Petroleum Hydrocarbons Pollution on the Sudanese Red Sea Coastal Water

Masoud G. Ahmed[1], Bashier M. Elhassan[2] and Maysara E. Mohyeldien[3],

[1]Civil Engineering Department, Sudan University of Science and Technology (SUST), Sudan
[2]Chemical Engineering department, University of Khartoum, Sudan
[3]College of Petroleum Engineering and Technology, Sudan University of Science and Technology (SUST), Sudan
masoudadli@yahoo.com

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ABSTRACT – The aim of this paper is to determine the extent of petroleum hydrocarbons pollution on the Sudanese Red Sea coast (Portsudan harbor and Bashayer Marine Terminal (BMT)), to achieve this goal laboratory work was conducted to determine hydrocarbons concentration. The highest concentration of Total Petroleum Hydrocarbons (TPH) in seawater was found at strip I (dockyard) with the average of 80.2 mg/l, the next to the highest concentration was generally occurred at strip IV (BMT), the ranges of concentrations were between 5.8 and 24.2 mg/l with mean value of 14.98 mg/l. Values of oil concentration at strip II (South port) are much lower than those of strip I (6.8 to 10 mg/l). Higher concentrations, ranging from nil to1320 mg/kg were detected in the sediment samples. It can be concluded on this basis that most of the Portsudan harbor and BMT suffers from oil pollution in different degrees according to UNEP and AIDMO. No oil contamination was observed at strip III (North port). The GC measurements proved those hydrocarbons contaminations were due to biologic and petrogenic origins, most oil samples light and middle fractions.

Keywords: *Red Sea, Portsudan harbor and Bashayer, Hydrocarbons Pollution, Cavitation, biologic and petrogenic origin.*

المستخلص *– تهدف هذه الورقه لتحديد مدي التلوث النفطي في الساحل السوداني لمياه البحر الاحمر(ميناء بورتسودان وميناء بشائر لتصدير النفط). للوصول لهذا الهدف أجريت تجارب معملية لايجاد تراكيز الهايدروكربونات. وجد اعلي تركيز للهايدروكربونات في القطاع1 (حوض السفن) بمتوسط تركيز80.2 ملجم/لتر يليه القطاع VI (ميناء بشائر) بتركيز يتراوح بين 5.8-24.2 ملجم/لتر ومتوسط تركيز يصل 14.98 ملجم/لتر. وجد أن تركيز الهايدروكربونات في القطاع II (الميناء الجنوبي) أقل بكثير من تركيزها في القطاع I بقيم تتراوح بين6.8-10 ملجم/لتر أما عينات الطين فوجدت فيها تركيزات اعلي تتراوح مابين 0-1320 ملجم/كجم. خلصت الدراسة أن معظم مناطق ساحل بورتسودان وميناء بشائر تعاني من التلوث بدرجات متفاوتة وفقا للدليل الاسترشادي العام الصادر من المنظمة العربية للتنمية الصناعية (AIDMO) وبرنامج الأمم المتحدة للبيئة(UNEP). وجد أن القطاع III (الميناء الشمالي) خالى من التلوث النفطي. قياسات كروموتوغرافيا الغاز أثبتت أن التلوث النفطي ناتج عن أصول حيوية وبترولية وأن معظم العينات تتكون من مركبات خفيفة ومتوسطة.*

INTRODUCTION

The world production of crude oil is about 3 billion tons per year and half of it is transported by sea1 being strategically positioned between the Indian Ocean and Mediterranean Sea, the Red Sea has been extensively used by international maritime

traffic. Oil shipping and refinement are crucial industries for the Sudan econom butare also potential threats to the coastal marine environment especially after Sudan has entered exportation phase which requires awareness from early stages to achieve sustainable development between oil resources development and environment. The important effects of oil on organisms include, effects on fish, shellfish, seabirds, plankton, marine mammals, vegetation, as well as its effect on Oxygen Regime, public health and tourism .The Red Sea is long semi–enclosed tropical body of water, the coastline of the Sudan on the Red Sea is about 750 km long, including embayments and inlets. The aim of this paper was to determine the degree of pollution caused by oil of Portsudan harbor and Bashayer Marine Terminal (BMT).

