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HYDROCARBON LEVELS IN TASAUL LAKE

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ABSTRACT

The paper presents data regarding the level of hydrocarbons collected in 2005 - 2007 from different sites round Tasaul Lake in monitoring system for water samples and also sediments in a station established in the middle of the lake.

The level of hydrocarbons in Tasaul Lake is influenced probably by diffuse pollution, mainly by air and also from the lake affluents, which use to carry discharges from domestic and industrial areas, roads and garage (cars, agriculture machines oil and combustible). In water, concentrations are higher than in sediments, where traces are met only on surface, as results of a recent influence.

KEY-WORDS: hydrocarbons, water, sediment, sources

AIMS AND BACKGROUND

On the water surface the hydrocarbons cause some physical, biological and social consequences. Propagated on the water surface, the petroleum pollutant has a specific physical-chemical evolution, varying with its nature and aquatic conditions. On dispersal, emulsifying and dissolving, the hydrocarbons alterate the quality of the aquatic environment by water pollution, concentrating in sediments, accumulating in organisms.

Crude oils are complex mixtures which vary widely in composition. However, they can be divided into three broad groups of compounds which help the responder assess the initial impacts and fate of the oil.

We use compositional data on crude oils to characterize them as to the amounts of each group present in the oil, and thus predict the behavior of the oil and the risk the oil poses to natural resources of concern.

1) Light-weight components are characterized, by:



- Hydrocarbon compounds containing up to ten carbon atoms;
- A boiling range up to 150°C;
- Rapid and complete evaporation, usually within a day;
- High water solubility; usually contributes >95% of water-soluble fraction;
- High acute toxicity because they contain the monoaromatic hydrocarbons (benzene, toluene, xylene) which are soluble and toxic;
- No potential for bioaccumulation (they evaporate instead);
- Mostly composed of alkanes and cycloalkanes which have relatively low solubility (and thus low acute toxicity potential)

2) Medium-weight components are characterized, by:

- Hydrocarbon compounds containing between 10 and 22 carbon atoms;
- A boiling range from about 150 to 400°;
- Evaporation rates of up to several days, although there will be some residue which does not evaporate at ambient temperatures;
- Low water-soluble fraction (at most a few mg/l);
- Moderate acute toxicity because they contain diaromatic hydrocarbons (naphthalenes) which are toxic in spite of their low solubilities;
- Moderate potential for bioaccumulation and chronic toxicities associated with the diaromatic hydrocarbons;
- Alkanes which are readily degraded.

These medium-weight components pose the greatest environmental risks to organisms because the compounds are more persistent, they are biologically available, and the PAHs have high toxicities.

3) The heavy-weight components are characterized by:

- Hydrocarbon compounds containing more than 20 carbon atoms;
- Almost no loss by evaporation;
- Almost no water-soluble fraction;
- Potential for bioaccumulation, via sorption onto sediments, otherwise not highly bioavailable;
- Potential for chronic toxicity, because they contain polynuclear aromatic hydrocarbons (phenanthrene, anthracene etc.)
- Most of the components are waxes, asphaltenes, and polar compounds which do not have any significant bioavailabilites or toxicities;
- Long-term persistence in sediments, as tar balls, or asphalt pavements.

These heavier components pose little acute toxicity risks, except that due to smothering, because of the very low solubilities of the individual compounds.

Animals have to be exposed via a sediment pathway or through the food chain. However, these are the most persistent components of an oil, and degradation rates will be very slow.

Weathering processes at oil spills as applied to resources at risk, oil persistence

Evaporation is the single most important weathering process in the first several days of an oil spill. Environmental factors which affect the rate of evaporation are:

- Area of slick exposed, which changes rapidly,
- Wind speed and water surface roughness,
- Air temperature and solar radiation,
- Formation of emulsions.

For light, refined products such as gasoline, evaporation will remove 100% of the spill within a very short time. For heavy refined products, evaporation will only remove 5-10% of the spill. For crude oils, the amount of the spill lost to evaporation can range from 20 to 60%. For spills of medium crude oils, a rule of thumb is that 20-30 percent of the oil is lost to evaporation within the first 24 hours.

Dissolution of petroleum hydrocarbons into the water column poses risks to aquatic organisms because of the acute toxicity of the compounds that have significant water solubility.

Factors affecting oil impacts on biota

Toxicity is defined as “the inherent potential or capacity of a material to cause adverse effects in a living organism” (Rand and Petrocelli 1985).

