"Atmospheric transboundary transport of pollutants in East Asia"

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- **Vladivostok (POI)**

Kanazawa

- **Taiga-Mounting St.**

Sapporo

Sampling of aerosols over the Sea of Japan

Sampling period: 3 May – 31 May 2011 г.
Air volume ~ 1750 м^3 for one sample.
PALLFLEX filters (200x250mm)
Total of 8 samples for the sampling period.

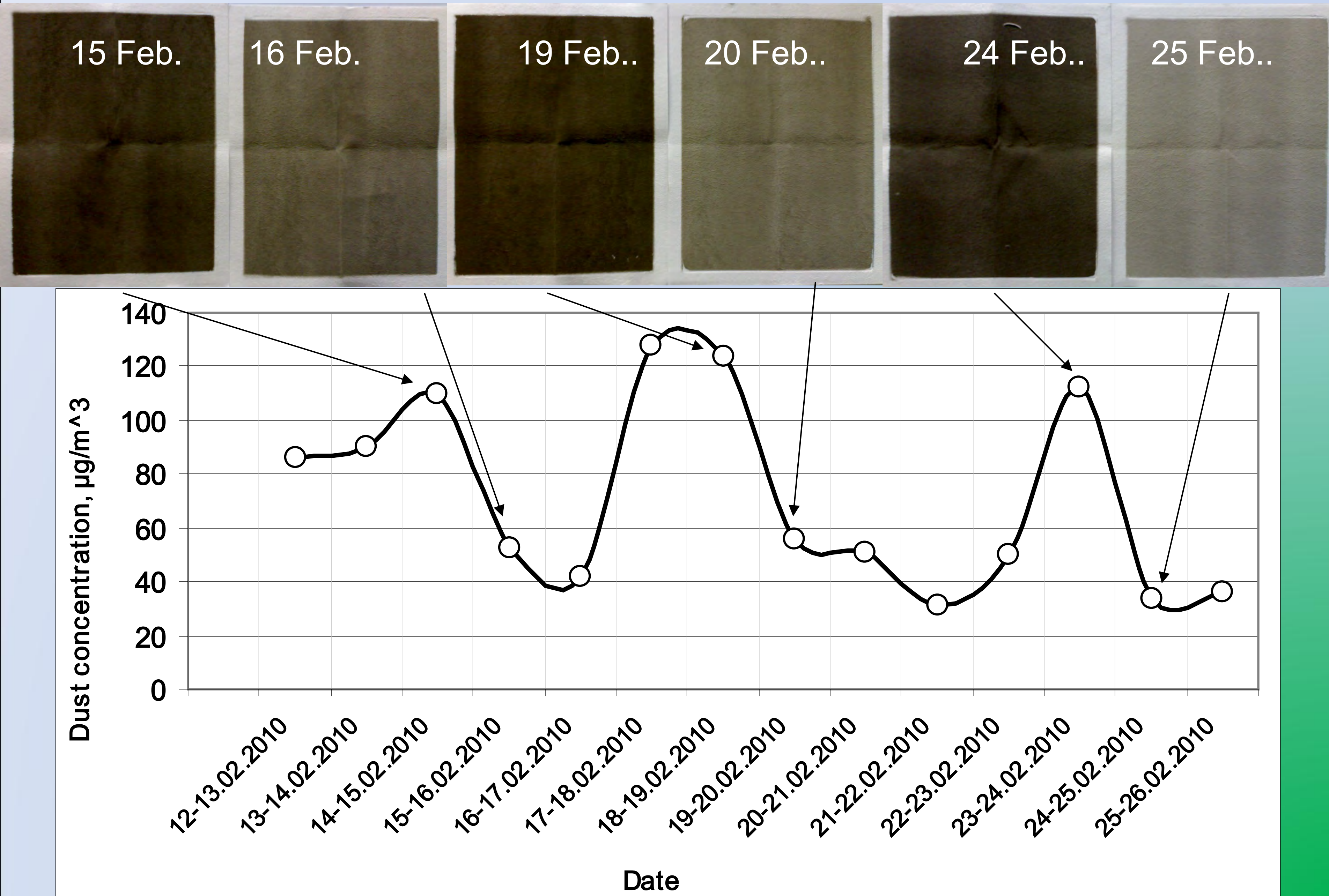
Sampling and analysis methods

Sampling of aerosols was made with japanese sampling pump (Kimoto, Japan)

Air volume ~ 4500 м^3 for one sample. 168h

The gamma-spectrometric analysis of weekly aerosol samples was performed in the Laboratory of Nuclear Oceanology, V.I.Il`ichev Pacific Oceanological Institute, Far Eastern Branch, Russian Academy of Sciences with gamma-spectrometer with a detector of High Purity Germanium GEM150.

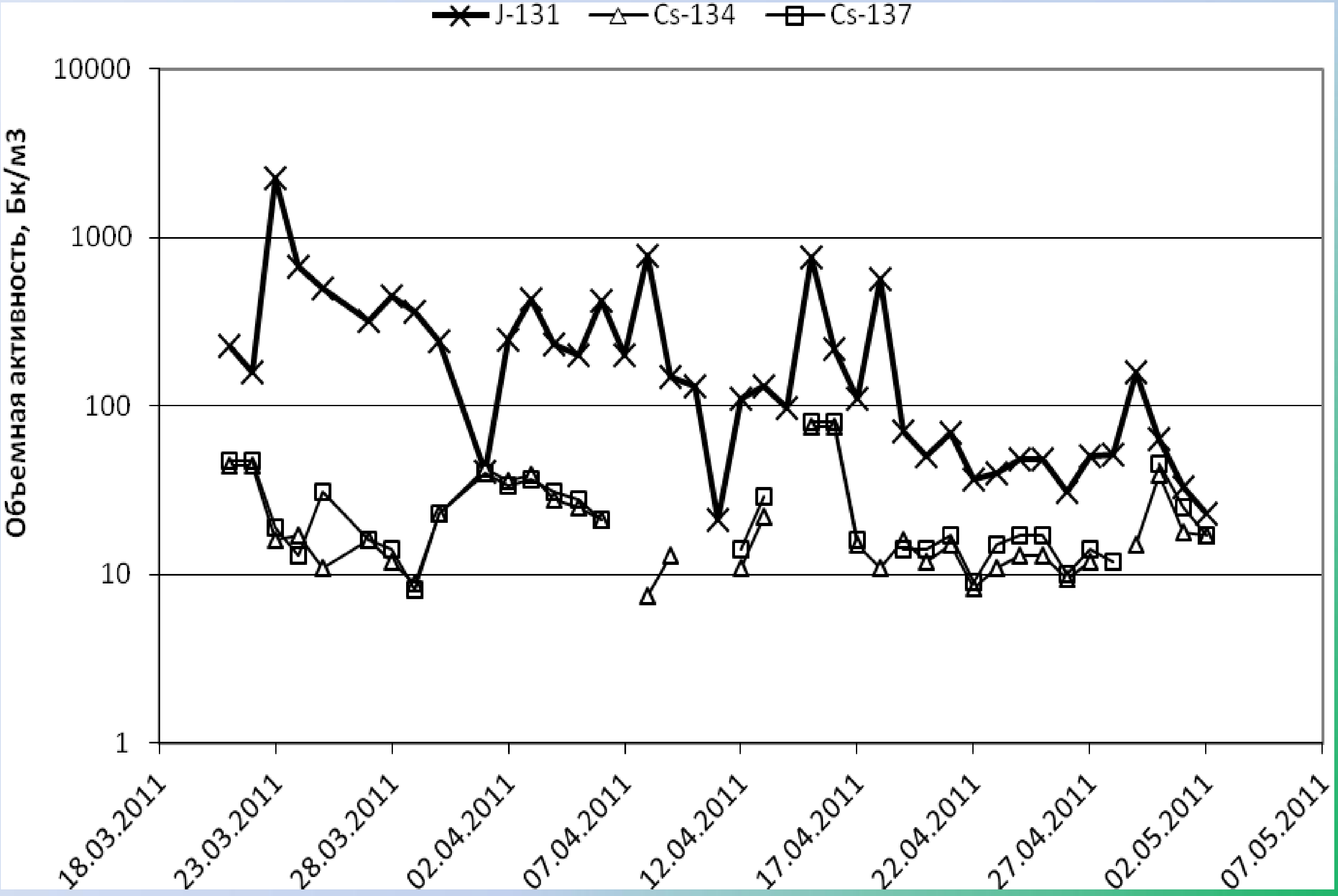
Color of daily sampled filters in Feb. 2010 in Vladivostok