MATERIAL AND METHODS SAMPLING STATIONS

Nineteen samples that including 13 seawater samples and 6 sediment samples from four research strips were collected and investigated for detection of hydrocarbons concentration at Red Sea coastal areas of Portsudan harbor and Bashayer Marine Terminal (BMT) port. The sampling stations were selected from four strips along Port Sudan coastline and BMT (Figures 1 and 2). The sampling stations located in the four strips, are expected to be the principal fixed sources of oil pollution. These strips are:

1. Strip I: Dock yard contains 3 stations for water sample (S1, S3 and S5) and 1 station for sediment sample (S1).

2. Strip II: South quay contains 2 stations for water sample (S7 and S9) and 2 stations for sediment sample (S6 and S7).

3. Strip III: North quay contains 3 stations for water sample (S10, S11 and S13) and 2 stations for sediment sample (S11 and S12).

4. Strip IV: BMT contains 5stations for water sample (S14 to S18) and 1station for sediment sample (S14). Sampling procedures Sea water sampling procedures to determine the concentration of TPH in the seawater, 500 ml sample glass stoppered bottles were used to contain the sample. Before used all bottles were cleaned with detergent, washed and cleaned by soap and tap water then by distilled water, dried and finally rinsed with solvent to remove any traces of oil and grease that may be attached to the walls of the bottles that may interfere with the analysis. Samples were collected from water 5-15 m from the shore where the depth of the water was nominally 0.5-1m at strip I and strip IV. Samples for control were collected from the entrance of the port (S13), with deep depth, they assumed to be unpolluted. For strip IV control sample (S18) was collected from about 2 km far from shore where the depth of the water is 54m approximately.

Strip I: dockyard, Strip II: South quay, Strip III: North quay, Strip IV: Bashayer Marine Terminal port (BMT)

Figure 1: Location of the sampling stations of Portsudan harbor

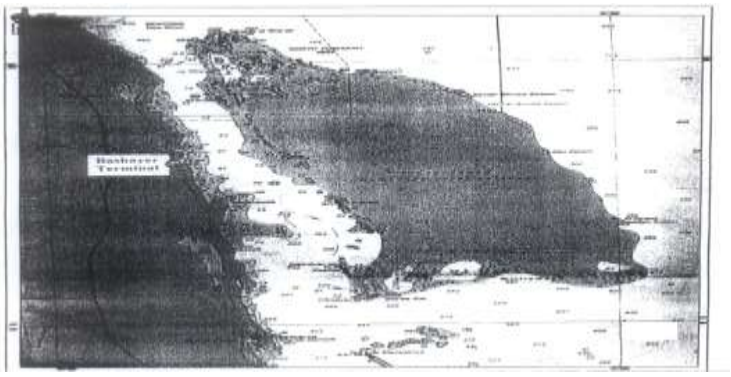


Figure 2a: Bashayer Marine Terminal (BMT) area

Figure 2a: Location of the sampling stations of BMT[2]

Sediment sampling procedures: Sediment samples were collected from 0.5-2 m water depth from stations strips 1 and IV, the distance from the shore was approximately 5-15m. Samples kept in plastic containers and labeled with markers according to the strip and stations numbers. A total number of 6 sediment samples were collected. It was not possible to collect control sample sediment because the place where the water sample control obtained (entrance of the harbor) is very deep.

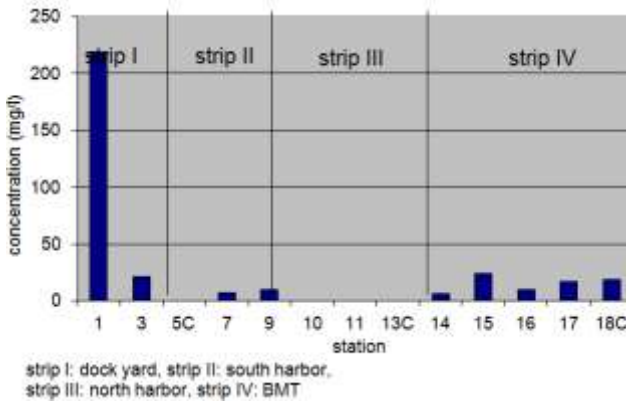
Laboratory Analyses: Quantitative determination of the Total Petroleum Hydrocarbons (TPH) was done by using gas chromatograph of model CP9001 Serial number 9486993 which was combined with flame ionization detector, the column used was WCOT fused silica type, with 25m column length and 0.25 mm inside diameter, the carrier gas was hydrogen with velocity of 40 cm/s. In this study, all laboratory tests were carried out in accordance with Standard Methods. Analysis of TPH has been done at Central Petroleum laboratories (CPL) at street 61-Khartoum, Sudan.