Concentration, duration of exposure, and sensitivity of the receptor organism will all determine the toxic effect. Sensitivity to toxic compounds varies greatly by species, by life stage within a particular species, and by individual.

Oil impacts between species groups vary. Though individual exceptions undoubtedly exist, a broad categorization can be made for the anticipated degree of impact as follows (NAS 1985):

- Little to no long-term effects: annelids, gastropods, copepods
- Some effects: macrophytes, barnacles
- Long-term effects: bivalves, decapod crustacea

Within one species, individual characteristics will also determine the degree of impact, including age, sex and contamination history.

Acute toxicity refers to immediate impacts that result in death of the organism. Acute toxicity will be dependent on the toxic properties of the oil (a combination of the oil type and weathering), and the concentration and dose that the organism receives.

Some toxic effects may not be evident immediately, or may not cause the death of the organism. These are called chronic, or sublethal effects, and they can impact an organisms' physiology, behavior, or reproductive capability. Chronic effects may ultimately impact the survival rates of species affected. Chronic effects are harder to detect than acute effects and may require more intensive studies conducted over a longer period of time. Many chronic effects result from stress responses in the physiology of an organism, such as increased metabolism, increased consumption of oxygen, and reduced respiration rate. These can be short term responses, but over extended periods of time, may cause other impacts to the organism. A common chronic response is reduced growth rates, for example in benthic organisms that live in chronically oiled sediments.

Bioaccumulation can be defined as the uptake of a contaminant by an organism from water directly or through consumption of contaminated food. Organisms that live in a contaminated environment, for example, mussels in oiled sediments, may appear to be healthy but still contain elevated levels of petroleum compounds in their tissue. Some components of oil can be bioaccumulated by aquatic organisms, particularly the group of longer lasting compounds known as polycyclic aromatic hydrocarbons (PAH).

MATERIALS AND METHODS

Sampling and analyses

The prelevation strategy of the abiotic samples for pollutants content determination has taken into account the following:

- the main hydrological and meteorological characteristics of the studied area;
- the spreading area of the pollutant load.

In order to analyse the total hydrocarbons content from the water samples collected from the eight stations settled on Tasaul Lake (1-8), the extraction of pollutant in acid medium with hexane/diclorometane mixture 3/1 was made.

For analysing the total hydrocarbons content from the sediment samples collected from the eight stations settled on Tasaul Lake, the extraction of pollutant in ultrasonic bath with hexane/diclorometan mixture 3/1 from the determined quantity of dry sediment was made.

The dry extracts on anhydrous Na_2SO_4 were analyzed spectrophotometrically in UV, 230-270 nm, using a HEWLETT PACKARD 834 apparatus.

The calibration was made with crude oil type *Danube Reference Oil*.

The banalization of PAHs from the sediments was made through the extraction of pollutant in of ultrasonic bath with hexane/diclorometane mixture 3/1, from a determined quantity of dry sediment. The extract, after the concentration, treatment with copper for removing the compounds with sulphur, separation on column with alumina, silicagel and anhydrous Na_2SO_4 was Gas-chromatographically analyzed with a HEWLETT PACKARD and mass Spectrometer detector.

RESULTS AND DISCUSSIONS

The investigations carried-out in 2005 concerning oil contaminant levels in water and surface sediments from the Tasaul have identified pollutants such as petroleum hydrocarbons and polyaromatic hydrocarbons.

The total hydrocarbon content analysis in water samples indicated the presence of petroleum pollutant in all investigated samples, in concentrations between 72.4 - 1305 $\mu\text{g/l}$ in waters and within the limits of 373.2 - 5355.9 $\mu\text{g/g dw}$ in surface sediments. (Fig. 1.).

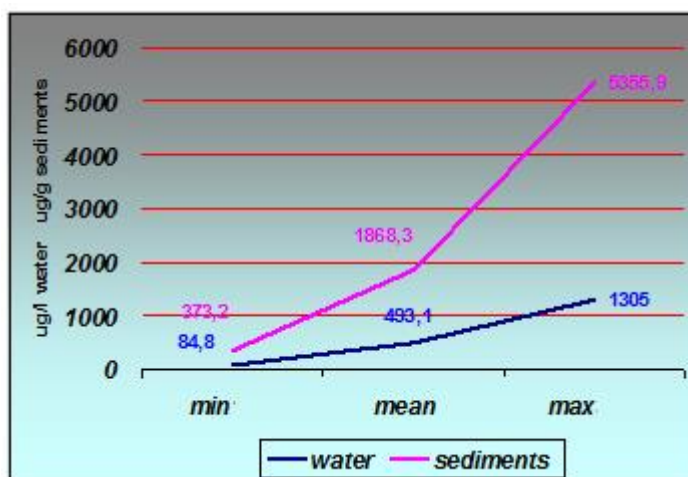


Fig. 1. Total petroleum hydrocarbon in abiotic samples collected in May-Nov. 2005

In conformity with literature data (M. Marchand and M.C. Caprais), there were assessed more levels regarding the pollution degree of surface waters based on the concentrations of detected hydrocarbons.