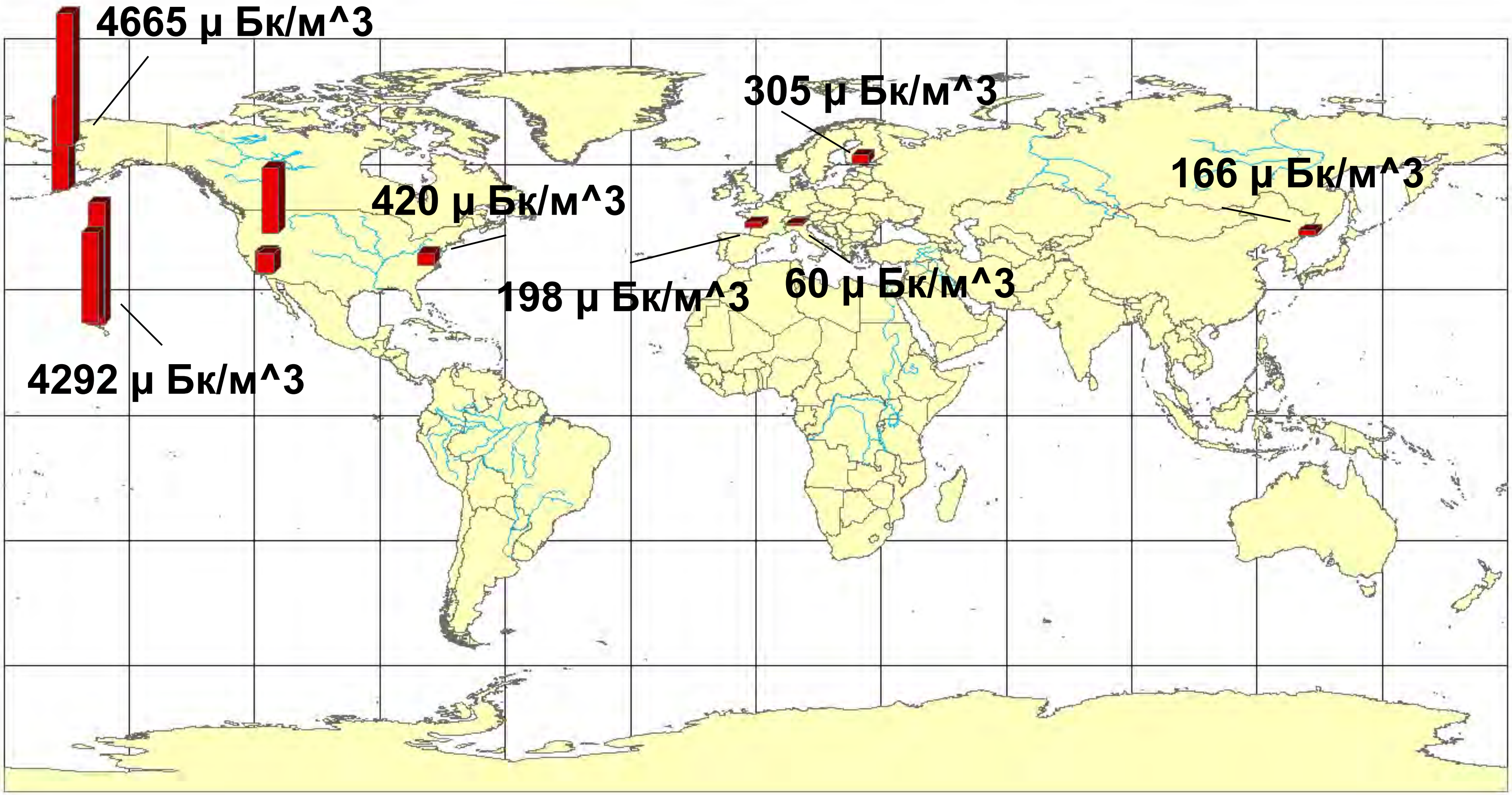
- 1. Concentrations of polynuclear aromatic hydrocarbons (PAHs) were determined by high pressure liquid chromatography.
- 2. Macro (Al, Ca, Mg, Na, K, Fe, Mn) and trace (Pb, Cd, Ni, Zn, Co, Cu, Cr) chemical elements were determined by atomic absorption spectrometer.
- Gamma activity and radioisotope composition have been determined by the gamma spectrometer with the high purity germanium detector GEM150 and a digital multi-channel analyzer DSPEC jr2.0, ORTEC Company.

Global atmospheric transboundary transport

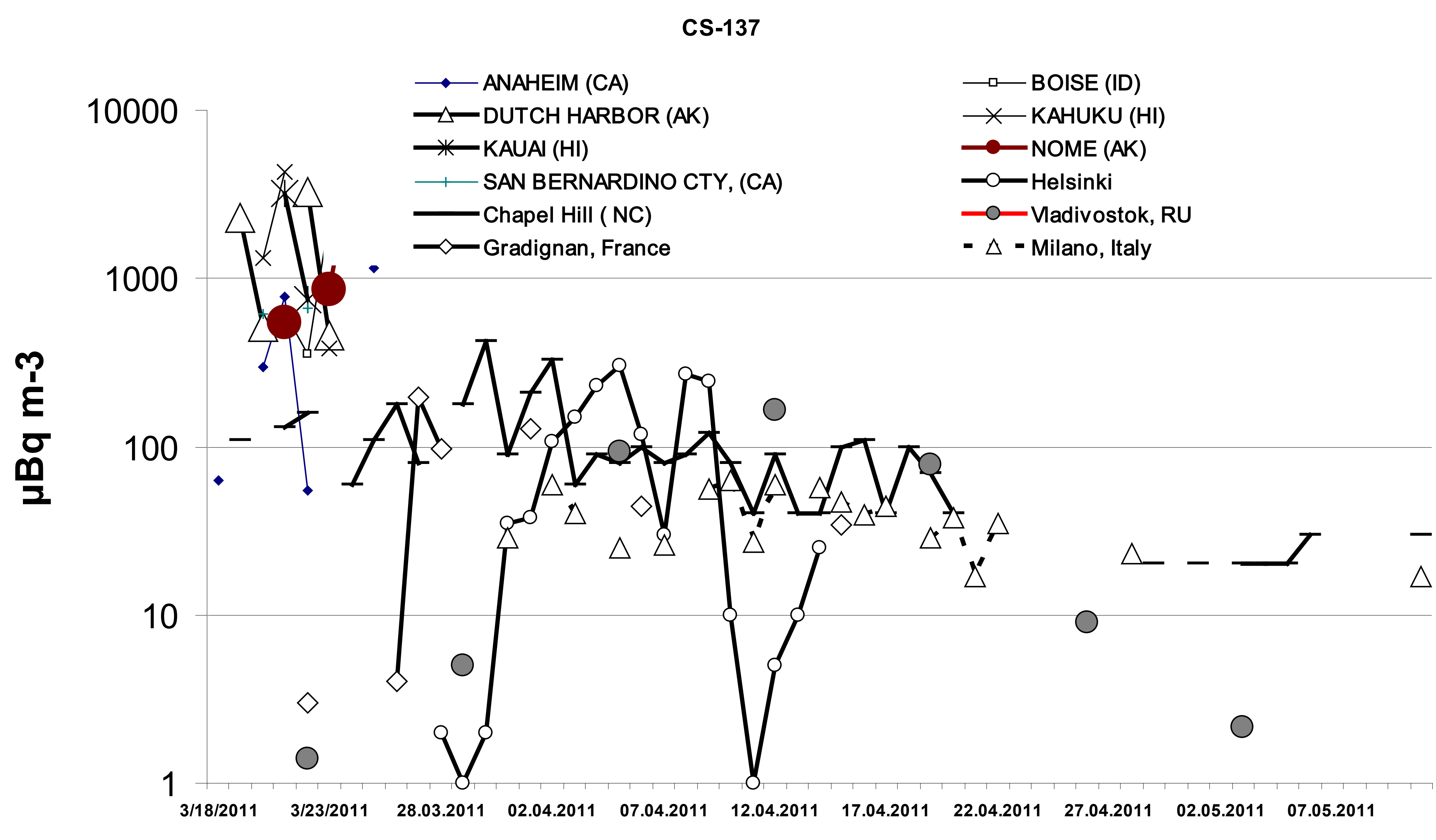
Activity of radionuclides near Fukushima (Tokyo Electric Power Company (http://www.tepco.co.jp/en/index-e.html))