NUMERICAL RESULTS

Hydrocarbons concentration in seawater

Strip I: This strip, contains stations located near electrical power station and dock yard, four samples were collected (three seawater samples plus one sediment) and examined for TPH and results are shown in Figure 3. Results show that hydrocarbons concentration varied greatly in this strip. The average concentration levels of the hydrocarbons in this strip was 80.2 mg/l. Maximum TPH concentration was found at station 1, with value of 219.2 mg/l which, represents the highest value recorded among all other thirteen research stations.

Station 5 which were selected as control sample and far away from assumed pollution areas, were free of pollution. The high level of petroleum concentration at these stations is probably due to their geographical locations, this strip is semi-enclosed basin and hence it affects physochemical processes which lead to degradation of oil content in sea water. The location of stations 1, 3 is close to power station, the main electrical power station is located on the Western side of the harbour.



Figur 3: ***Hydrocarbons Concentration in Seawater at Portsudan Harbor and B***

This plant has been discharging the waste oil directly into the sea; therefore, these areas have the potential to be contaminated with oil from this station. Other sources is the discharges from the dock yard where many shipping activities and repair are done, the location of station 3 is close and facing to maritime workshop. Therefore, these areas have the potential to be contaminated the adjacent waters with oil. These data suggest that the level of petroleum hydrocarbonss is higher than the level fixed by the UNEP and Arab Industrial Development and Mining Organization AIDMO[2].

Therefore, this strip could be classified as highly polluted. Gas chromatographic analysis was used to identify the source of contaminants. It gives information about the qualitative and quantitative determination of hydrocarbons and their paraffinic distribution. It showed the existence of fifteen hydrocarbons components at station 1. (Table 1), n-paraffins ranging from n-hexadecane (C-16) to n-triacontane (C-30).

Highest component concentration was n-eicosane (C-20) with 16.02% and the lowest one was n-hexadecane (C-1) with only 0.49%. In case of station 3, thirteen hydrocarbons components were detected ranging from n-pentadecane (C-15; bp=514.71 F) to n-triacontane (C-30) (Table 2). Highest component concentration was n-eicosane (C-20) representing 11.01% were the lowest concentration recorded according to the GC analysis was C-27 with 3.07%.

Gas chromatographic analysis was also used to identify the source and the origin of contaminants based on the ratio of the sum of the amounts of even to odd carbon numbered alkanes. Blumer and Sass[3] suggested that the amount of hydrocarbons with even numbers of carbon atoms were indicative of petroleum residues. In contrast, natural hydrocarbons originating from biological synthesis are predominately those having odd numbers of carbon atoms in their molecules4. The capillary gas chromatography of paraffin distribution of the studied oil samples can be identified into three fractions, light, middle and heavy fractions; Light fraction: C12-C22; Middle fraction: C23-C30; heavy fraction C31-C405. According to this classification it has been found that most oil samples belong to light and middle fraction.

Table 1: Hydrocarbons concentrations in seawater at station 1 (C=219.2 mg/l)

Components	Results (%)
C16	0.49
C17	2.84
C18	7.85
C19	11.70
C20	16.02
C21	15.28
C22	13.42
C23	9.75
C24	8.40
C25	5.60
C26	4.65
C27	1.84
C28	1.03
C29	0.56
C30	0.56
Odd	47.58
Even	52.42
Even/Odd	1.1

In general, petroleum hydrocarbons having a ratio approaching 1.0, while the indigenous hydrocarbons derived from biological sources exhibit ratios nearer to zero. The calculated

ratios for each study station are shown in Table 1 and 2. The ratios showed that station 1 have a predominance of even numbers alkanes (even/odd=1.1 and 1.04) which indicated that there is petroleum hydrocarbons. The absence of very light carbon components and presence of light one at this strip indicated that weathering process was going on at the time of sampling at this strip.