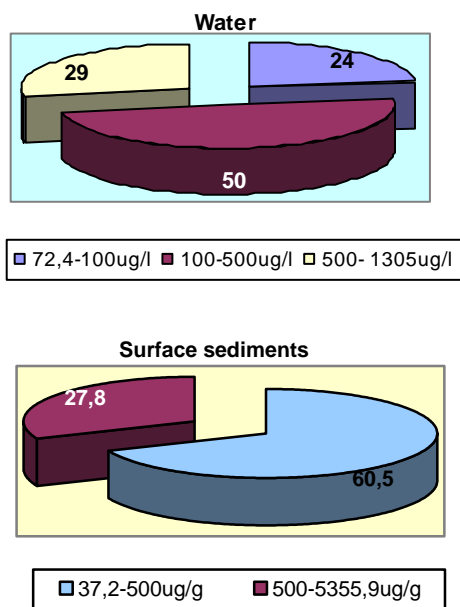


Fig. 2. Percentage distribution of hydrocarbon concentration in abiotic samples collected from Tasaul in 2005

Table 1. Assessment of hydrocarbon pollution levels depending on the level and frequency of concentrations

Level of pollution	Hydrocarbon concentration mg/l	Frequency of detection in the concentration zone
Lack of pollution	0.001	10
Slight pollution	0.002	up to 25
Hydrocarbon pollution	0.002	75
Hydrocarbon pollution	0.005	45
Significant pollution	0.010	35
Significant pollution	0.05	5
Significant pollution	0.100	2

In 2005, the mean value with total hydrocarbons content of Tasaul Lake was 381.2 $\mu\text{g./l.}$ In August, the highest level of loading was noted, the mean value being 813.03 $\mu\text{g/ l,}$ 4.9 higher comparatively with May and 5.1 higher than in November. The level of concentrations and frequency of 79.1% of concentrations higher than 100 $\mu\text{g/l}$ determined in the waters mean that there is a chronic pollution with hydrocarbons in this area (Fig. 2).

The spatial distribution of the concentrations identified all long investigation period showed a specific aspect of evolution of hydrocarbons pollution for each of the studied zones, depending on the dominance of meteorological, hydrological and anthropogenic factors (Fig. 3).

The quality of waters from Tasaul Lake is influenced by the vicinity of Petrochemical Plant from Midia, as well as a high diversity of activities developed on lakesides, urban and rural settlements, animal and fish farms, and mining exploitation.

As a consequence of significant loading with hydrocarbons of waters is the accumulation of pollutants in the superficial sediments (Fig. 4). In May 2005, the mean content of total hydrocarbons determined in sediments was 2126.4 $\mu\text{g/g dw.}$

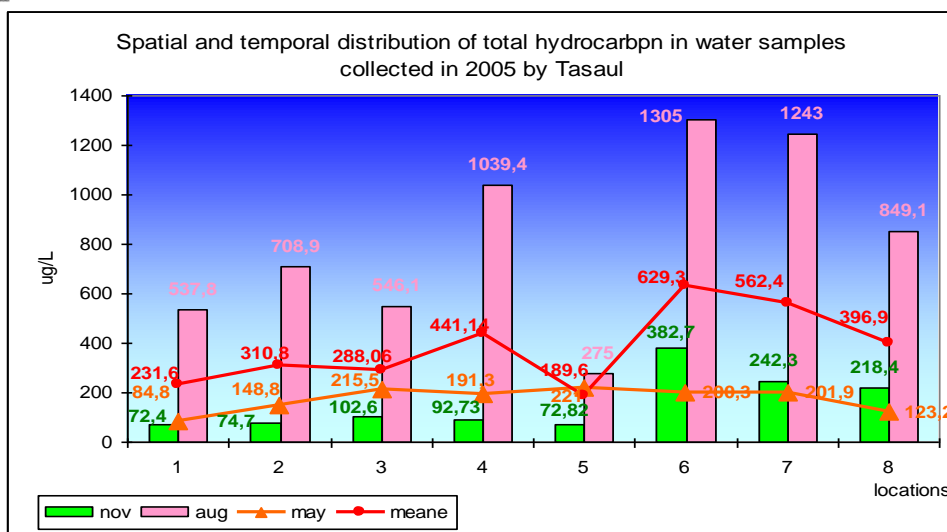


Fig. 3 Spatial and temporal distribution of total hydrocarbons in water samples collected in 2005 from Tasaul

