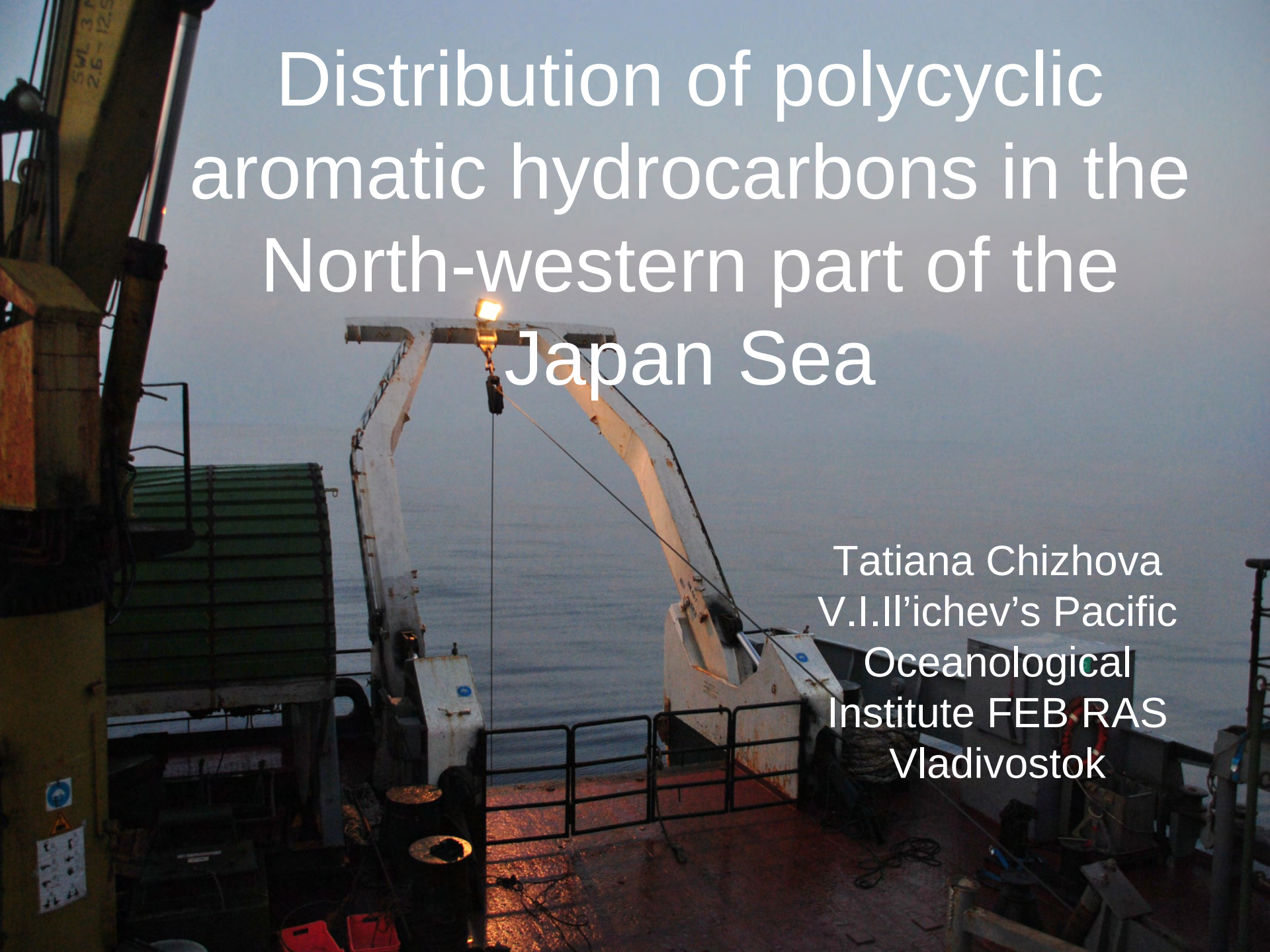
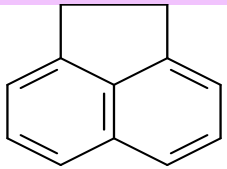
Distribution of polycyclic aromatic hydrocarbons in the North-western part of the Japan Sea

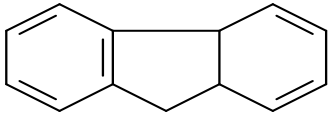


Tatiana Chizhova
V.I.Il'ichev's Pacific Oceanological Institute FEB RAS
Vladivostok

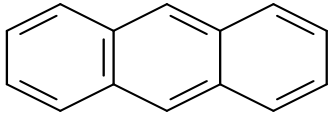
Polycyclic aromatic hydrocarbons (PAHs):



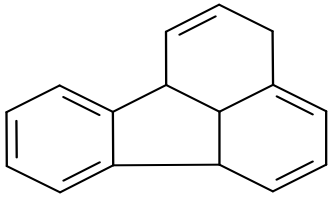
acenaphthene (Ace)