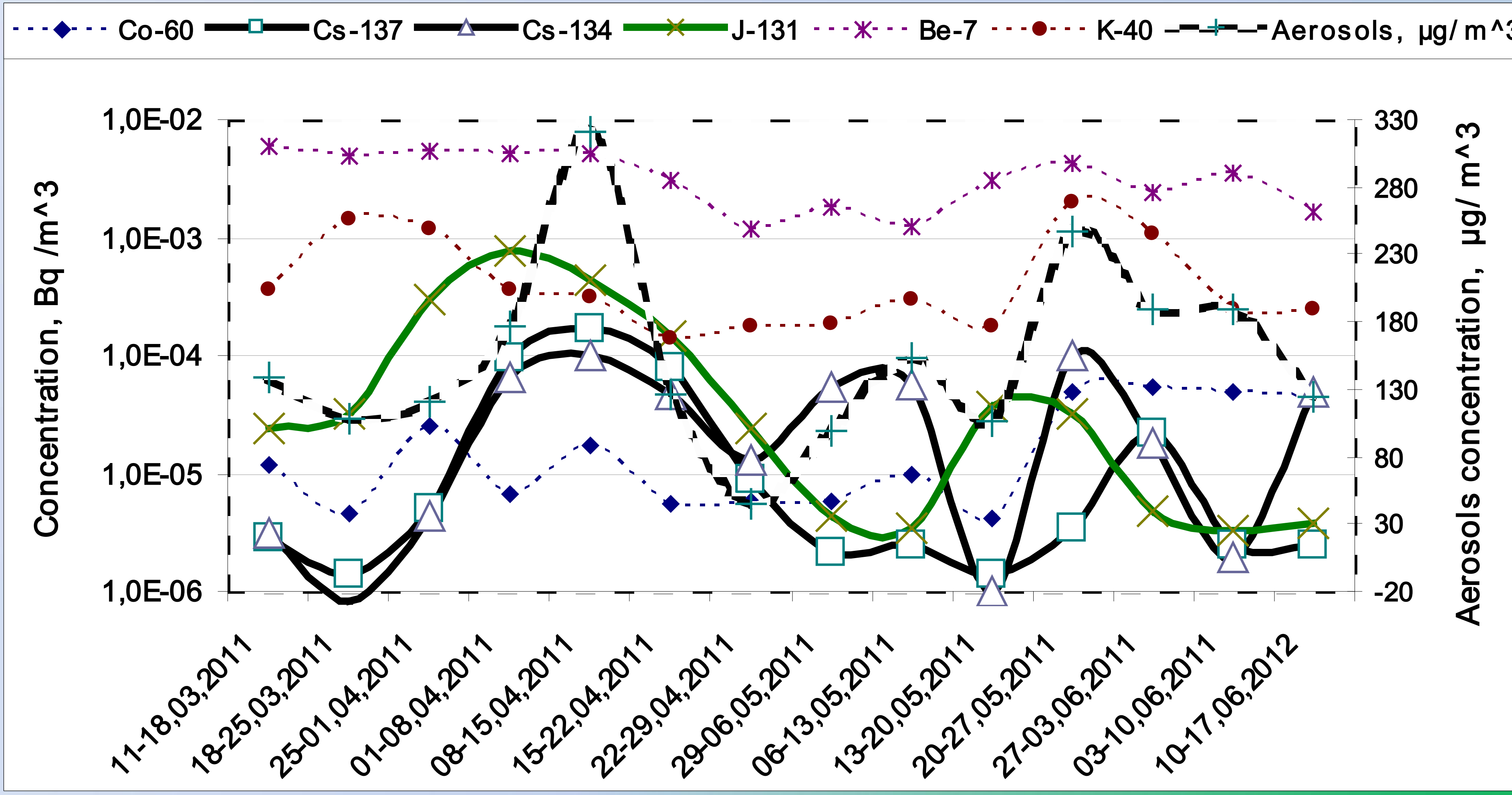
Maximal concentrations of Cs-137 in aerosols in different parts of World after Fukushima accident .



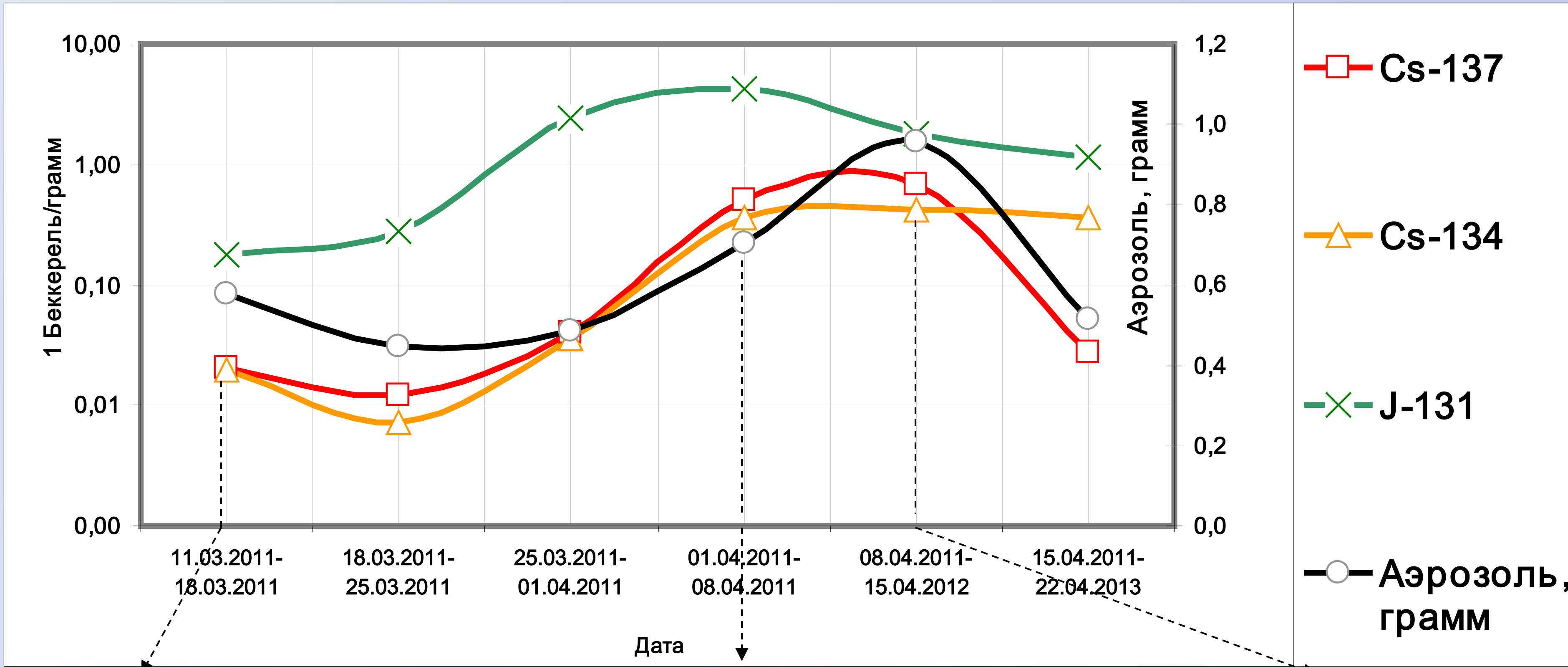
Temporal and spacial distribution of Cs-137 in aerosols

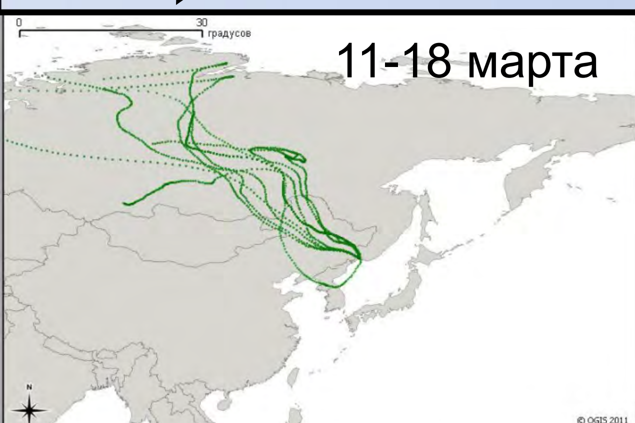


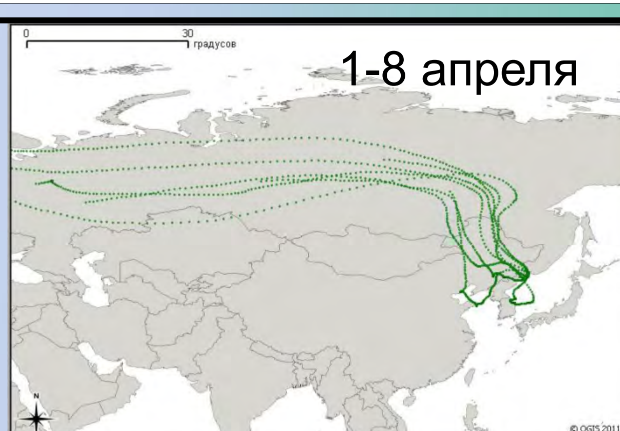
Activity of radionuclides (Bq/m^3) and concentration of aerosols (µg/m^3) near Vladivostok