The frequency of 100% of concentrations higher than 100 $\mu\text{g/g dw}$ in sediments showed a very intense process of concentration of mineral oil pollutant in substrata (Fig. 2).

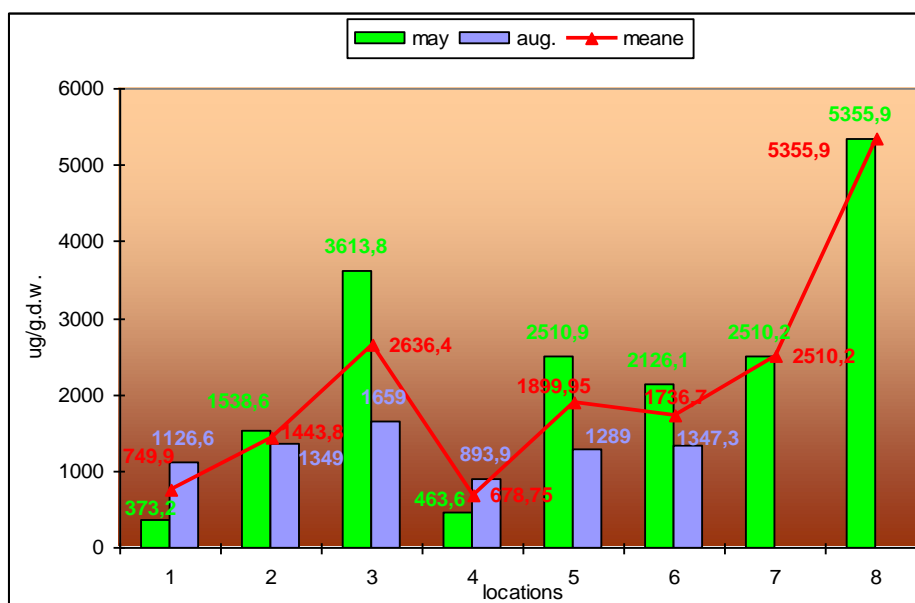


Fig. 4. Spatial and temporal distribution of total hydrocarbons in sediment samples collected in 2005 from Tasaul

The polyaromatic hydrocarbons are compounds of a large scale of contaminants, which are differentiated through the number of benzenic nuclei, their position in the molecular structure and through the nature and position of substitutes in the molecule.

The PAHs analysis from the sediments collected in 2005 indicated the presence of these pollutants in all the samples, the concentrations being comprised among 24 and 1,098 ng/g dw. (Table 2, Fig. 5).

Table 2. PAHs concentrations determined in sediment samples collected in May 2005 from Tasaul (ng/ g dw)

	Tasaul 1	Tasaul 2	Tasaul 3	Tasaul 4	Tasaul 5	Tasaul 6	Tasaul 7	Tasaul 8
Naphthalene	1	121					13	
Acenaphthylene	8		115	18	25	4	44	27
Acenaphthene	2			17	21	2	19	1
Fluorene		250		65	64	25	64	3
Phenanthrene		21	117	23	4	15	32	2
Anthracene		22	122	124	36	4	33	2
Fluoranthene	13		2					1
Pyrene				1		1		
Benzo[a]anthracene		37	37	46	15	21	16	39
Crysene		28	28	35	11	16	12	29
Benzo[k]fluoranthene		2	30	13	1	2	3	2
Benzo[a]pyrene		12	9	306	4	19	12	43
Benzo[ghi]perylene		310	276	213	210	289	588	539
Dibenzo[a,h]anthracene		136		27	93	126	261	231
Indeno[1,2,3-c,d]pyrene		1	1	1	2	2	1	

The sediments collected in May 2005 contained 4 (station 1) up to 13 (stations 4, 6 and 7) PAH compounds.

