

# Effect of crude oil pollution on organic carbon and humus content in grey-brown soils in Mangyshlak, Pre-Caspian Sea Region

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**Abstract:** The organic carbon and humus content in oil polluted brown and grey-brown soils in Mangyshlak, Pre-Caspian Sea Region, was analyzed from 2000 to 2008. The results indicated that bitumen substances from crude oil pollution deteriorated the soil property, however, the organic carbon content increased significantly. The products of oil pollution changed the composition of carbonaceous substances which formed soil humus, and changed the ratios of the humus components. Residual insoluble carbon increased with the rise of oil organic carbon. The mobility of humus components was significantly increased because of the high oxidation-reduction process in the topsoil, and the humus content and microorganism activity increased. The organic carbon content increased significantly, while it decreased with the distance away from the oil well. The rearrangement of physical, physical-chemical and chemical properties of the polluted soils was significant.

**Keywords:** oil-chemical pollution; humus; transformation; degradation; Pre-Caspian Sea Region

## 1 Introduction

Oil-chemical pollution of soil is a central environmental issue in the Caspian Sea Region due to oil and gas exploitation. Irrational use of raw material resources, a progressive increase in anthropogenic influence on the soil, and frequent oil-spills resulted in the formation of oil 'pits' and 'polygons' in the ecologically destabilized territories. The geochemical condition, carbon-nitrogen balance and element composition of the soil may be significantly modified by severe oil pollution.

Oil pollution caused by oil industry wastes, leaching from equipment and spills has led to  $5 \times 10^5$  hm<sup>2</sup> salinization soil and the degradation of ecosystems (Saparov *et al.*, 2006). In the oil-polluted soils, the important genetic indices created by nature over thousands of years are altered, including change of humus content and composition, formation of bitumen crusts, disturbance of soil-absorbing complexes, and decreases in porosity, aeration, water-air properties and ecological stability. Toxic chemicals accumulate in the soil and have caused many human diseases, such as hepatitis, lung diseases, tuberculosis and cancers. The

increase of 'professional diseases' among local people and the loss of cattle have been related to these toxic chemicals (Bigaliyev *et al.*, 2002). Oil exploitation, refining, sewage treatment and tankers increase the pollution of the Pre-Caspian Sea. Pollution by crude oil, which contains 20%–25% hydrogen sulfide, caused the deaths of water birds, migratory birds and mammals. The death of these animals had a negative effect on the bio-productivity of the Caspian Sea (Dusenov, 2001).

The oil pollution problems of Kazakhstan have not been solved and require further comprehensive study. Decontamination of the environment in the oil-industry regions of Kazakhstan is an urgent task for the government. It is necessary to detect centralized oil-polluted regions, the regularity of their geochemical migration, the composition and toxicity of the pollutant. The aim of the present study is to clarify the effect of oil pollution on organic carbon content, humus content and composition in the grey-brown soil.

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Received 2009-11-06, accepted 2010-04-16  
doi: 10.3724/SP.J.1227.2010.00133

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## 2 Materials and methods

The research was carried out on the monitoring sites of Zhanaozen oil-field (grey-brown soils) and Dossor oil-field (brown soils) in the Pre-Caspian Sea Region. Both sites were polluted by crude oil and oil industry wastes from 2000 to 2008. The soil was saline, being composed of loam, sandy-loam, sands and clay. Twenty-eight monitoring holes were drilled in the affected soils by oil wells representing a total area of 10,000 m<sup>2</sup>.

The soil profiles were drawn, and the soil samples were selected according to the soil horizons (Ponamareva *et al.*, 1975). The group and fractional composition of humus, total content of organic carbon and humus were measured using Turin methods (Turin, 1937). The comparative-ecological analyses of soils were undertaken according to common methods in soil science (Arinushkina, 1961).

## 3 Results and discussion

### 3.1 Organic carbon and salt contents in the oil-polluted soil

The results of the research indicated that the oxidation of organic substance in the unpolluted soil was least. The organic carbon content reached the

maximal (0.98%) in the topsoil, and decreased with soil depth. It was undetected in the 51–80 cm horizon (Table 1).

The organic carbon contents in the polluted soil, compared with the control soil, increased sharply in the topsoil. The organic carbon content reached 5.87% in the P-2 polluted topsoil, which was higher than the other soil horizons (Table 2). The organic carbon content in the alluvial 0–4 cm horizon in the section of P-1 near the well was 4.68% and the buried 4–20 cm horizon was 1.18%, whereas it was 0.56% in the 20–40 cm horizon. The organic carbon content in topsoil horizons of the polluted soils differed markedly from that in the correspondent horizons of the unpolluted soils (Table 1). However, it was no difference below the 20 cm horizons.

The speed of oxidization increased with increasing soil organic carbon content. In the polluted soils, insoluble organic carbon residuum accumulation was significant because of solidification. This is the beginning of the formation on the soil surface of solid salted crust. The salt content in the lower layer of solid saline soils was significant lower than that of topsoil. Total salt concentration in the surface layer was more than 1% (Table 2).