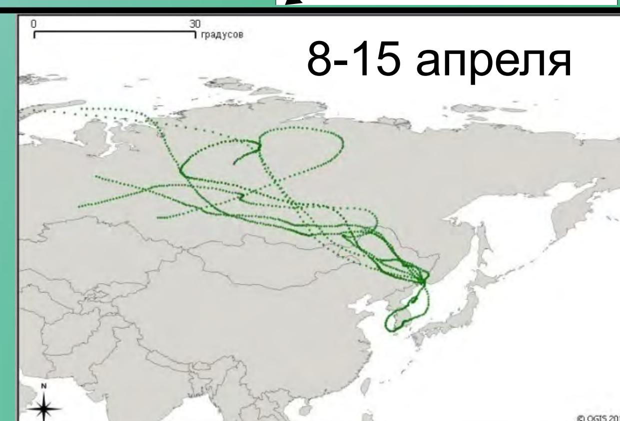


Back trajectories of air movement to Vladivostok (100 m) in mach-April 2011





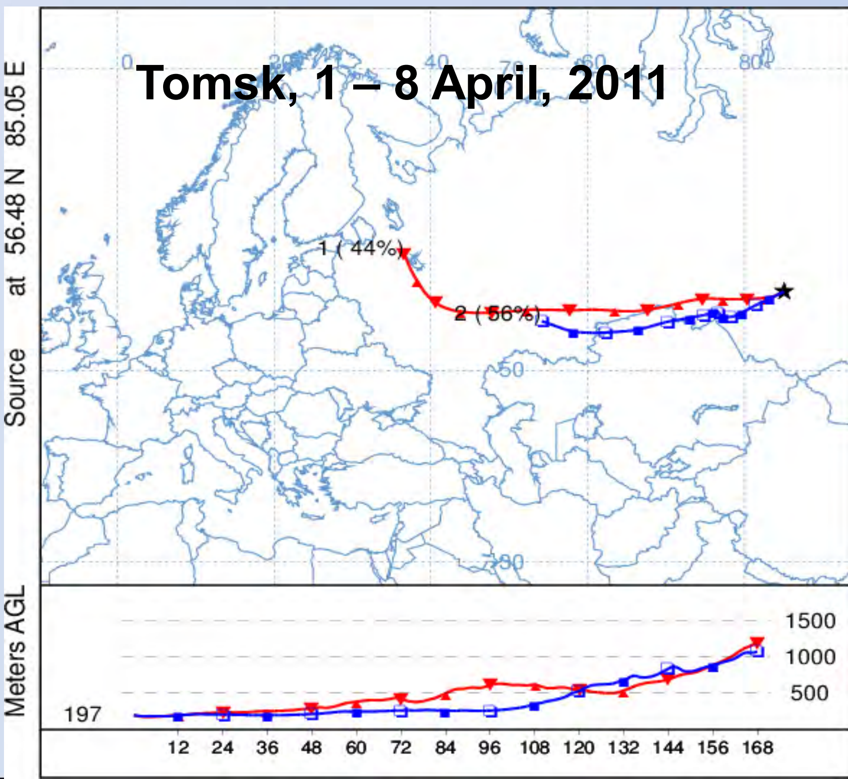


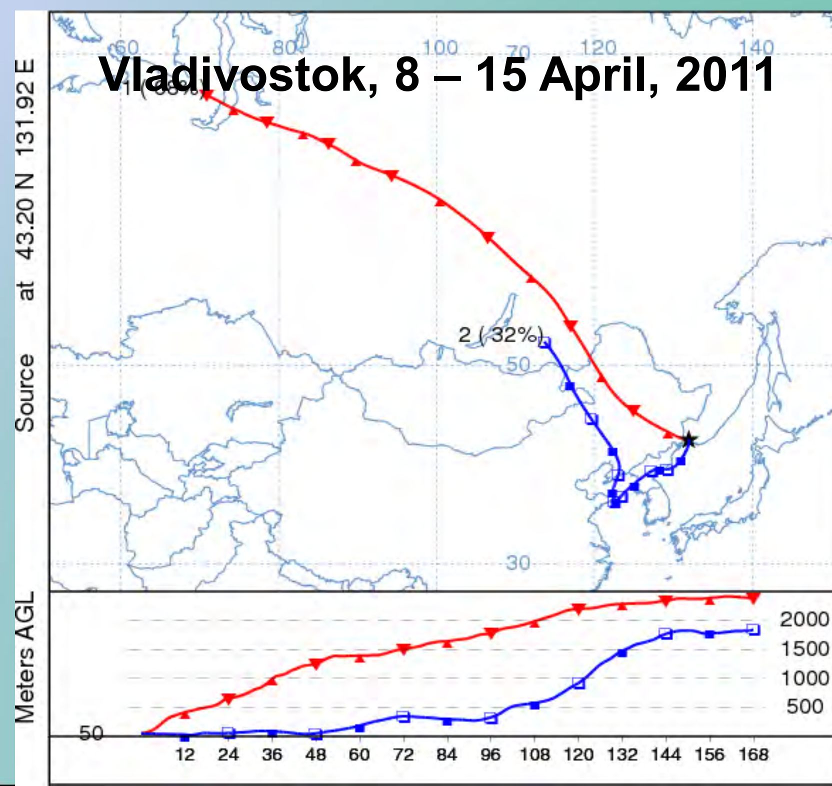


Mean 7-day back trajectory for the main trajectory clusters at Vladivostok and Tomsk for 1 – 8 April (Tomsk) and 8 – 15 April (Vladivostok).

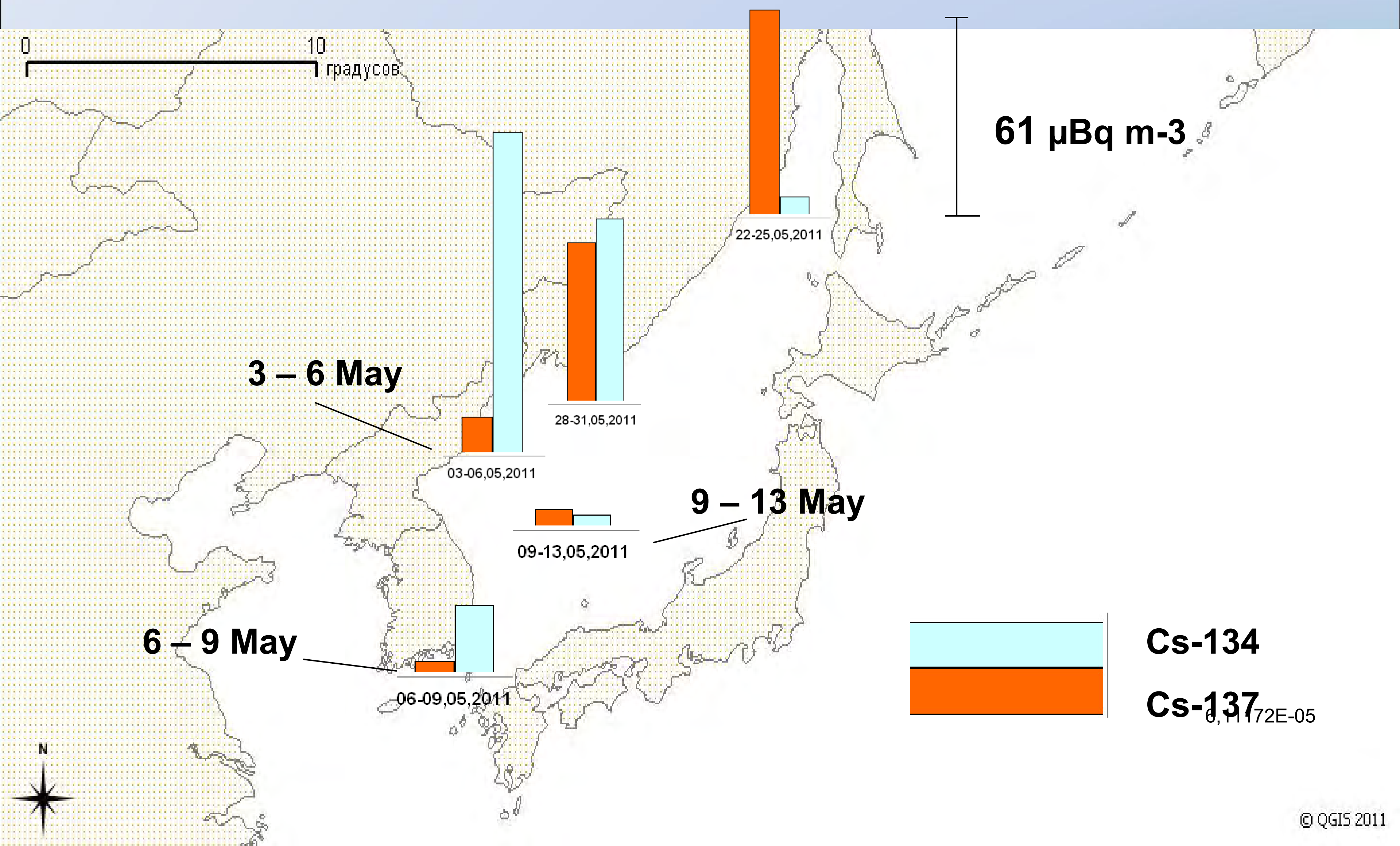
Maximal values of Cs-137 and Cs -134 concentrations (213.8 µBq/m3 and 84.5 µBq/m3 respectively) were reached in samples taken <u>from 1 to 8 April</u>

Maximal values of Cs-137 and Cs -134 concentrations (166 µBq/m3 and 169 µBq/m3 respectively) were reached in samples taken <u>from 8 to 15 April</u>