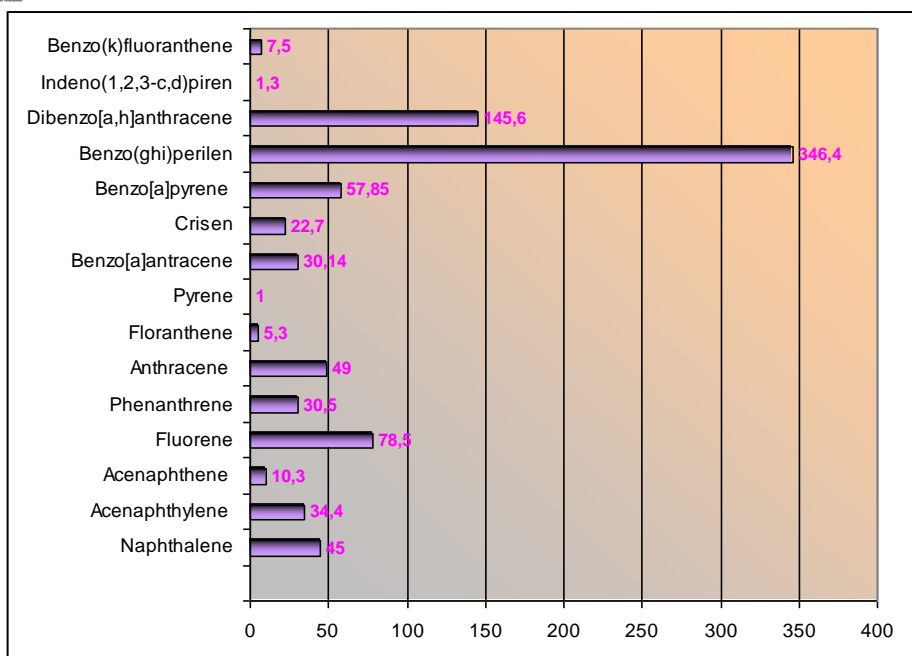


Fig. 5. The mean values of PAH compounds determined in sediments collected in May 2005 (ng/g dw)

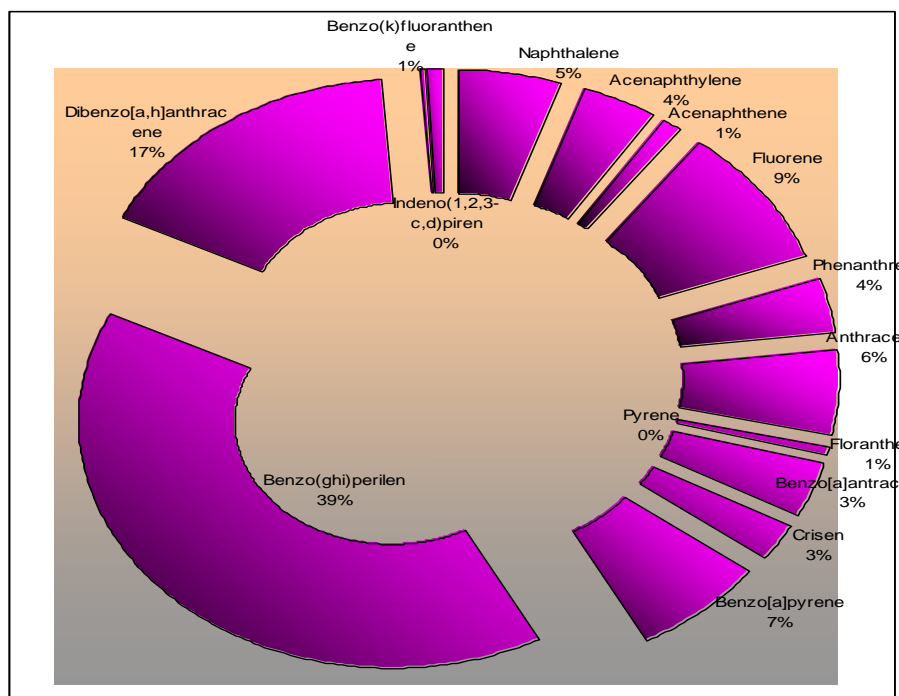


Fig. 6. Percentage composition of mean loading of PAHs Determined in sediments collected in May 2005

The analyses of sediments collected in May 2005 indicated the increased values of PAH compounds with big number of condensed benzene nuclei: benzo (g,h,i) - perylene 39%, dibenzo[a,h]anthracene 17%, benzo-a-pyrene 7%, fluorene 9%, anthracene 6%. These compounds are characterized by increased remanence and toxicity, being included in the List with priority dangerous chemicals, Annex 1 of *Action Programme for reducing the pollution of aquatic environment and underground waters caused by the hazardous substances*, approved through GD No. 118/2006 (Fig. 6).