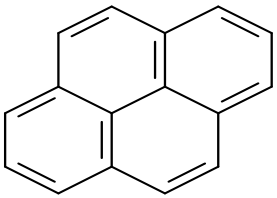
fluorene (Fle)



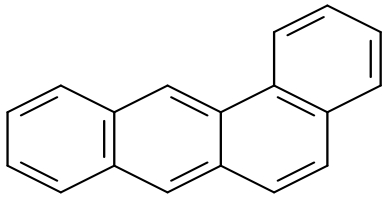
anthracene (Ant)



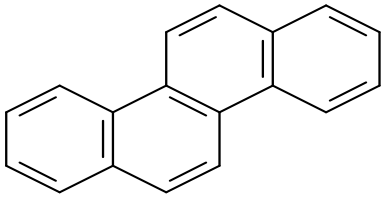
fluoranthene (Flu)



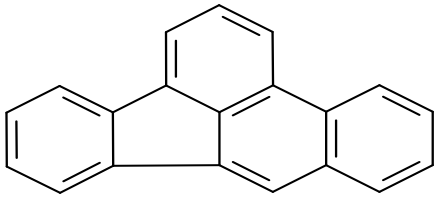
pyrene (Pyr)



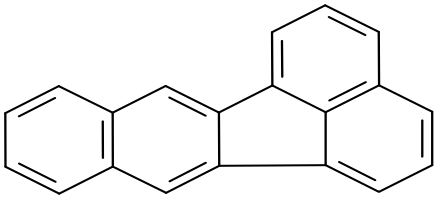
benz[a]anthracene (BaA)



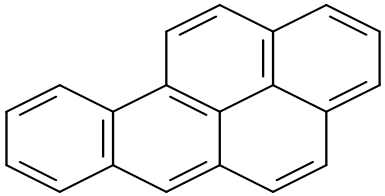
chrysene (Chr)



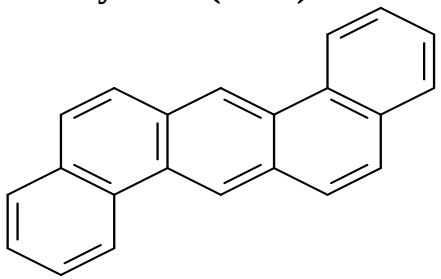
benzo[b]fluoranthene (BbF)



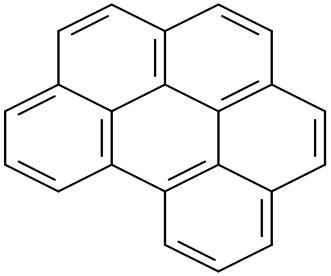
benzo[k]fluoranthene (BkF)



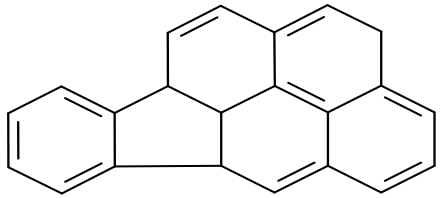
benzo[a]pyrene (BaP)



dibenz[a,h]anthracene (BaA)



benzo[g,h,i]perylene (BgPe)



indeno[1,2,3-c,d]pyrene (IDP)

Mechanisms of PAHs formation:

- **Pyrogenic -**

very rapid, high temperature (~700°C) incomplete combustion or pyrolysis of organic materials

- **Petrogenic -**

very slow (millions of years) rearrangement and transformation of biogenic organic materials at moderate temperatures of 100-300°C to form fossil fuels

- **Diagenic -**

relatively rapid (days to years) transformation of certain classes of organic compounds in soils and sediments

- **Biogenic -**

direct biosynthesis by organisms

Sources of PAHs:

PAHs

natural sources

CTD/Rosette system

Rosette with 12 pcs. of Niskin bottles (the volume is 5 or 12 liters for each) for seawater sampling

SBE 9plus Underwater Unit (Manufacturer Sea-Bird Electronics, Inc.)