Table 2: Hydrocarbons concentrations in seawater at station 3 (C=21.4 mg/l)

Components	Results (%)
C15	15.18
C17	12.20
C18	10.29
C20	11.01
C21	7.92
C22	8.57
C24	6.31
C25	6.36
C26	7.77
C27	3.07
C28	3.53
C29	4.12
C30	3.67
Odd	48.85
Even	51.15
Even/Odd	1.04

Strip II

The highest level of total hydrocarbons detected was 10 mg/l at station 9. Concentration recorded at station 7 was 6.8 mg/l. Station 13 was selected to be as control sample, it is located at the entrance of the harbor, which is a pit far from assumed oil sources pollution. Analysis proved that control station was free from oil pollution. The values of oil concentration recorded at station 9 and 7 could be attributed to the fact that the coast of south harbor is slightly polluted by direct discharges of oil from ships activities and loading and unloading tankers cargos at the terminal. Values of TPH concentration at this strip are much lower than those of strip I. The mean concentration at this strip was 8.4 mg/l, which is mean the level of petroleum hydrocarbons is lower than the level fixed by the UNEP and Arab Industrial Development and Mining Organization [2].

Strip III

Stations forming strip III are located at the North part of the harbor. The results obtained in the study of this strip showed no oil contamination was observed. This strip does not subject to the same degree of pollution as strip I, II and IV, in addition to that, this strip due its location at the entrance of the harbor, near open sea, is exposed to high action of sea current and prevailing wind which is assist both physio-chemical and biological weathering process of spilled oil in marine and coastal environment at this area. Strip IV Total Petroleum Hydrocarbons (TPH) concentration at this strip (BMT) varied between 5.8 at station 14 and 24.2 mg/l at station 15. The mean values of oil concentration in this strip were 14.98 mg/l. With the exception of station 14 and 16 the rest of the samples gave evidence of oil pollution. The relatively low mean value of hydrocarbons concentration at this strip when compared to strip I, probably due to the fact that, Bashayer marine terminal is a new port, protection and safety procedures against pollution are considered, the pumping mechanism of oil into tanks is good, which reflects the discipline of application of rules and regulations governing the operation processes of the terminal.

There is very big variation in hydrocarbons component numbers in this strip. Gas chromatograms showed the existence of hydrocarbons components range from four at station 18 to fourteen hydrocarbons components at station 16 (Table 3 to 7), n-paraffins ranging from n-pentadecane (C-8) at station 15 to n-triacontane (C-30) at stations 16. Studying the characteristic feature for chromatogram of station number 15 (Table 4) we can say that, this station has low boiling point components up to n-C19. This suggests relatively recent oil input at this station and or a slow weathering rate (evaporation and dissolution) of spilled oil.

Table 3: Hydrocarbons concentrations in seawater at station 14 (C=5.80 mg/l)

Components	Results (%)
C15	7.81
C17	9.23
C18	10.91
C19	16.06
C20	20.89
C21	12.90
C22	11.57
C24	10.62
Odd	46
Even	54
Even/Odd	1.17

Table 4: Hydrocarbons concentrations in seawater at station 15 (C=24.2 mg/l)

Components	Results (%)
C8	5.99
C9	6.53
C10	5.69
C19	5.72
C20	8.34
C21	12.77
C22	13.10
C23	14.03
C25	11.57
C26	9.34
C27	6.93
Odd	57.54
Even	42.46
Even/Odd	0.73

Stations 17 and 18 (Table 6 and 7) are characterized by a profile typical to highly weathered crude oils. Their n-paraffin peaks are shown to be greatly affected by weathering processes (natural and biochemical weathering). The presence of both weathered and highly weathered profiles give an indication of continuous petroleum inputs. The calculated ratios for each study station are shown in Table 3 to 7. The ratios show that station 15 and 17 (Table 4 and Table 6) have a predominance of odd numbers alkanes (even/odd=0.73, 0.48 for station 15 and 17 respectively) which indicate some input of hydrocarbons from cultural sources, hydrocarbons formed by biological synthesis also constitute a minor but continuing contribution to the natural organic matter in the marine environment. The ratios show that, station 14, 16 and 18 was higher (0.99 to 1.17) which is indicate that there is petroleum hydrocarbons sources.