The spatial distribution of PAH concentration shows different concentrations among the studied locations. Station 1 registered the lowest level of contamination of sediments with hydrocarbons, in May, namely 24 ng/g dw, values 33 times lower then the mean value (Fig. 7).

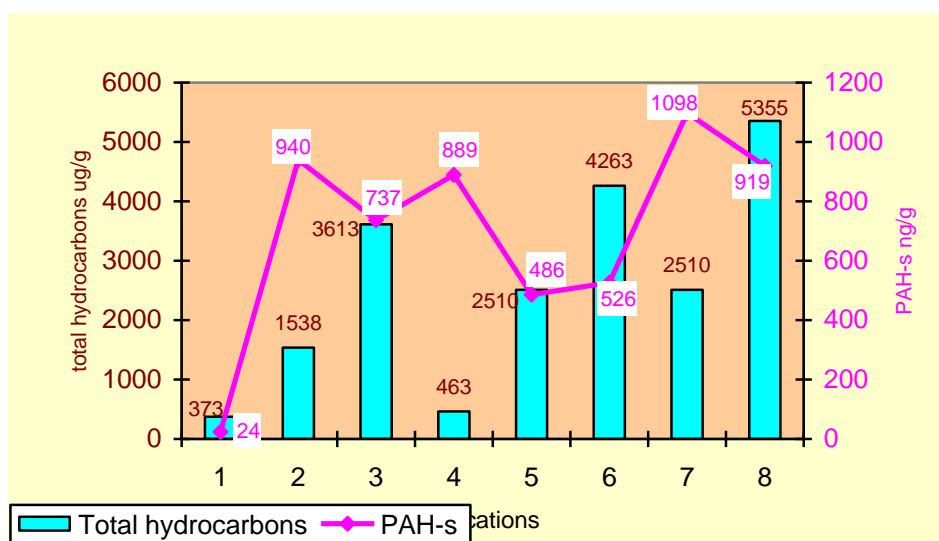


Fig. 7. Spatial distribution of total hydrocarbons and PAH concentrations in sediments samples collected in May 2005

Analyses of core-boxes collected in September 2005 from the stations 3 and 6 evolved an intensification of accumulation process of mineral oil pollutants in the sediments (Fig.no. 8, 9, 10).

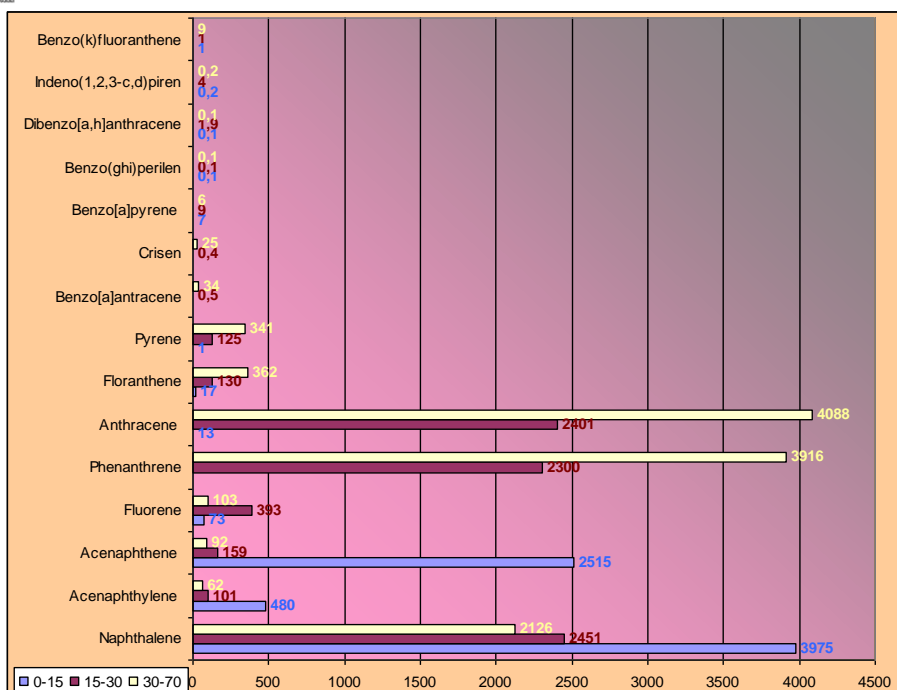


Fig. 8. PAHs in sediment samples collected in September 2005 from Tasaul 3 location (ng/g dw)

