BIOGENIC STUDIES OF POLICYCLIC CARBONS DISCHARGE FROM THE AMUR RIVER INTO THE FAR EASTERN SEAS

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INTRODUCTION

The Amur River discharges into the Far Eastern seas various chemical elements and organic substances. It is rather difficult to assess the impact that each biochemical component produces on the marine ecosystems. It is also hard to determine priority factors that regulate interrelations between production and destruction processes. Productivity of the Far Eastern seas depends on many abiotic and biotic factors and among them toxic substances, which impact is of noticeable importance for the development of primary producers (phytoplankton), energy transport though the trophic chains and for mechanisms of different-genesis organic substance destruction with the microbial complexes participation.

The priority task of the Amur-Okhotsk Project is to reveal factors that regulated the Okhotsk Sea productivity. An important focus is given to biogeochemical transport from terrestrial ecosystems to the Amur River and further on from the Amur to the Okhotsk Sea (Narita, Shiraiwa and Nakatsuka, 2004).

The guiding scientific concept is based on revealing regularities of iron ion impact on marine ecosystem productivity, including studies of biogeochemistry of iron in seawater and the role of riverine input from the Amur River to the estuarine mixing systems and coastal waters in the Okhotsk Sea. Special focus is given to the river discharge of suspanded substances, which also include humic substances, i.e. stable organic substances of natural origin. Iron can dissolve as the complexes with humic substances and the suspended particles (Kuma, 2004; Terashima, Nagao, 2007). Suspended matter may also include other stable organic compounds.

There are many factors of the Amur River pollution with stable organic substances, including chlorine-containing pesticides, biphenyls and polycyclic aromatic hydrocarbons (Kondratjeva, 2005). The most significant factors are the transboundary pollution of the Amur from the neighboring Chinese territory, emission from electric power facilities and vehicles, forest fires and the Bureya dam, being filled in at present (Kondratjeva et al., 2007). Studies of water ecosystem pollution with polycyclic aromatic hydrocarbons (PAHs) are of great importance as these substances are highly toxic for organisms of all organization levels, can fully accumulate in hydrobionts and transport through the trophic chains.

SOURCES OF PAH PENETRATION INTO ECOSYSTEMS

At present PAH contaminate all biosphere components. They penetrate to the atmosphere with industrial wastes, exhausts of vehicles, emissions of power plants and forest fire smoke. Sources of PAH in water ecosystems are atmospheric precipitation, surface water runoff, and waste water discharge from oil refineries. Being transferred through the atmosphere PAHs contaminate soils, ground and surface waters. In spring a volley discharge of PAH accumulated in winter is formed due to snow and river ice melting.

Anthropogenic PAH are mostly the products of organic matter pyrolysis, including oil, coal, peat, shale, etc. Hundreds of cancerous and mutagenic active compounds are identified among anthropogenic PAH and their analogs. Indicators of industrial pollution are pyrene, fluoranthene, 1,12-benzperylene, 3,4-benzfluoranthene и 2,3-o-phenylenepyrene. 1,12-benzperylene prevails in internal combustion engine emissions.

Intensity of PAH transfer and their stability depends on the time of the year. In winter when much coal, wood and hydrocarbons are burnt such PAH as chrysene, benzperylene, benzfluoranthenes and anthracene are transferred through atmosphere and contaminate the snow cover. In summer phynanthrene, fluoranthene, pyrene, chrysene and benzperylene, present in rain waters, can be transferred with the surface runoff into water ecosystems, contaminate soils and be absorbed by plants (Rovinsky et al., 1988).

In bound state PAH can be transferred for long distances and distributed far from their sources of origin. During fires**,** when lots of smoke is produced and photochemical oxidation is reduced, the degree of ecological risks of PAH transfer to other regions and sedimentation on soil and water surface increases. Although carcinogenicity of PAH has not been proved for all these substances, it is known that all of them tend to accumulate in different organisms and are highly toxic. Moreover, PAH mixtures with other substances may increase toxicity of water media.