Collection samples of seawater and suspended matter

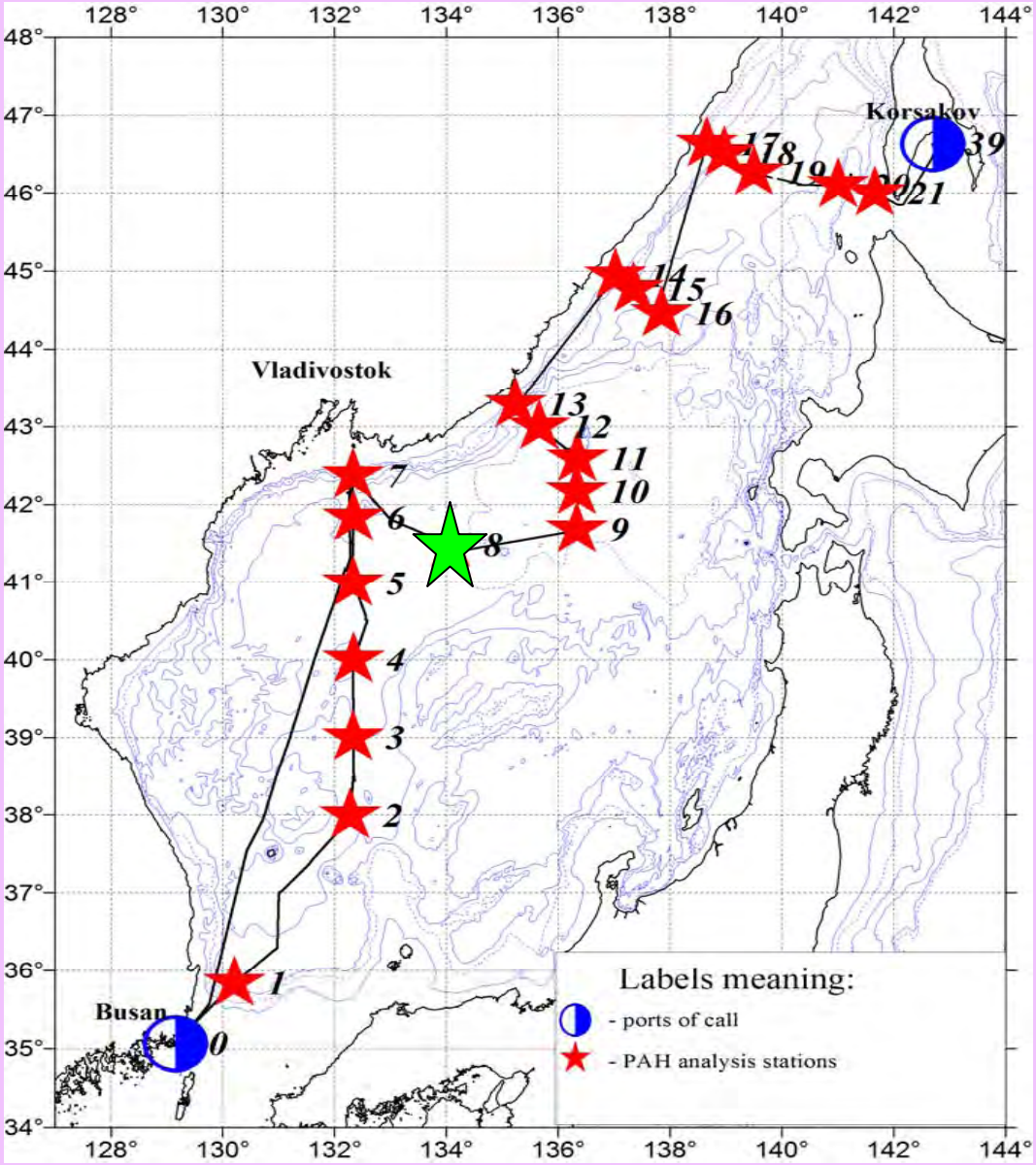
Filtration

0.5 µm pore glass fiber filter

Water	**Suspended matter – SM**
Cartridge **C18** (preconditioned 5 ml EtOH, 5 ml distilled water), flow rate 10 ml/min	
Dried under vacuum condition	Dried in the air about 1 h

Kept in the refrigerator at 4°C

2009, July/03-20. Cruise. Japan Sea



At the all stations water samples were collected from the surface layer.

At the station 8 water samples were collected at the following depths (m): 3480 (bottom), 3000, 2500, 2000, 1500, 1000, 500, 300, 200, 100, 50 and 33.

PAHs extraction:

Analysis

C18		
(water)	Desorption	15 ml dichloromethane
	Clean up	Silica gel cartridge, hexane:acetone 9:1
	Dry	
	Diluted in acetonitrile	200 µl DMSO + 800 µl acetonitrile
Filter		
(SM)	Ultrasonic extraction	30 ml mixture benzene:ethanol 3:1
	Liquid-liquid extraction	5%NaOH, 20%H_2SO_4, distilled H_2O
	Clean up	Silica gel cartridge, hexane:acetone 9:1
	Dry	
	Diluted in ethanol	100 µl DMSO + 900 µl ethanol

PAHs analysis system

The HPLC system:

2 Hitachi L-2130 pumps; Hitachi degasser; Hitachi L-2485 fluorescence detector; Hitachi organizer.

Analytical column - Inertsil ODS-P (4.6i.d.×250mm, 5μm, GL Sciences)