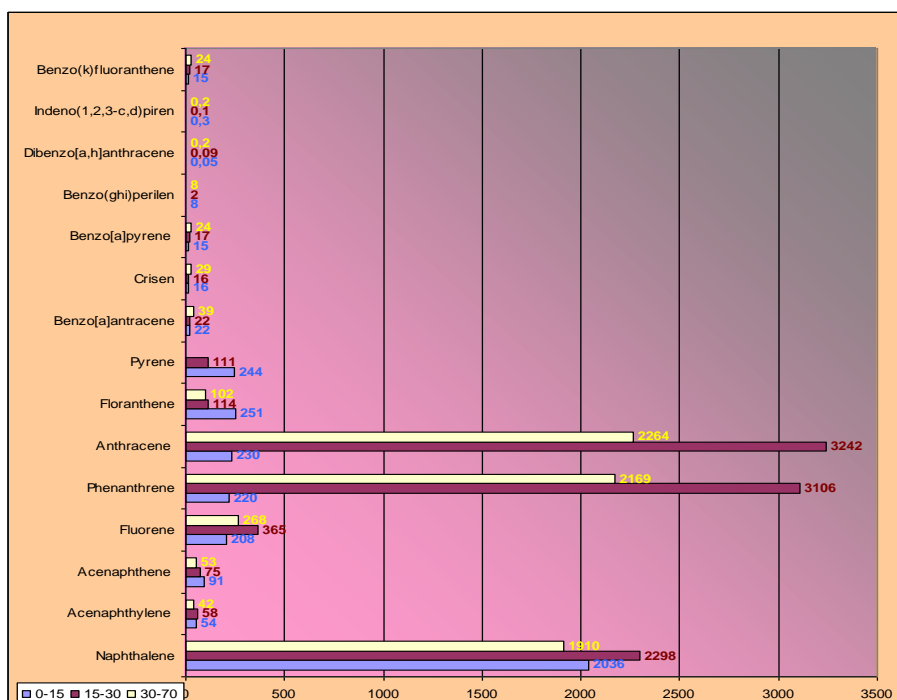


Fig. 9. PAHs in sediment samples collected in September 2005 from Tasaul 6 location (ng/g dw)

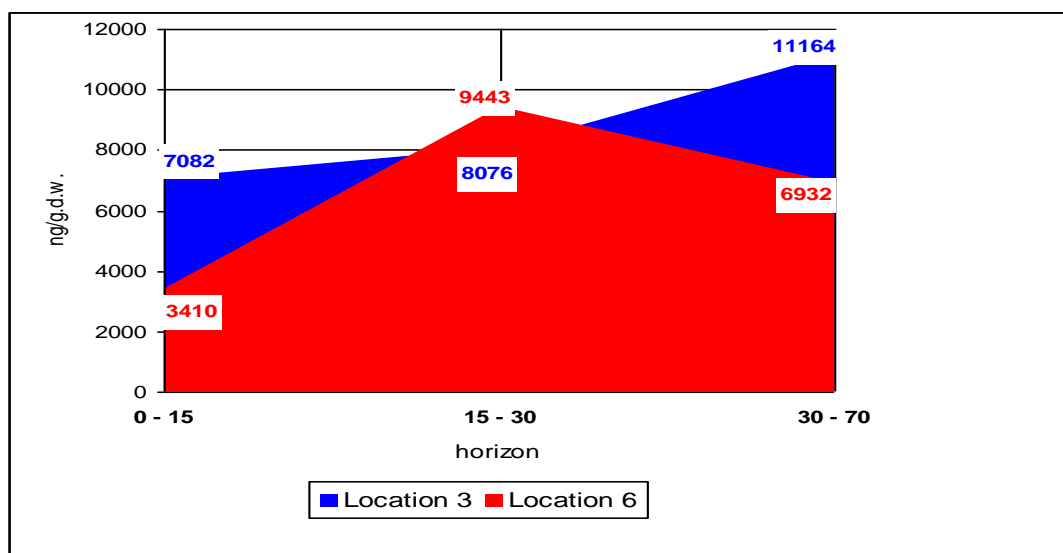


Fig. 10. Concentration distribution of the total PAH load in sediments by different horizons of locations 3 and 6 in September 2005

The results of analyses of PAH content of the core-boxes collected in stations 3 and 6 demonstrated the intensity of accumulation and transformation processes of mineral oil pollutants in the sediments. The upper layer (0-15 cm) had the lowest content of PAHs, diminished 1.5 times in station 3, and 2.6 times in station 6 comparatively with the PAHs loading from the 30-70 cm layer.