The World Health Organization (WHO) proposed 16 priority substances to assess ecological risks of PAH pollution, such as naphthalene, acenaphthalene, acenaphthene, anthracene, fluorene, phynanthrene, fluoranthene, pyrene, chrysene, tetraphene, 3,4-benzfluoranthene, 11,12- benzfluoranthene, 3,4-benzpyrene, 1,12- benzperylene, 2,3-o-phenylenepyrene, 1,2,5,6-dibenzanthracene. Due to WHO's recommendations PAH concentrations in drinking water should not exceed 0.2 mg/l (Maistrenko et al., 1996). There are no recommendations on total PAH content in fishing waters due to the possibility of their accumulation in various organs and tissue of hydrobionts. Some PAH substances cause endocrine system diseases, reproduction function disorders, pregnancy complications, spontaneous abortions, infantile mortality, new-born children pathology (abnormalities and genetic changes), mental retardation and children development anomalies. Adolescents under PAH impact can develop disorders of organs of sense, bone and muscular system, immune and hormone status and other functions.

STUDIES OF THE AMUR RIVER POLLUTION WITH PAH

Studies of PAH content assessment in Amur water lower Khabarovsk city were conducted in 2002 under the interdisciplinary project "Ecological crisis on the Amur and health conditions of indigenous peoples of the North" sponsored by a charity organization «Landesverband der Inneren Mission E.V.» (Munster, Germany) (Kondratjeva, 2005). Up to present difference nature conservation services and the Far Eastern Nature Resource Department did not monitor stable toxic substances in the surface waters of the Amur. The analysis of the seasonal pollution of the Amur River with PAH showed that in summer in the certain river passages lower Khabarovsk the total PAH content in water 10 times exceed their winter values.

In summer forest fires contribute much to the Amur pollution with stable organic substances. In 2002 research of natural water pollution with PAH was carried out based on highly efficient liquid chromatography following international standards (EPA 625). The analysis of seasonal contamination of the Amur River with persistent polyaromatic hydrocarbons revealed that in summer, at some sites of the River lower Khabarovsk, their overall concentration was 10 times greater than in winter.

All water samples collected in 2004 in the Amur from the Sungari juncture to Nickolaevsk-on-Amur revealed benz(b)fluoranthene. In fact, this hydrocarbon did not decompose and is discharged from the river to the Amur liman (Tab. 1).

Table 1. PAH Qualitative Composition in Water Samples, Selected in the Amur River and the Amur Liman in Summer 2004.

Sampling Sites	Dominating Compounds
1.Middle Amur (mouths rivers Zeya, Bureya, Sungari)	Benz(a)anthracene Benz(b)fluoranthene Chrysene
2. Lower Amur (from Khabarovsk to Nickolaevsk-on-Amur)	Naphthalene Anthracene Fluorene Phynanthrene Benz(b)fluoranthene
3. Amur liman (in the direction of the Okhotsk sea)	Naphthalene Phynanthrene Fluorene Benz(b)fluoranthene Benz(g,h,i) perylene
4. Amur liman (in the direction of the sea of Japan)	Anthracene Dibenz(a,h)anthracene Phynanthrene

As shown in Table 1 maximal PAH diversity occurs in summer time and most of them are discharged with the river runoff in the Okhotsk Sea direction. In river freezing time ¾ of the river runoff is directed to the Sea of Japan. At low temperatures the rate of stable organic matter transportation and destruction reduces. Thus is seems most important to study spatial distribution of PAH in the Amur Liman in winter and assess ecological risks of PAH transport into the Sea of Japan with the Amur runoff.

In August 2005 more detailed studies of Amur pollution with PAH were undertaken in the Amur tributary junctions from Blagoveschensk to Khabarovsk (Kondratjeva et al., 2007). Various combinations of PAH were identified in water samples collected at different hydrological stations. Most changes in PAH content were revealed in the transboundary river passages. For example, at the Sungari juncture anthracene and pyrene with concentrations of 0.014 ng/l prevailed at the left bank, which belongs to Russia, in the middle of the river they were lower the detection limit, where as at the left bank, which belongs to China (Heihe city), phenanthrene (0.032 ng/l) and anthracene (0.021 ng/l) were identified.

Even higher phenanthrene and anthracene concentrations were found in surface and bottom water layers at the Bureya juncture. There are lots of PAH potential sources in the Upper Bureya region, such as coal mines, coal combustion for power, swampy areas, flooding soils and forest vegetation to form Bureya dam. Our studies showed that phenanthrene and anthracene prevail in the Bureya mouth. They are supposed to originate from the water drainage area including the Bureya dam. Sunken wood also contributed to PAH migration into the water media. Less PAHs were carried with Zeya waters. Lower the Amurzet check point down the Amur River water samples revealed the dominance of anthracene.