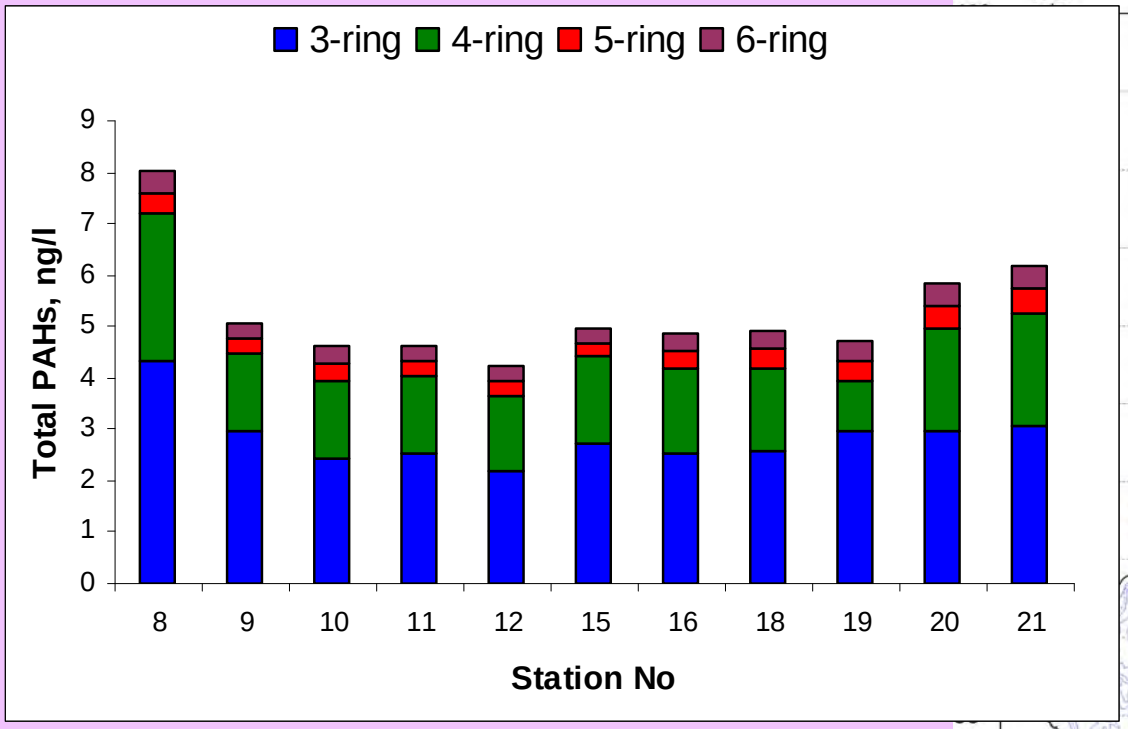
Guard column - Inertsil ODS-P (4.0i.d.×10mm, 5μm, GL Sciences)

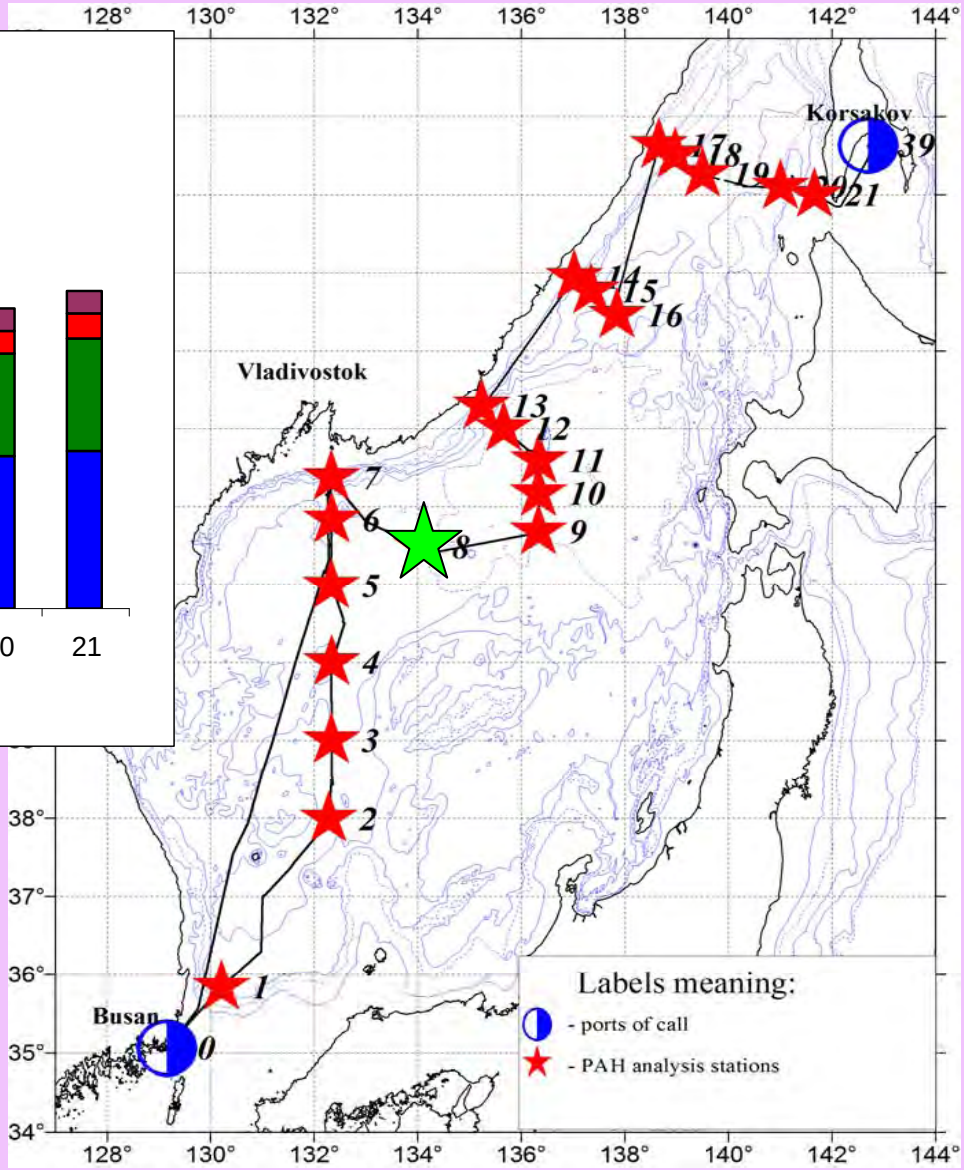
Mobile phase - mixture of acetonitrile and distilled water