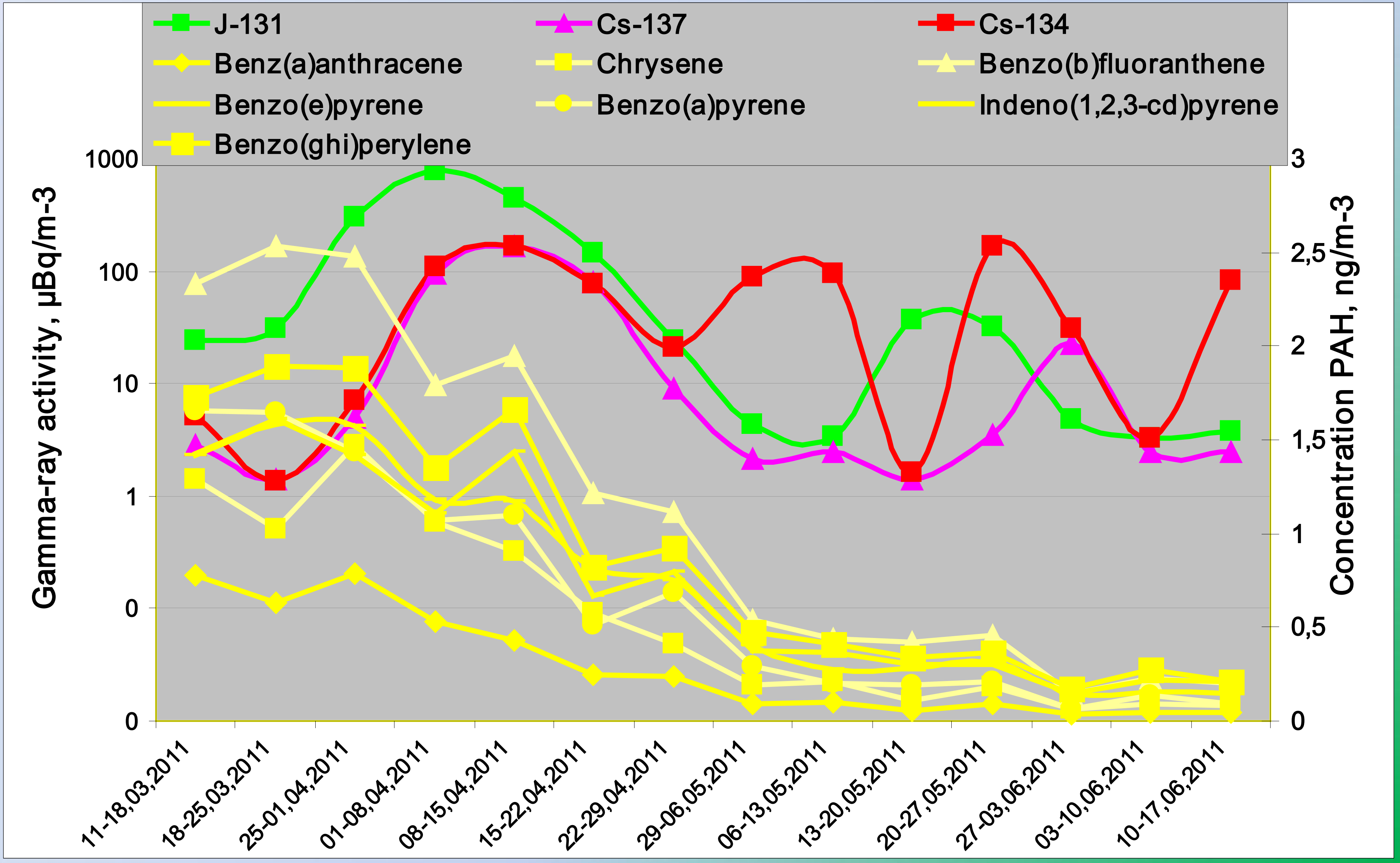




Gamma-ray activity of Cs -134, Cs-137 in the aerosols of Sea of Japan

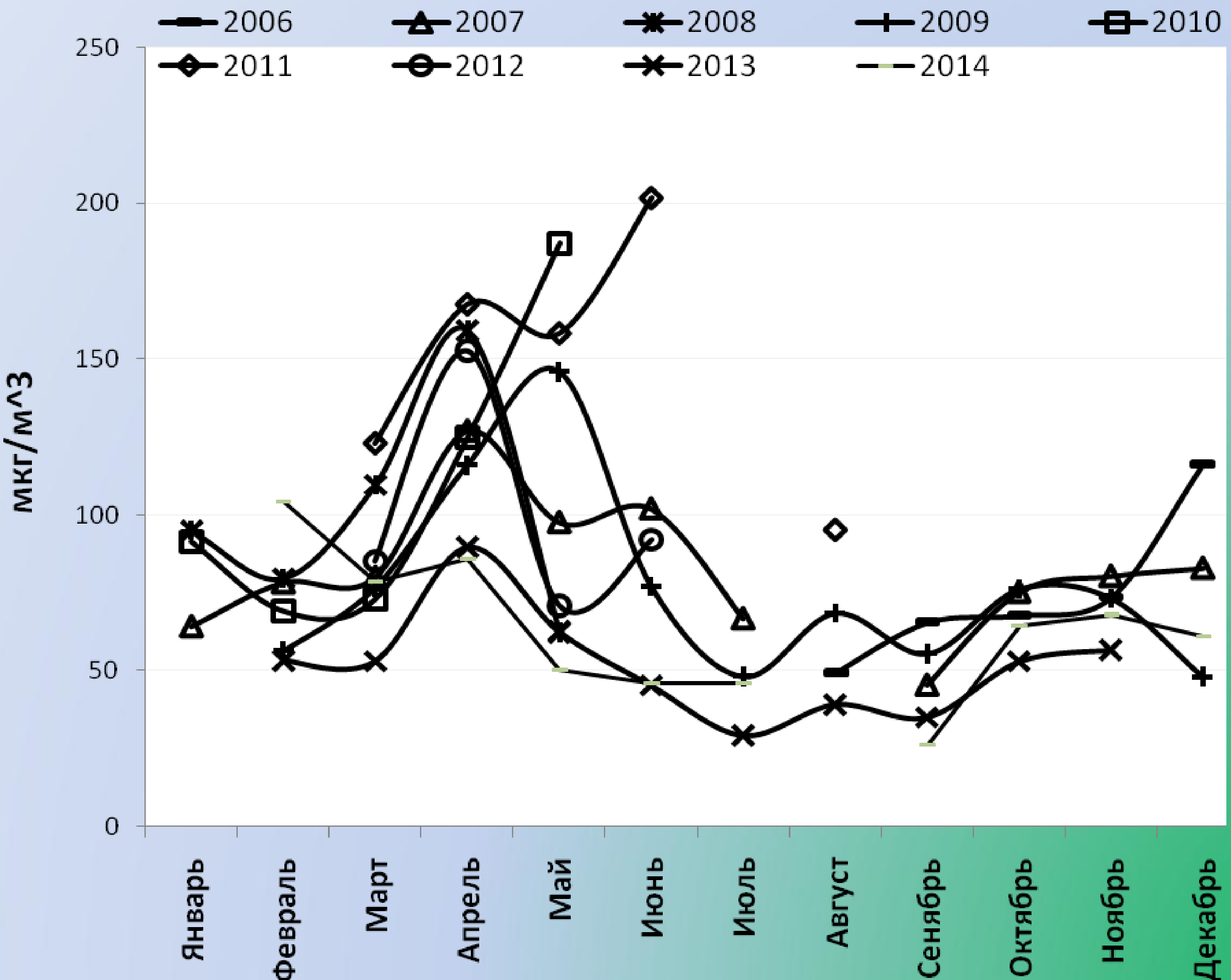


Polycyclic aromatic hydrocarbons and Gamma-ray activity of Cs -134, Cs-137, I-131 in the aerosols for spring 2011(Vladivostok)