TRANSBOUNDARY POLLUTION WITH PAH

Our studies showed that the Amur tributaries discharge different combinations of PAH (Kondratjeva et al., 2007**)**. Thus, the Sungari discharged benz(b)fluoranthene in the highest amount (Fig. 1). Benz(b)fluoranthene mostly originates from petroleum and coal combustion, diesel and benzene engines work. It is known that oil refinery process results in production of phenanthrene, fluoranthene and benzene derivatives.

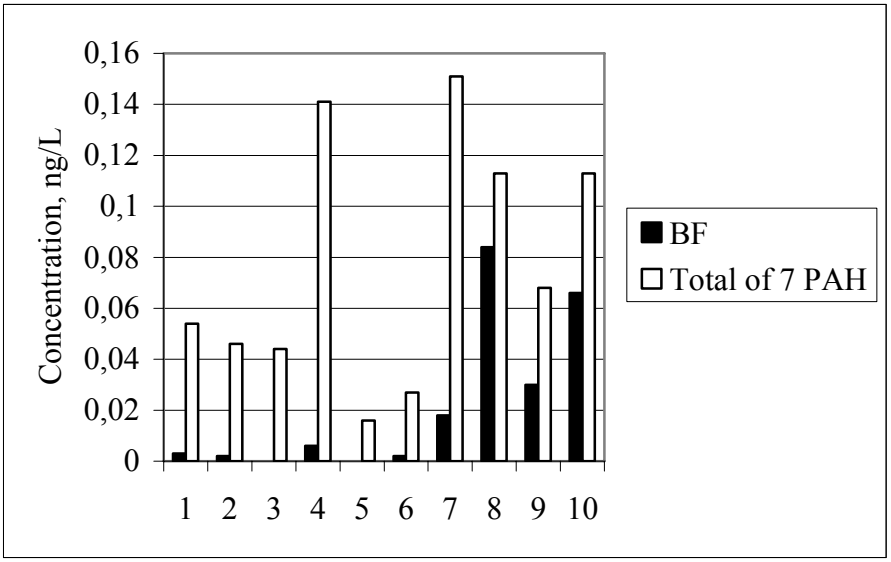

Fig. 1. Benz(b)fluoranthene (BF) content and the total content of 7 PAH components in surface water of different Amur river passages: 1- 2 km upper Blagoveschenck city, 2 – Zeya mouth, 3 - 1 km upper the Bureya juncture, 4 - the Bureya juncture, 5 – Amurzet check point, 6, 7, 8 - 4 km lower the Sungari juncture (left bank, middle, right bank), 9, 10 - 5 km upper Khabarovsk (middle, right bank).

PAHs were not revealed at the control stations (Amurzet). In the upper river passages it was found in micro admixtures. Most differences were found in samples, collected 4 km lower the Sungari juncture at the left (Russian) and right (Chinese) banks.

Additional data on the transboundary pollution of the Amur with PAH were collected after the technogenic accident at the oil refinery in China (Jilin city) in November 2005. The accident aftereffect analysis showed that the river water flow, contaminated with nitrobenzene, accelerated PAH concentrations. It happened due to PAH capacity to dissolve in water. In fact, this accident in China had a lot of inherent ecological aftereffect to be revealed in the long future and cause an unpredictable impact on the Sungari and Amur ecosystems. In this respect seasonal fluctuations of maximal ecological risks should be noted. In winter benzene was identified in ice and a part of toxic elements sedimented at the river bottom.

In March 2006 the Russian-Chinese monitoring of the Sungari basin revealed pyrene. Fluoranthene was identified across the river section with maximum values at the bottom layers. Twenty kilometers upper the Sungari juncture only naphthalene was revealed in the surface waters. Marked high concentrations of naphthalene were found in bottom waters at the middle of the river near the city of Fuyan (16.1 microg/l). It may be explained with PAH destruction in the bottom sediment layers and their migration into the water mass.