Flow rate of mobile phase - 1.0 mL/min

The sample was detected by fluorescence detector for which the excitation and emission wavelengths were automatically set by a time program.

The total concentrations of PAHs in the surface samples of seawater

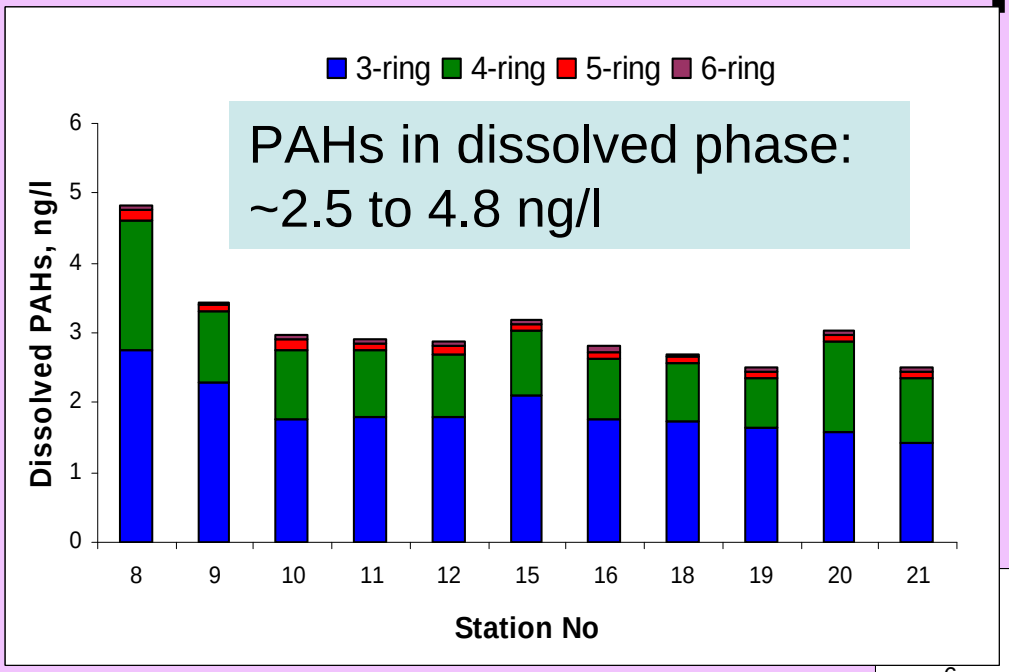