Table 5: Hydrocarbons concentrations in seawater at station 16 (C=9.7 mg/l)

Components	Results (%)
C17	2.86
C18	7.89
C19	11.76
C20	16.10
C21	15.35
C22	13.49
C23	9.80
C24	8.44
C25	5.63
C26	4.67
C27	1.85
C28	1.03
C29	0.56
C30	0.56
Odd	47.81
Even	52.19
Even/Odd	1.09

Table 6: Hydrocarbons concentrations in seawater at station17 (C=16.4 mg/l)

Components	Results (%)
C21	45.15
C22	10.14
C23	11.96
C24	11.60
C25	10.23
C26	10.92
Odd	67.34
Even	32.66
Even/Odd	0.48

Table 7: Hydrocarbons concentrations in seawater at station 18 (C=18.8 mg/l)

Components	Results (%)
C22	20.79
C23	24.42
C24	29.04
C25	25.75
Odd	50.17
Even	49.83
Even/Odd	0.99

Table 8 shows total hydrocarbons concentration in the study area compared to concentration found by several authors in other coastal water.

Table 8: Petroleum hydrocarbons concentrations in seawaters of comparable areas

Area	Concentration (mg/l)	Reference
Kuwait	2.1-3.6	El-Samra et al., 1986
Oman	1.3-28.9	Badawy et al., 1993
Saudi Arabia (Gulf Coast)	0.19-3.47	Ehrhardt and Burns., 1980
Arabian sea (Coast zone)	0.6-18.8	Gupta et al., 1980
English Channel	0.3-14	Fileman and Law, 1988
Saudi Arabia (Red sea coast)	1.8-17.9	Sultan and Turkey, 1997
Sudan (Red Sea coast)	6.8-219.2	Present study, 2006
BMT	5.8-24.2	"

Hydrocarbons concentration in sediment

In addition to the quantitative analysis of hydrocarbons in the seawater sediments analysis was done to evaluate the history of the oil in the studied area. Hydrocarbons present in sediments are generally believed to indicate the past influx of hydrocarbons into the overlying waters [7]. The adsorption of aliphatic hydrocarbons on suspended material could be taking place at different rates within the area investigated. This could lead to flocculation and incorporation of the material into the bottom sediments. Analysis of the bottom sediments for aliphatic hydrocarbons may reveal this phenomenon. The development of black layers in the sand, indicating that biodegradation had started [7]. Six sediment samples were taken from the total four strips, one from strip I, IV, two samples from each strip II, III. Results obtained are presented and shown as a histogram in the Figure 4.

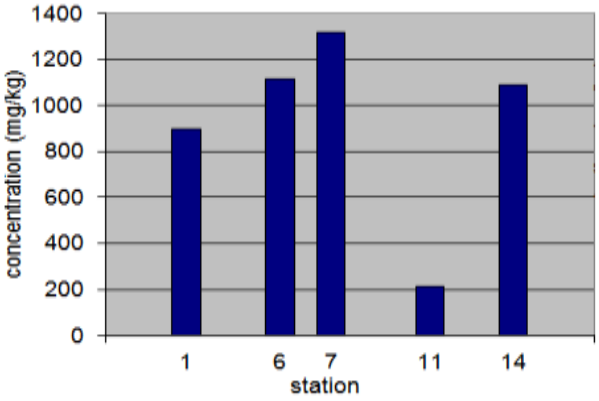


Figure 4: Hydrocarbons concentration in sediment

The values of hydrocarbons concentration in sediment in Portsudan harbor and BMT varies between 215 mg/kg at station 11(strip III) to 1320 mg/kg at station 7 (strip II). These higher values are considered to be toxic and have a negative impact to the surrounding marine environment. Eva8 defined significantly contaminate as concentration greater than 20 ug/g, this indicate that the south harbor of Portsudan is highly polluted. These higher values of hydrocarbons in sediment recorded at station 6 and 7 could be attributed to the fact that the south harbor (Gas chromatograms showed the existence of hydrocarbons components range from seven at station 6 to fourteen hydrocarbons components at station 11 (Table 9 to 13), n-paraffins ranging from (C-17) at station 7 and11 to (C-24) at station 6.