Three months after the technogenic accident it was found that water, ice and bottom sediments in the Sungari River were contaminated with PAH. Total content of 14 PAH components in surface waters upper Harbin city was 0.109 microg/l. High PAH concentrations remained up to the Sungari lower reaches. Lower the Sungari juncture near Nizhneleninskoe phenanthrene, pyrene and benz(b)fluoranthene were identified. Ice, most polluted with different ingredients, was near Tsyamusi city close to the right bank of the river. This ice contained many clay particles and had a strong smell. In this ice the highest

concentration of total PAH (0. 348 microg /l) and maximal phenanthrene concentration (0. 131 microg /l) were observed. Components that were present in water during the nitrobenzene spill participated in the chemical composition of this ice. High concentrations (microg /kg) of such PAH as pyrene (31,4), perylene (26,6), benz(e) pyrene (24,4), chrysene (13,6), naphthalene (8,6) were revealed in bottom sediments of the Sungari River. In the Amur bottom sediments collected in the zone of the Sungari impact PAH concentrations were even higher. For example, perylene concentration was 128 microg /kg and benz(b+j)fluoranthene concentrations was 112 microg /kg. Bottom sediments lower the Sungari juncture had a high capacity to accumulate many toxicants including PAH, phthalates and trace metal ions.

After river freezing the main amount of benzene and PAH passed into water media. Thus in May 2006 fluoranthene and pyrene dominated in Sungari waters in the passage Harbin – Tsyamusi – Tuntsyan. Total PAH in the Amur upper the Sungari juncture was 0.015 microg /l. Lower the Sungari juncture PAH content at the right river bank was 0.036 microg /l (surface waters) and 0.021 microg/l (bottom waters). Most soluble in water PAH are not carcinogenic, but when exposed to ultra-violet radiation they transform to compounds highly toxic for water organisms and water fowl. That is why the number of potential risk factors due to the technogenic accident increased in summer.

BIOGENIC STUDIES IN THE AMUR LIMAN

Complex quality assessment of water in the Amur liman was carried out in August 1997. Significant differences in water quality formation were found between discharge directions into the Okhotsk Sea and the Sea of Japan. The major portion of organic matter of different origin and maximum phenol compounds content were identified in the main stream opposite the Orimif Island. Organic matter, difficult to mineralize, was found discharged more into the Okhotsk Sea than to the Sea of Japan. Higher content of labile forms of phenol compounds (0.009 mg/l) was also evident. Bioindication did not reveal labile nitrogen-containing organic matter in the water samples. Near the Pronge village (Sea of Japan direction) hydrobiologic water quality parameters were much better. In fresh and seawater mixing zone at the Sakhalin traverse water quality improves as compared to the Orimif Island area. Nevertheless, labile and persistent organic substances are registered. These though preliminary data allow concluding that in summer time River discharge cause active processes of organic matter production and destruction in the shallow Amur River liman. The main portion of persistent components is carried out in the Okhotsk Sea direction. A much lower self-purifying parameter is also registered here (Kondratjeva, 2004).

In 2004 the share of river discharge in pollution of marine areas with PAH was estimated with a bio-indication method. Water sampling stations in the Amur Liman were grouped according to river runoff distribution specifics in summer as follows: 1 group – the northern part with a maximal discharge of pollutants from the Amur; 2 group – the southern part with a minimal substance discharge in the direction of the Tatar Strait. Correlation analysis was used to study the interrelations between the structure of microbial complexes (TGB– total number of heterotrophic bacteria , AMB – ammonifying bacteria, NB– nitrifying

bacteria, PhOB – phenol-oxidizing bacteria), which take part in different-genesis organic matter destruction and transport, and the content of easy-accessible carbohydrates in water (glucose – Gl), hydrocarbons (Hyd), naphthalene (Naph) and products of PAH transformation, i.e. salicylic acid (Sal), pyrocatechol (Pyr). It was revealed that in the zone of the main Amur runoff along the Northern waterway towards the Okhotsk Sea (Table 2) that the correlation between the total number of microorganisms (TGB) and their capacity to utilize salicylic acid, one of PAH transformation products, is high and positive (r=0.92). The correlations between the number of phenol-oxidizing bacteria (PhOB) and their activity to utilize salicylic acid and naphthalene, intermediate product of cyclic hydrocarbon transformation were as high as r=0.99 and r=0.93 respectively and the correlation between the bacteria growth rate in naphthalene and its transformation product pyrocatechol was r=0.92.

Such results give grounds to confirm that the Amur River discharges various aromatic compounds of phenol group, including products of microbiologic transformation of PAH. It is shown with PhOB growing in number, their capacity to destruct and transform PAH in model systems. Correlations with hydrocarbon pollution were not revealed. This factor turned out to be less important for microbiocoenose development.