Total PAHs = Dissolved PAHs

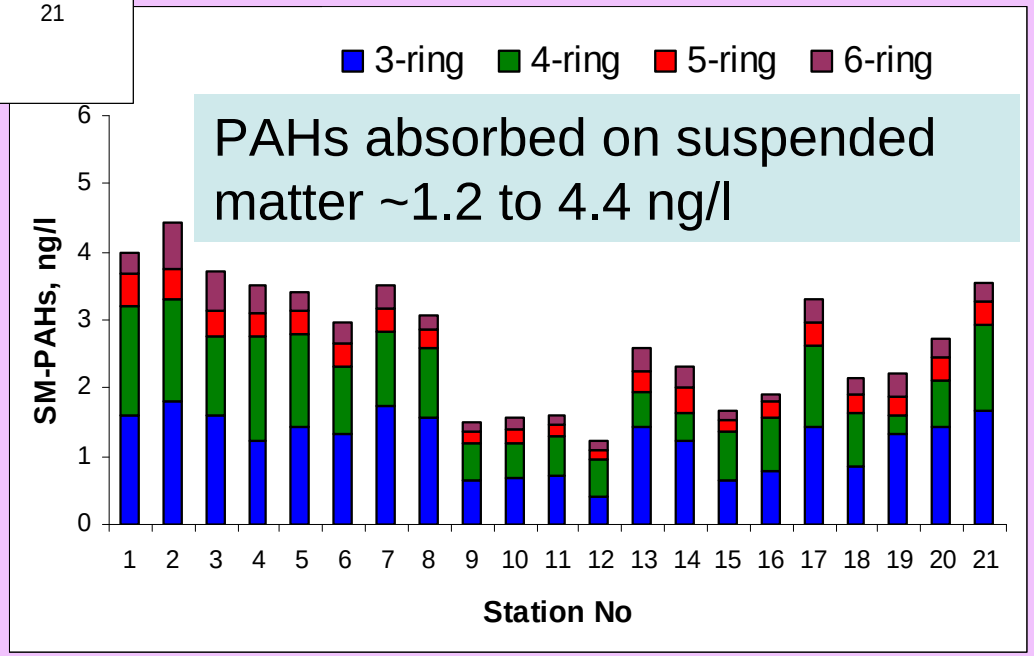
+ PAHs sorbed on SM

Concentrations of DPAHs and SM-PAHs in the surface samples of seawater

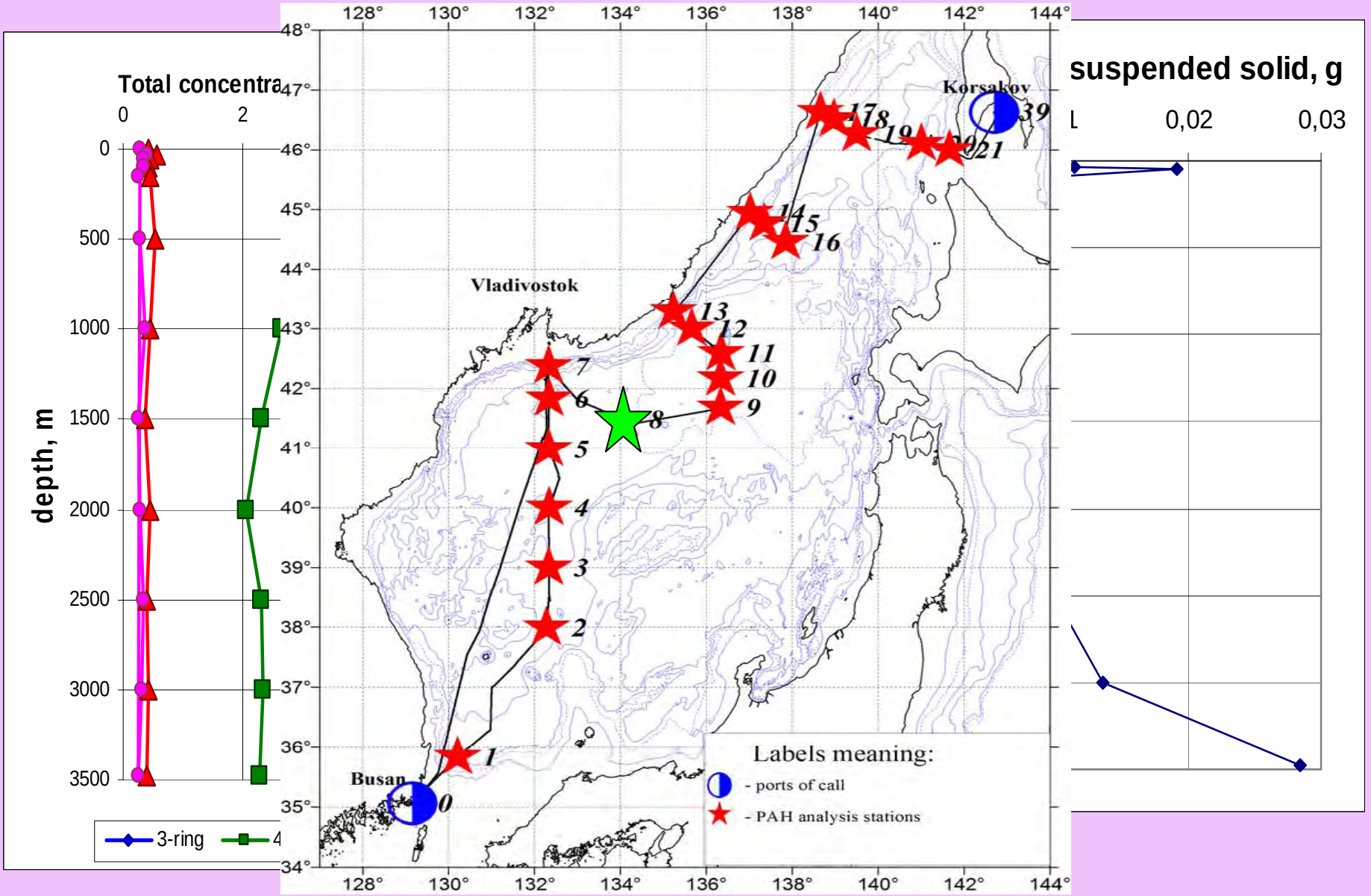


- **DPAHs – Dissolved PAHs**
