coal Basin (Tertiary) are shown for comparison.

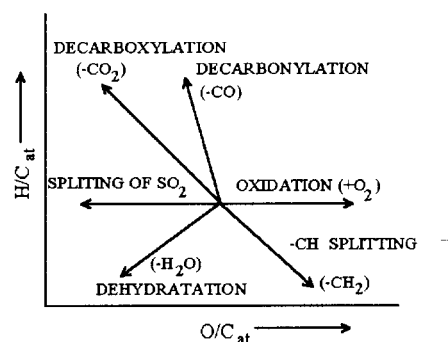


Figure 4. Characteristic direction of reactions proceeding during experimental oxidation of organic matter expressed in the H/C vs. O/C plot.

most reactive centres predominates breaking of water or carbon oxides during this initial period of oxidation. This stage of oxidation is represented in Figure 3 by its initial part characteristic of monotonous increase in O/C atomic ratio right to the point where the diagram curve turns to lower values of O/C and H/C atomic ratio. This turning point of the curve appears after 32 hours

in the case of humic (coal-type) organic matter from Tertiary sediments and after 16 hours for organic matter from the Carboniferous organic matter from the Plzeň Coal Basin. During the second stage of oxidation, the decomposition or condensation of oxygenated species, producing especially water and carbon oxides becomes temporarily the dominating chemical reaction. Not until after exhausting entire oxidizable species, the new equilibrium between the oxygen consumption and reaction products formation is established which is governed by the oxidation rate of other more difficult oxidizable species of substrate. This period begins earlier for sample from the Plzeň Coal Basin (after 32 – 64 hours) than for sample of coal-type organic matter from the Sokolov Coal Basin. In the third stage of the oxidation, the oxygen consumption and reaction product formation are in equilibrium similarly as in the case of aliphatic organic matter oxidation.

Conclusions

The study of fossil organic matter at tips of brown coal mines at the Plzeň Basin has shown that significant amount of oxidation products (humic substances) is produced during weathering. From the agrochemical point of view, the weathering of organic matter affects namely the sorption capacity of rocks dumped on the tips. Both the long-term weathering and the experimental oxidation of the organic matter manifest themselves namely by the decrease of the hydrogen content in their structure. This is evidenced by the decrease of the vibration intensity of aliphatic C-H bonds and by increase in the vibration intensity of carbonyl and carboxyl groups. In contrast to the oxidation of aliphatic (algae-type) organic matter, the oxidation of coal-type organic matter is more complex. Very quick consumption of oxygen dominates the initial stage of oxidation and is followed by a temporary period when dehydration- and decarboxylation-reactions predominate. In the final stage of the oxidation, the oxygen consumption and reaction product formation are in equilibrium.

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