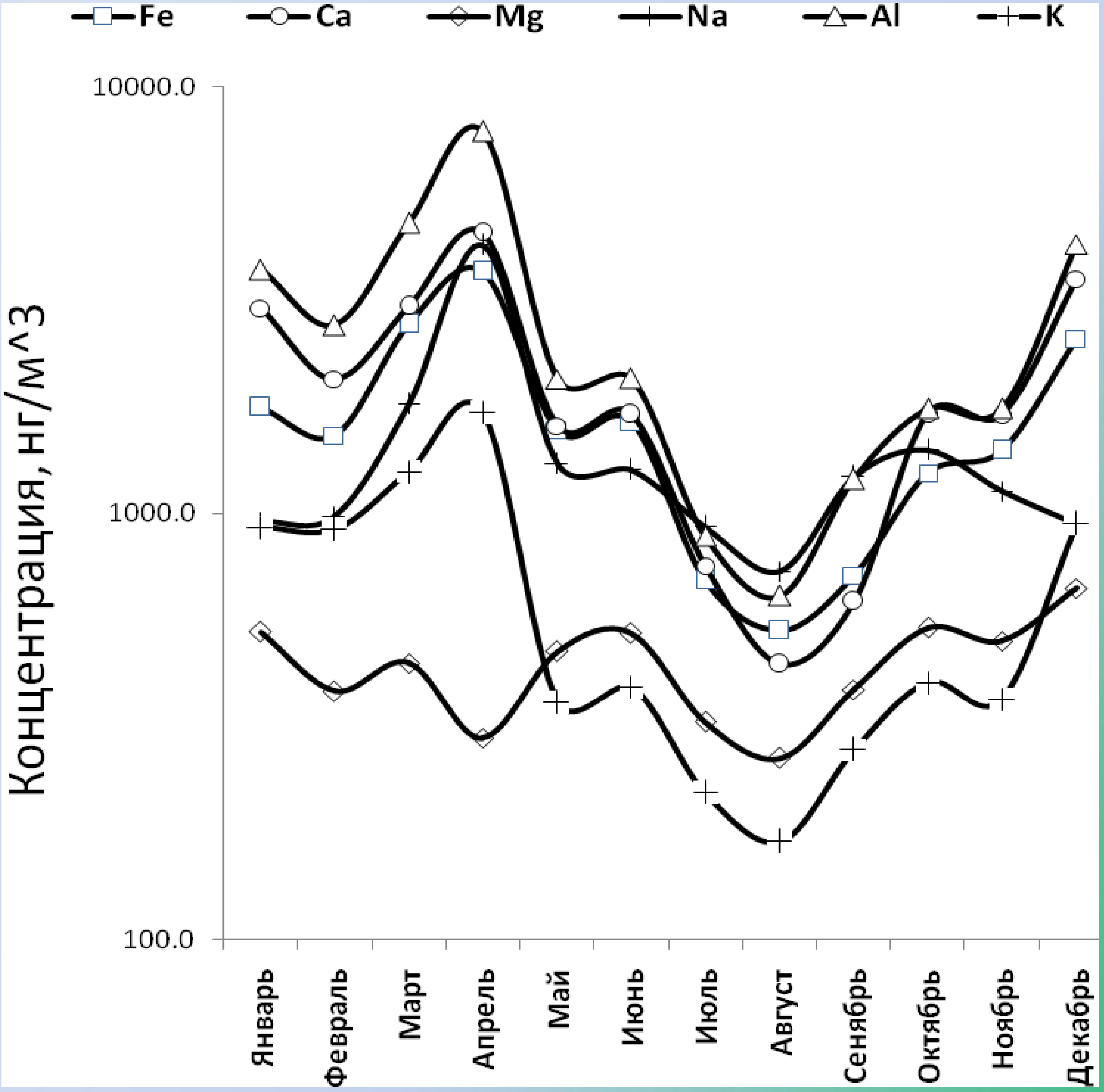


Regional atmospheric transboundary transport

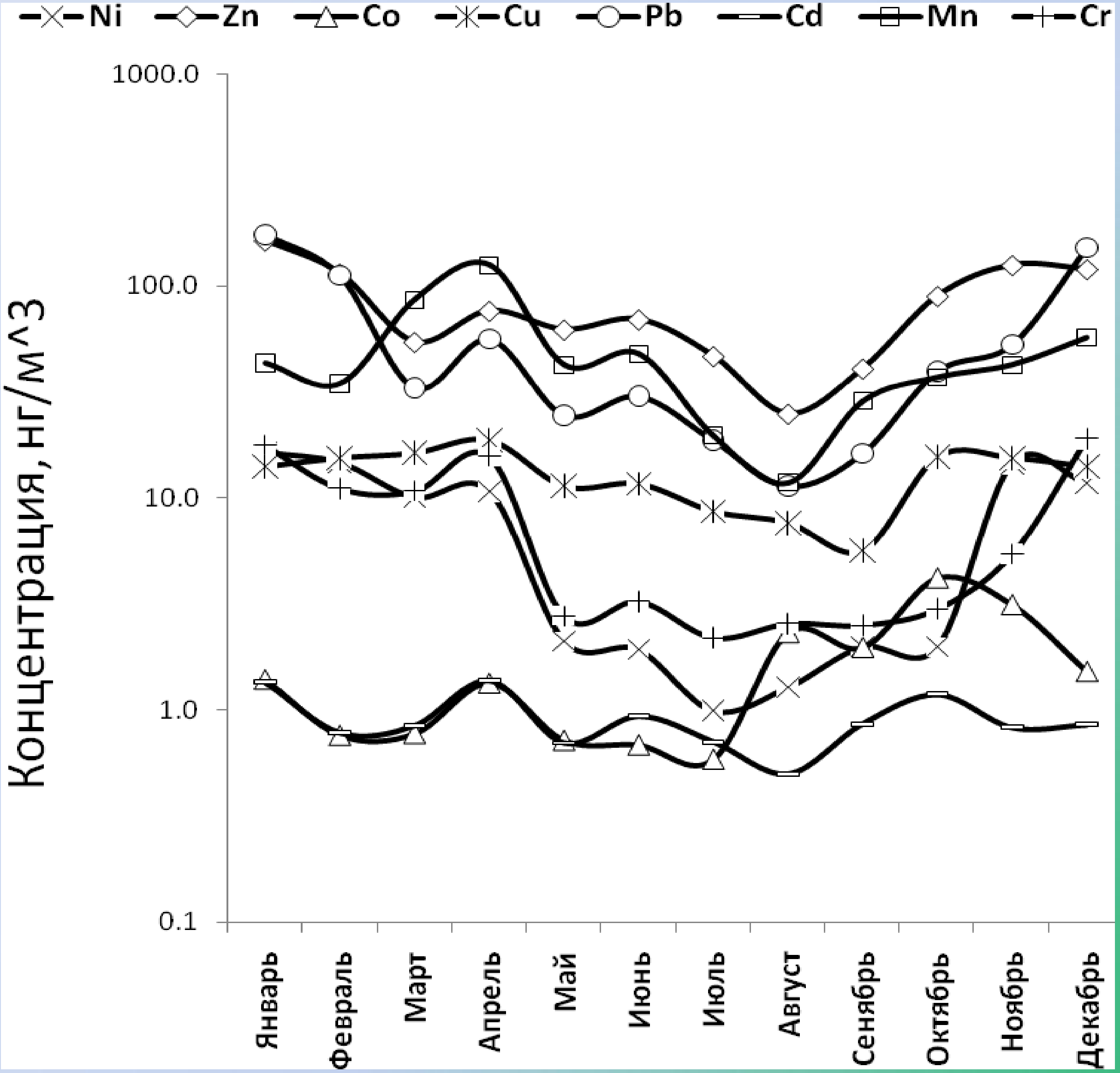
Monthly average concentrations of aerosols over Vladivostok from 2006 to 2014



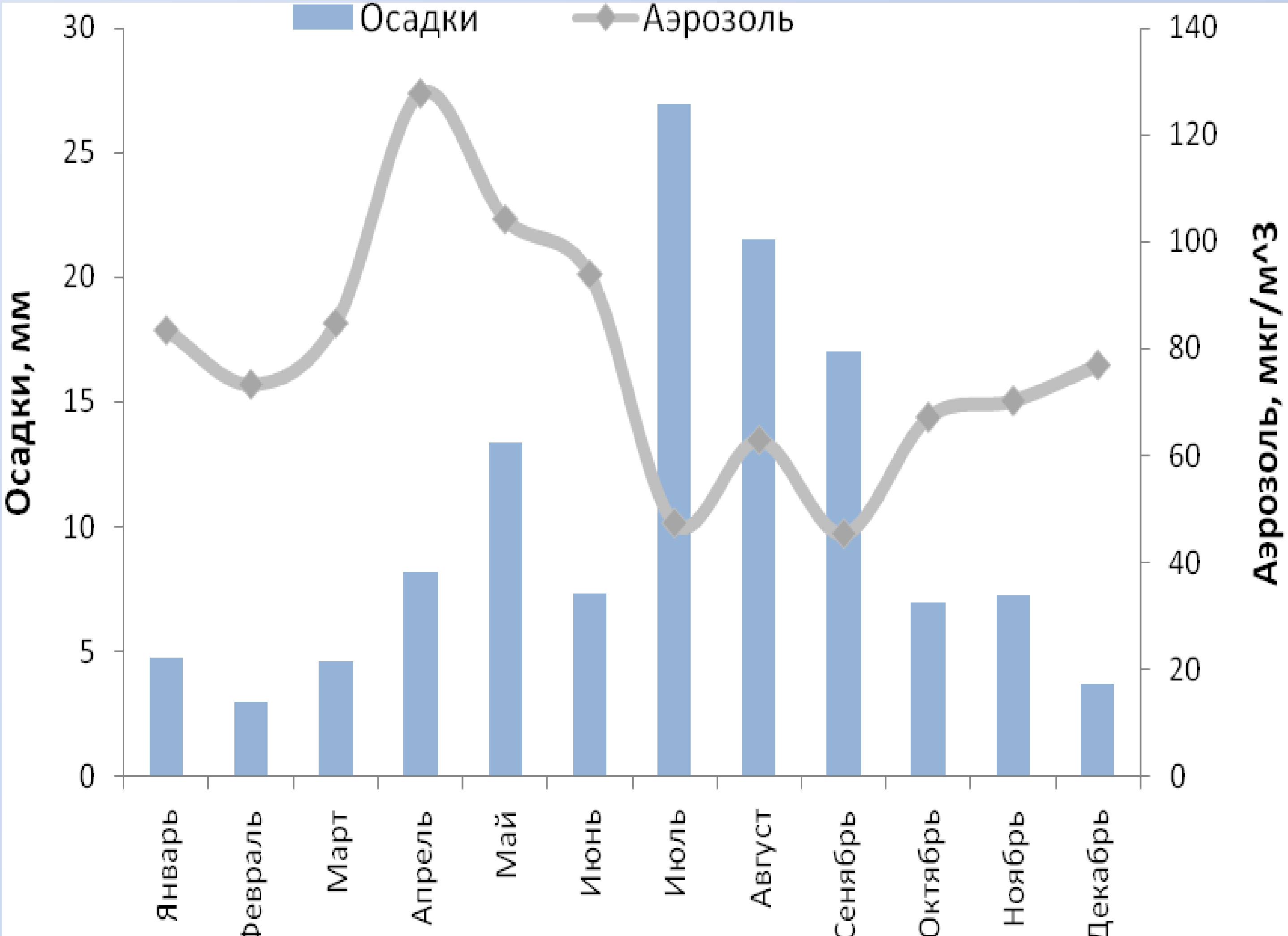
Monthly averaged macro element concentrations in air over Vladivostok from 2009 to 2013