- **SM-PAHs – PAHs sorbed on suspended matter (SM)**

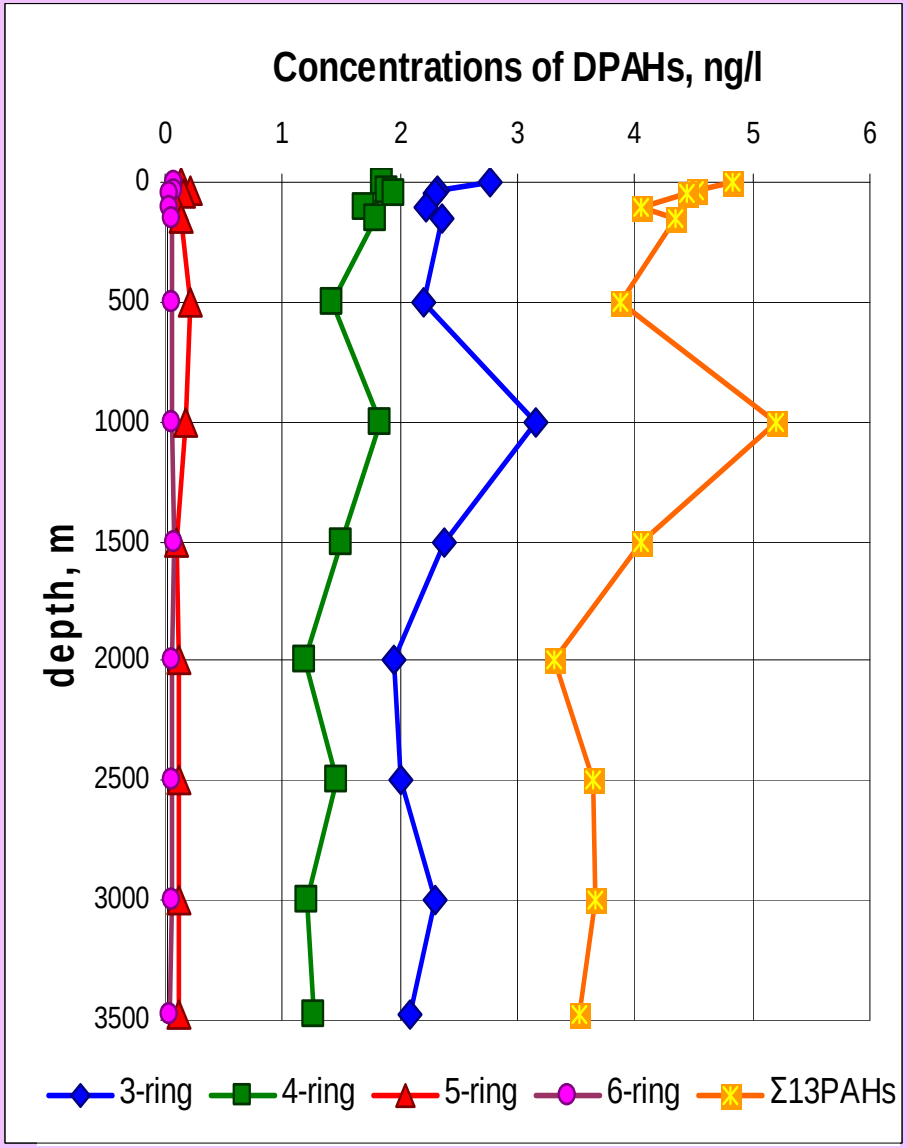
3-4 ring PAHs are dominated also, but concentrations of 5-6 ring PAHs are increasing from 0.11 to 0.24 ng/l for 5-ring PAHs and from 0.06 to 0.19 ng/l for 6-ring PAHs comparison with dissolved phase