CONCLUSIONS

During May-November 2005, in the abiotic elements of the Tasaul Lake ecosystem there were identified pollutants of mineral oil origin, assessed at a mean level of 381.2 $\mu\text{g/l}$ in water and 2126.4 $\mu\text{g/l}$ in superficial sediments.

The frequency of 79.1% of concentrations higher than 100 $\mu\text{g/l}$ total hydrocarbons in water indicated the settlement of a chronic pollution with hydrocarbons in this zone.

All the samples analysed in 2005 contained polyaromatic hydrocarbons, the mean content being 702.3 ng/g dw in superficial sediments.

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REFERENCES

1. Chen Z., Huang G. H., Chakma A., 1998 , Integrated environmental risk assessment for petroleum-contaminated sites - a North American case study, Wat. Sci. Tech., 38, 131-138;
 2. Nadim F., Hoag G.E., Liu S., Carley R.J., Zack P., 2000, Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview, Journal of Petroleum Science and Engineering 26, 169 -178;
 3. Pecheanu, I., Oros A., Piescu V., Stoica E., Dumitrache C., Coatu, V., 2002, Taux des substances nuisibles pour le milieu marin dans les zones de dépôt des sédiments dragués du port Constanta, Cercetari Marine, vol. 34, pp.183-196, ISSN: 0250-3069;
 4. Piescu V., Coatu V., Oros A., Patrascu V., Pecheanu I., 2004, Assessment of dangerous substances level off the Danube mouth, Cercetari Marine, Vol.35,pp.39-59,ISSN:0250-3069;
 5. Victoria Piescu, Valentina Coatu, Andra Oros, V. Patrascu, I. Pecheanu, 2004, Assessment of dangerous substances level off the Danube mouths, Cercetari Marine, I.N.C.D.M., Nr. 35, pg. 39-59;
 6. Piescu Victoria, Coatu Valentina, 2004, Nivelul contaminantilor derivati de hidrocarburi in zona marina de exploatare petroliera, Sesiunea stiintifica MENER noiembrie 2004, Bucuresti, Romania, Volumul de lucrari al Sesiunii, A 38-A 46;
 7. Victoria Piescu, Andra Oros, Valentina Coatu, Ioan Pecheanu, 2005, *Levels of some dangerous substances in the marine environment in front the danube mouths between 1996-2004*;
http://www.researchgate.net/publication/242283160_LEVELS_OF_SOME_DANGEROUS_SUBSTANCES_IN_THE_MARINE_ENVIRONMENT_IN_FRONT_THE_DANUBE_MOUTHS_BETWEEN_1996-2004;
 8. Stoica, E., Cociasu, A., Coatu, V., Oros A., Piescu, V., 2004, Present state of the Romanian Black Sea bathing waters quality, Cercetari Marine, vol. 35, pp.109, -121, ISSN: 0250-3069;
 9. Stoica, E., Piescu, V., Coatu, V., Oros, A., 2003, The impact of land-based sources of pollution on the Romanian coastal waters quality (Black Sea), Proceedings of The International Conference on Energy and Environment (CIEM), October 2003, Romanian Academy, Bucharest, Vol. 2, pp.455-460, ISBN: 973-27-1032-2;
 10. Stoica E., Piescu, V., Coatu, V., Oros, A., 2003, Impactul surselor de poluare de pe uscat asupra calitatii apelor costiere romanesti (Marea Neagra), Conferinta internationala ENERGIE MEDIU (CIEM), 29-31 octombrie 2003, Bucuresti, Lucrarile Conferintei, volumul II, 55-60;
 11. Weaver J.W., Charbeneau R.J., Tauxe J.D., Lien B. K., Provost J. B., 1995, The Hydrocarbon Spill Screening Model -HSSM, EPA, EPA/600/R-94/039a.US EPA;
- ***Directive 96/82/EC on the control of major accident hazards involving dangerous substances, 1997, Official Journal of the European Union, No L0/13;
- ***Directive 2003/105/EC am ending Council Directive 96/82/EC on the control of major - accident hazards involving dangerous substances, 2003, Official Journal of the European Union, No L345/973.