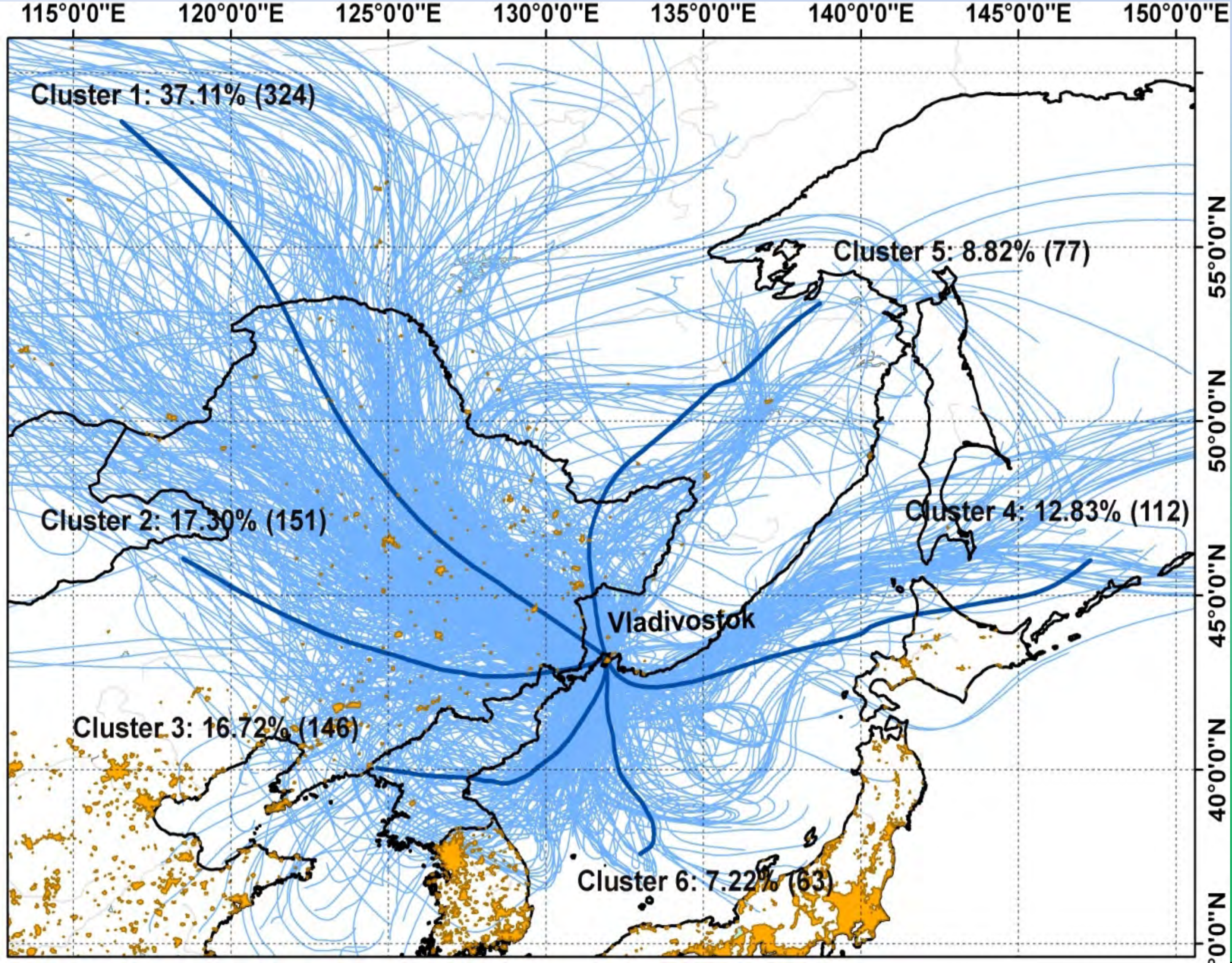
Monthly averaged trace element concentrations in air over Vladivostok from 2009 to 2013



Monthly averaged atmospheric precipitations and monthly averaged aerosol concentrations from 2006-2014



6 clusters of air mass backward trajectories for Vladivostok. Thin lines are individual trajectories, dotted lines are cluster means. Industrial regions are marked by orange color.



Target Transformation Factor Analysis.

DATA INPUT $X(m,n)$

INPUT OF TEST-VECTORS B (b_{ik}) (Tabl.2,3)

Account of correlation matrix $C(n,n) = (XV)^t (XV)$

V - matrix with elements $v_{ij} = \delta_{ij} (\Sigma \quad x_{ij}^2)^{-1/2}$, $\delta_{ij} =0$ $(i \neq j)$, $\delta_{ij} =1$ $(i=j)$

t - operation of transposing of a matrix

Calculation of own significances and own vectors $Q(n,n)$

$Q^{-1} C Q = \Lambda$, $Q^t = Q^{-1}$, $Q^t (XV)^t (XV) Q = \Lambda$

Λ - diagonal matrix of own significances

Calculation of factor loads $A = XVQ$ and factor significances $F = Q^t V^{-1}$

Calculation of matrix R of rotation vectors $r = \Lambda^{-1} A^t b$

of profiles of sources $B = A R$

of investment of sources $F' = R^{-1} F$

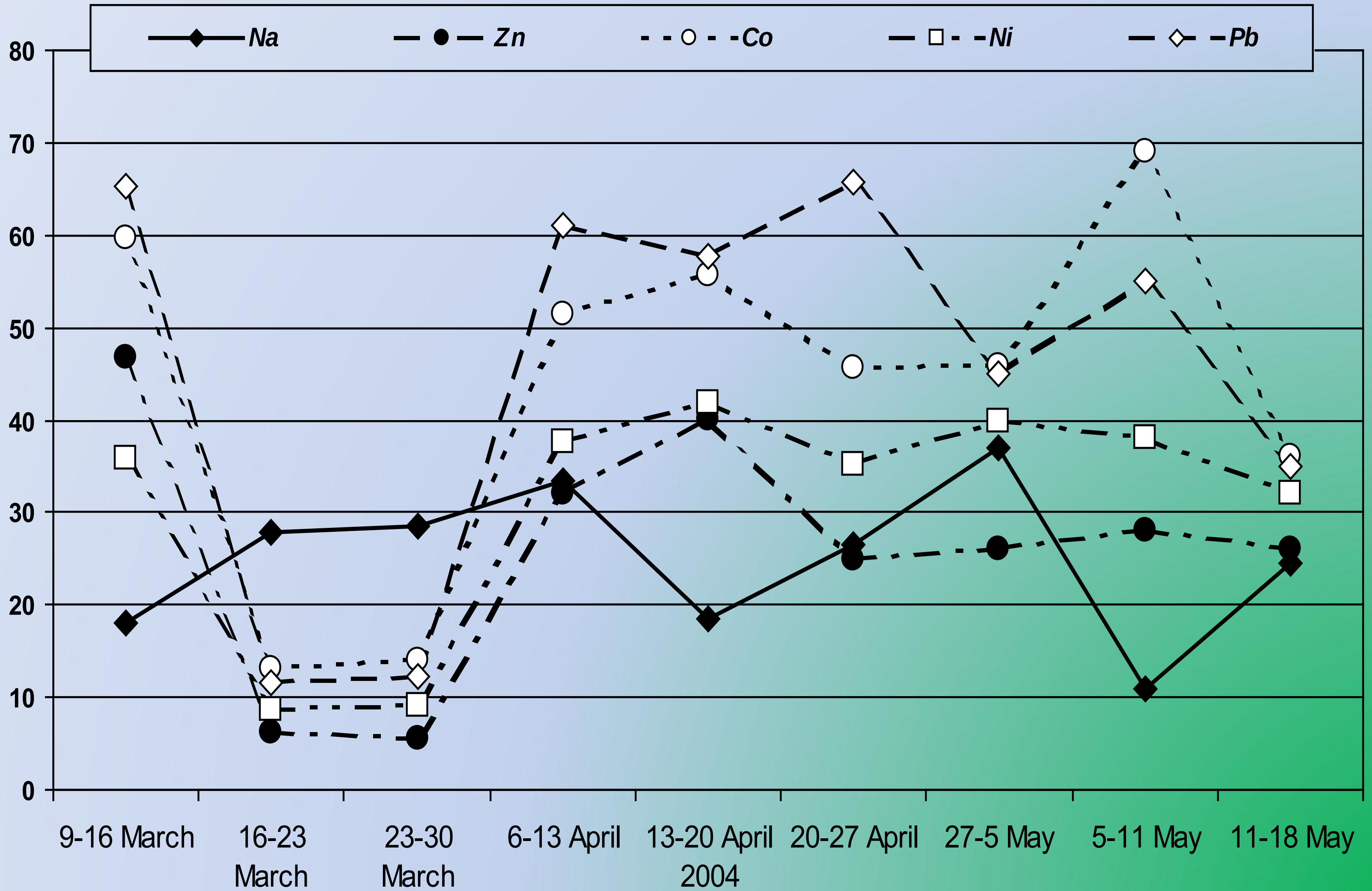
Concentration of elements in different natural sources (g/g of dry weight)

Element	Soil [8,10]	Clay and slates[8]	Sand-stones [8]	Carbo-nates [8]	Stone meteor ashes [8]	Volcanic ashes [9]	Fly ashes of burning plants [15]	Sea salt in drops after bubble bursting [20]
Na	6300	6600	3300	400	7000	16000	12000	307700
Mn	850	670	1	1100	2000	2000	6300	5,9
Fe	38000	33300	9800	3800	250000	23000	1400	590
Co	10	20	0,3	0,1	800	15	5	0,047
Ni	40	95	2	20	13500	---	90	---
Cu	20	57	1	4	100	270	420	5,7
Zn	50	80	16	20	50	780	5000	2800
Se	0,01	0,6	0,05	0,08	10	---	20	---
Ag	0,01	0,1	0,01	0,01	0,094	---	3	---
Cd	0,5	0,3	0,01	0,035	0,1	4	30	8,2
Sb	2	2	0,01	0,2	0,1	6,7	6	1,1
Cs	5	12	0,1	0,1	0,1	8,3	7,8	---
Ba	500	800	10	10	6	---	430	---
Hg	0,01	0,4	0,03	0,04	3	0,83	1,5	14
Pb	10	20	7	9	0,2	150	140	3,5

Mean concentration of elements in different anthropogenic sources (g/g of dry weight)

Ele-ment	Coal fly ash [12,14,16,17,18,19]	Fuel Fly ash [13,14]	Fly ash of burning of city waste products [11]	Ash of car exhaust [11,13]	Industrial aerosols [10,15]
Na	2800	5000	120000	270	8200
Mn	300	270	420	36	1200
Fe	76000	1000	5500	5500	29000
Co	48	230	10	1,8	13
Ni	180	3400	---	39	510
Cu	140	750	3600	190	1000
Zn	360	260	48000	1800	4000
Se	19	17	---	---	21
Ag	1,3	1	150	---	18
Cd	10	15	500	----	41
Ba	640	770	390	640	-----
Hg	0,85	0,06	----	-----	21
Pb	230	410	17000	120000	6200

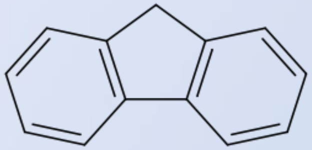
Temporal variation in the relative contribution of ash of coal (in %) to chemical composition of aerosols over the Vladivostok in 2004.