In the southern part of the Amur Liman biochemical processes significantly differed from those in the Northern waterway (Table 3). First of all, a high correlation (r=0. 83) between the total number of microbial complexes and their growth rate on glucose. It may be associated with an intensive growth of autotrophic organisms (phytoplankton and macrophytes) in shallow water, as well as with their excretion products of carbohydrate nature. High correlations between PhOB growth in number and their capacity to grow on pyrocatechol (r=0. 99) and salicylic acid (r=0. 99) were also registered. Pyrocatechol and salicylic acid may result from the destruction of aromatic compounds of autochthonic origin and of PAH that belong to suspended matter, accumulated in bottom sediments. When water sampling was carried out navigation, especially open-coal shipments, was very active in the Tatar Strait. Anthracene, found in water, indicates atmospheric transfer of coal dust that explains its presence in suspended matter.

Table 2. Matrix of Correlations between Microbial Complex Structure and their Activity on Different Substances in the Amur Liman North

	TGB	AMB	NB	PhOB	Hyd	Sal	Naph	Pyr	Gl
TGB	1,00								
AMB	0,98	1,00							
NB	0,99	1,00	1,00						
PhOB	0,84	0,70	0,74	1,00					
Hyd	-0,74	-0,57	-0,62	-0,99	1,00				
Sal	0,92	0,81	0,84	0,99	-0,94	1,00			
Naph	0,58	0,38	0,44	0,93	-0,98	0,85	1,00		
Pyr	0,22	-0,01	0,06	0,71	-0,82	0,59	0,92	1,00	
Gl	0,44	0,63	0,58	-0,11	0,28	0,05	-0,47	-0,78	1,00

Table 2. Matrix of Correlations between Microbial Complex Structure and their Activity on Different Substances in the Amur Liman South

	TGB	AMB	NB	PhOB	Hyd	Sal	Naph	Pyr	Gl
TGB	1,00								
AMB	0,97	1,00							
NB	-0,89	-0,74	1,00						
PhOB	-0,81	-0,94	0,45	1,00					
Hyd	-0,65	-0,43	0,93	0,08	1,00				
Sal	-0,71	-0,87	0,30	0,99	-0,08	1,00			
Naph	-0,92	-0,78	0,99	0,52	0,90	0,37	1,00		
Pyr	-0,83	-0,94	0,47	0,99	0,11	0,98	0,54	1,00	
Gl	0,83	0,65	-0,99	-0,35	-0,96	-0,19	-0,98	-0,37	1,00

A positive correlation between hydrocarbon content in water medium and active transformation of naphthalene (r=0. 90) proves that water in contaminated with hydrocarbons and PAH from the sea vessels.

The method of initiated communities was used to assess potential capacity of water microbial complexes (MC) to transform PAH. Naphthalene and phenanthrene was added to a sterile mineral solution M9 (10mg/10ml). Surface water from the Amur Liman was used as inoculum. Solution colority changes (600 nm) and biomass accumulation (490 nm) served as indicators of transformation intensity. Cultivation temperature was 23-25^{o}C. The experiment lasted from 30 to 140 days. Numerous PAH, discharged into the Amur from its tributaries, especially those combined with suspended matter do not fully transform in the mainstream and are discharged in the Amur Liman. MC from the Amur Liman revealed 2 phases of phenanthrene transformations: colority changes were observed in the first 30 days and biomass accumulation took place in the next 100 days. This not only proves PAH transformations, but also indicates intermediator utilization. Pyrocatechole and hydroquinone analogs were identified in colored products. MC adapted to naphthalene grew well on pyrocatechole. Most active were MCs from shallow water areas, where suspended matter from the Amur River sediments.

CONCLUSION

Thus, Amur River pollution with stable polycyclic aromatic hydrocarbons is caused be various anthropogenic factors. Mort significant are forest fires, Bureya river runoff and transboundary transfer of PAH with water and suspended substances from the Sungari river, most dominant of which are being of the anthropogenic origin. There are zones of PAH accumulation in bottom sediments lower the Sungari juncture and in the Amur lower reaches. Most PAH slowly decompose in bottom sediments and their decomposition products penetrate into water media and form sources of chronic pollution of water ecosystems with

aromatic substances. Most stable PAH migrate throughout the entire Amur stream, come to the floodplain lakes and are discharged into the sea areas. Considering a high biological activity of polycyclic aromatic hydrocarbons it is vitally important to implement deep and detailed studies of fish resources state in the Amur lower reaches, the Amur Liman and bio-productivity of the Okhotsk Sea, as there is a significant threat of toxic organic substance accumulation in organisms and transport through the trophic chains. They constitute a high risks for hydrobionts, birds, animals and health of people.

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