Table 9: Hydrocarbons concentrations in sediment at station 1 (C=900 mg/kg)

Components	Results (%)
C19	3.95
C24	72.24
C25	1.69
C26	3.55
C27	2.97
C28	1.93
C29	3.21
C30	2.49
C32	3.34
C33	1.61
C34	3.02
Odd	13.43
Even	86.57
Even/Odd	6.4

Table 10: Hydrocarbons concentrations in sediment at station 6 (C= 1115 mg/kg**)**

Components	Results (%)
C24	70.97
C25	2.37
C26	4.10
C28	5.94
C29	6.59
C30	2.81
C31	7.22
Odd	16.18
Even	83.82
Even/Odd	5.18

Table 11: Hydrocarbons concentrations in sediment at station 7 (C= =1320 mg/kg)

Components	Results (%)
C17	12.31
C18	14.89
C19	14.45
C20	13.68
C21	11.16
C22	9.29
C23	7.98
C24	6.14
C25	5.62
C26	4.47
Odd	51.52
Even	48.48
Even/Odd	0.94

Table 12: Hydrocarbons concentrations in sediment at station 11 (C=215 mg/kg)

Components	Results (%)
C17	9.00
C18	10.88
C19	10.68
C20	10.08
C21	8.41
C22	6.68
C23	5.66
C24	4.11
C25	3.79
C26	2.90
C27	5.79
C28	14.92
C29	3.12
C30	4.00
Odd	46.43
Even	53.57
Even/Odd	1.15

Table 13: Hydrocarbons concentrations in sediment at station 14 (**C=1090 mg/kg)**

Components	Results (%)
C18	13.94
C19	3.22
C22	4.23
C24	45.52
C25	9.24
C26	4.72
C27	2.45
C28	3.84
C30	2.83
C31	2.78
C32	2.44
C33	2.54
C34	2.25
Odd	20.23
Even	79.77
Even/Odd	3.84

n-C24 is shown to be predominating peak in the gas chromatographic chromatograms for most of studied samples were n-C26 representing the lowest concentration.

The predominant of even numbers of carbon atoms in their molecules in these stations indicated that the source of the pollutant is hydrocarbons petroleum. Strip (II) is polluted by direct discharge of oil from loading and unloading and shipping activities.

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CONCLUSION

Surface Red Sea water and sediment analysis show that strip I could be classified as highly polluted with total petroleum hydrocarbons, the next to the highest value was recorded at strip IV. These higher values are considered to be toxic and have a negative impact on the surrounding marine environment according to UNEP and AIDMO standards. Strip III is free

from oil pollution. The bottom sediment of Port Sudan harbor and BMT are highly polluted. The GC measurements proved that hydrocarbons contaminations are due to biologic and petrogenic origin. Most oil samples belong to light and middle fractions, all samples have paraffins but in different percentages.

REFERENCES

[1] Clark R. B. (1992), "Maine Pollution" 3rd ed., Clarendon Press.

[2] UNEP, AIDMO, (2001), "United Nation Environment Program: The maximum limits for discharge of industrial pollutants in the water environment", PP. 6 - 10,

[3] Blumer, M. and Sass, J. (1972), "Indigenous and petroleum-derived hydrocarbonss in a polluted sediment", Mar. Pollut. Bull., Vol. 3, PP. 92-94.

[4] Han J., McCarthy E. D., Van Hoeven W., Calvin M. and Bradley W. H. (1968), "Organic geochemical studies, II. A preliminary report on the distribution of aliphatic hydrocarbonss in algae, in bacteria, and in a recent lake sediment" Proc. N. A. S., Vol. 59, PP. 29-34.

[5] Elnagar A. W. (1999), "Hydrocarbons evaluation of new, used and refined marine oil, 3rd international conference on petroleum and environment", PP. 109-122.

[6] Giger W., Reinhard. M., Schafner C. and Stumm., W. (1974), "Petroleum-derived and indigenous hydrocarbons in recent sediments of Lake Zug", Switzerland. Env. Sci. Tech., Tech., Vol. 10, PP. 454-455.

[7] Mooly F. Spooner. (1977), "Oil spill in Hong Kong", Marine Pollution Bulletin, Vol.8(3), PP. 62-65.

[8] Eva J. Hoffma and James G. Quinn (1979), "Gas chromatographic analyses of Argo Merchant oil and sediment hydrocarbonss at the wreck site", marine pollution bulletin, Vol. 10, PP. 20-24, program press ltd.