The thin soil crust was formed when the soil dried up. Eventually, all of clay and loam surfaces may be

**Table 1** Organic carbon content and salt composition in the unpolluted grey-brown soils

No. of soil section	Depth (cm)	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total salt	CO <sub>2</sub>	Organic carbon
							(%)				
Unpolluted grey-brown soil	0–3	0.018	0.130	0.419	0.037	0.015	0.219	0.001	0.839	12.05	0.98
	3–14	0.015	0.241	0.483	0.051	0.020	0.277	0.001	1.193	12.35	0.88
	14–35	0.018	0.133	0.528	0.050	0.030	0.232	0.002	0.993	10.82	0.59
	35–51	0.015	0.208	0.541	0.060	0.021	0.290	0.002	1.137	10.21	0.42
	51–80	0.006	0.102	0.818	0.288	0.017	0.098	0.001	1.330	11.07	–

**Table 2** Organic carbon content and salt composition of oil-polluted saline soils

No. of soil section	Depth (cm)	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total salt	CO <sub>2</sub>	Organic carbon
							(%)				
P-1	0–4	0.019	1.088	0.954	0.326	0.097	0.605	0.010	3.097	13.92	4.68
	4–20	0.016	0.340	0.322	0.126	0.030	0.177	0.004	2.015	11.31	1.18
	20–40	0.007	0.058	0.712	0.261	0.018	0.041	0.002	2.104	12.37	0.56
	40–120	0.080	0.077	0.786	0.280	0.021	0.066	0.002	1.240	11.78	–
P-2	0–21	0.019	0.098	0.529	0.182	0.021	0.072	0.005	0.921	9.07	5.87
	21–46	0.012	0.044	0.672	0.233	0.018	0.051	0.003	1.033	10.58	0.65
	46–75	0.010	0.053	0.749	0.270	0.024	0.039	0.002	1.147	10.96	0.46

covered by the crust. These processes were accompanied by desertification. Finally, in the region of accumulation, the soil surface would be transformed into solid saline soils.

### 3.2 Organic carbon content changes with time in the oil-polluted soil

Oil degradation was observed in polluted soil by oil stream 15 years ago. The bitumen substances were gradually transformed into insoluble chemicals and humic materials in the soils. This implies the change of organic carbon content in the soils with degradation of the bitumen substances. It showed that the multiple oil pollution of the soil could increase the organic carbon content continuously (Dusenov, 2001). The organic carbon content accumulated in the soil during the period of three years (Table 3). The organic carbon content decreased with increasing distance from the well. Compared with the unpolluted soil, the organic carbon content increased by 32.9% in the 0–10 cm topsoil horizon, which was 50 m away from the well. The organic carbon content in the 10–30 cm layer changed slightly. However, it decreased by 16.2% in the 30–50 cm layer (Table 3).

**Table 3** Organic carbon content in the oil polluted soils at different times

Soil depth (cm)	P-control, unpolluted soil (%)	P-1N, polluted soil (%)		
		Age of pollution		
		The distance away from the well		
		3 years	15 years	
		10 m	50 m	10 m
0–10	0.91	1.81	1.21	2.09
10–30	0.75	0.85	0.80	1.80
30–50	0.62	0.78	0.52	0.97

The organic carbon content increased markedly in the 0–30 cm horizon in 15-year polluted soils but did not change significantly in the 30–50 cm horizon (Table 3). This result implied the bitumen substance in polluted soils was decomposed with time.

### 3.3 Humus content and composition in the oil-polluted soil

The composition of organic acids in the profile of grey-brown soils was shown in Table 4. The organic carbon content of the polluted soil and the amount of unhydrolyzed residual increased significantly compared with the unpolluted soil. The humic and fulvic acids and the ratio of humic acid to fulvic acid also changed (Table 4).

Increasing oxidation in the horizon of 0–10 cm could be attributed to the increase of fulvic acid in humus, which could be more easily oxidized than humic acid (Pikovsky, 1981). On the other hand, the higher oxidization of organic substance in the polluted topsoil could be related with higher molecular oxygen concentration. The oxidization of organic carbon decreased sharply in the 30–40 cm horizon due to the increase of humic acid content or the reduction conditions caused by insufficient molecular oxygen. In the 60–70 cm soil layer, oxidization of the organic carbon increased again because of more utilizable organic acids of low molecular weight dominated in this horizon (Table 4).

## 4 Conclusion

Chemical composition, properties, and structure of the soil were altered by crude oil pollution, with the humic horizon being most strongly affected. The content and mobility of humus components increased

**Table 4** Group and fractional composition of organic substances in saline grey-brown loam soils

No. of soil section	Depth (cm)	Organic carbon content in soil (%)	Unhydrolyzed residual (%)	Decalcine (%)	Humic acid (%)				Fulvic acid (%)				Humic acid/fulvic acid
					I	II	III	Sum	I	II	III	Sum	
P-6 polluted soil	0–10	6.48	30.69	5.57	0.34	10.65	26.29	37.28	14.63	7.25	4.57	26.45	1.40
	30–40	3.29	62.32	10.79	0.67	4.19	4.19	9.05	6.17	2.79	5.87	14.83	0.61
	60–70	4.65	84.64	5.82	0.24	2.97	2.06	5.27	0.97	8.84	2.99	4.26	1.23
P-7 unpolluted	0–6	0.78	14.74	3.46	1.41	13.2	22.05	36.66	29.61	8.84	6.67	45.12	1.35
	6–13	0.50	30.40	8.20	2.20	16.0	15.20	33.40	11.20	8.00	8.80	28.00	1.19
	20–30	0.57	15.96	9.65	5.96	N/A	10.88	16.84	4.91	24.21	28.42	57.45	0.29

significantly in the soil due to long-term changes in oxidation-reduction conditions. Meanwhile, the continued oil-pollution led to the increase of organic carbon content in the soils.

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## Acknowledgements

The research was supported by Government Order of the Ministry of Education and Science of the Republic of Kazakhstan (0106 RK).