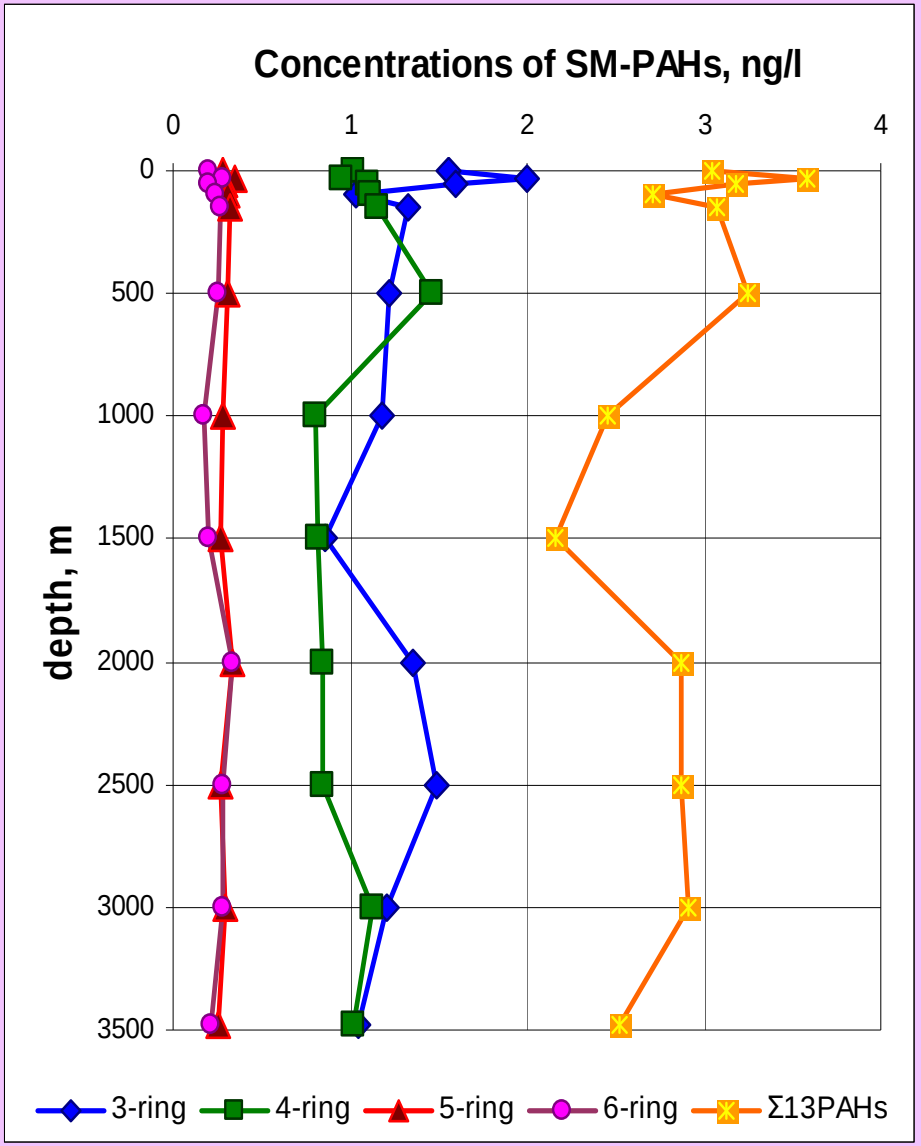


Vertical distribution PAHs at the station 8



Vertical distribution of DPAHs and SM-PAHs





PAHs ratios as markers of PAHs sources:

PAHs ratios	Petrogenic sources	Pyrogenic sources	
		Petroleum combustion	*Coal combustion*
Flu/(Flu+Pyr)	<0.4	0.4–0.5	>0.5
IDP/(IDP+BgPe)	<0.2	0.2–0.5	>0.5
BaA/(BaA+Chr)	<0.2	0.2–0.35	>0.35

	8	**9**	**10**	**11**	**12**	**15**	**16**	**18**	**19**	**20**	**21**
Flu/(Flu+Pyr)	**0,30**	**0,32**	**0,36**	**0,30**	**0,37**	**0,32**	**0,19**	**0,21**	**0,31**	**0,17**	**0,26**
IDP/(IDP+BgPe)	**0,46**	**0,53**	**0,55**	**0,49**	**0,43**	**0,45**	**0,40**	**0,46**	**0,55**	**0,47**	**0,50**
BaA/(BaA+Chr)	**0,45**	**0,48**	**0,45**	**0,40**	**0,44**	**0,45**	**0,46**	**0,49**	**0,41**	**0,43**	**0,45**

Conclusions:

- At first time was measured the levels of PAHs in the Japan Sea (DPAHs ~2.5 to 4.8 ng/l; SM-PAHs ~1.2 to 4.4 ng/l with highest content of 3-ring PAHs)
- The main source of PAHs in the Japan Sea is the atmosphere
- The markers point to different origins of PAHs in the Japan Sea:

crude oil, petroleum combustion, coal combustion (heating season)

Acknowledgments:

- Japan-Russian Youth Exchange Centre, Tokyo, Japan

- Kanazawa University, Kanazawa, Japan


Thank you for your attention