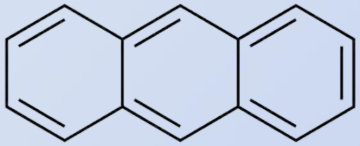
Точки отбора проб аэрозоля в регионе Восточной Азии.

4

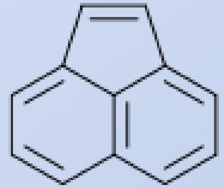
Polycyclic aromatic hydrocarbon in the aerosols over Vladivostok for 11 March – 17 June 2011



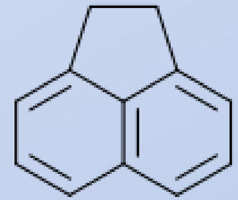
Fluorene



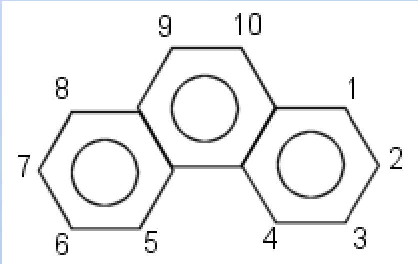
Anthracene



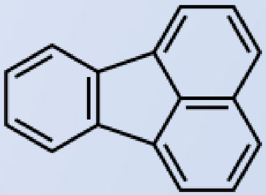
Acenaphthylene



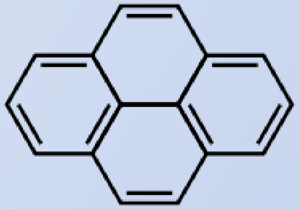
Acenaphthene



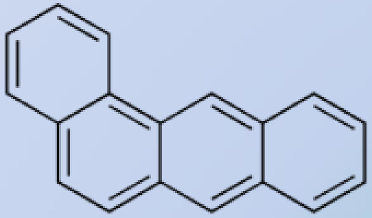
Phenanthrene



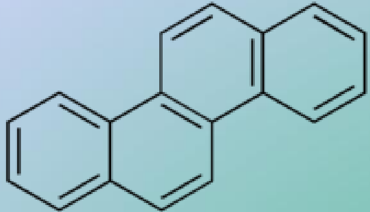
Fluoranthene



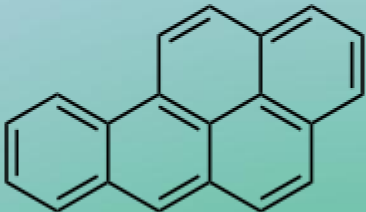
Pyrene



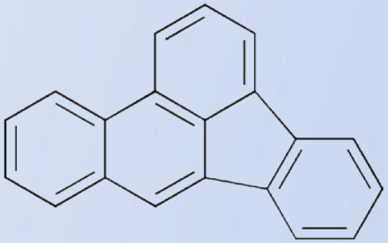
Benz(*a*)anthracene



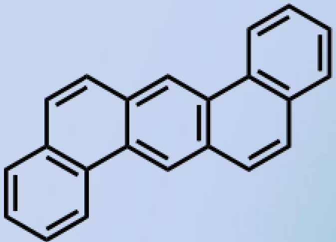
Chrysene



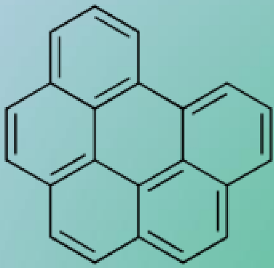
Benzo(*a*)pyrene



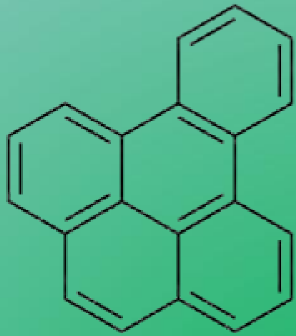
Benzo(*b*)fluoranthene



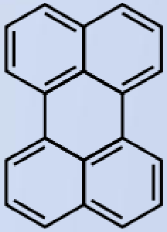
Dibenz(*a,h*)anthracene



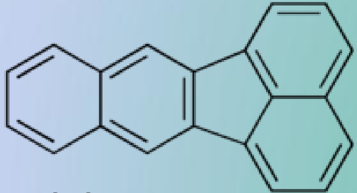
Benzo(*ghi*)perylene



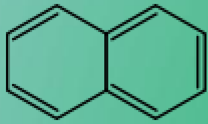
Benzo(*e*)pyrene



Perylene

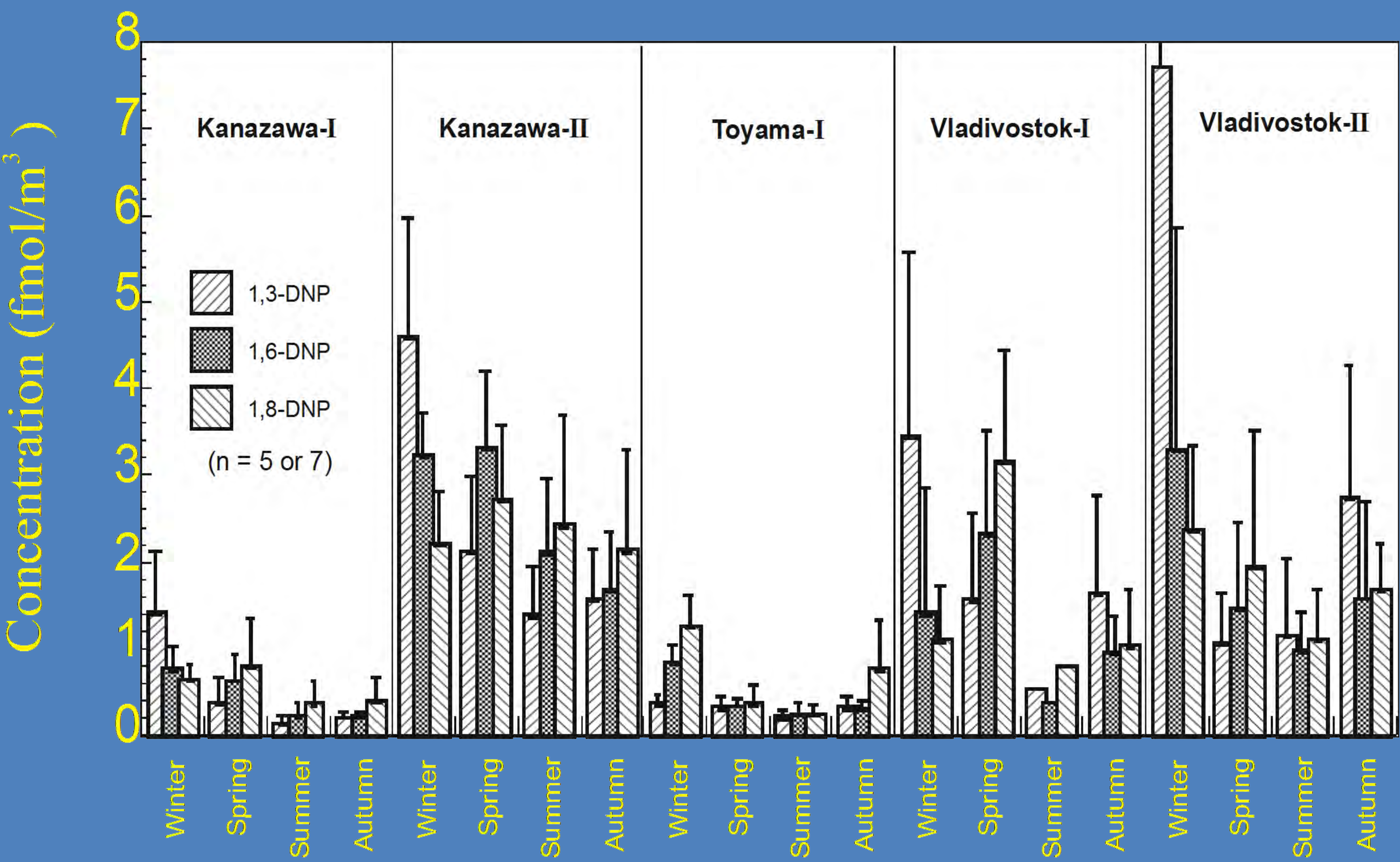


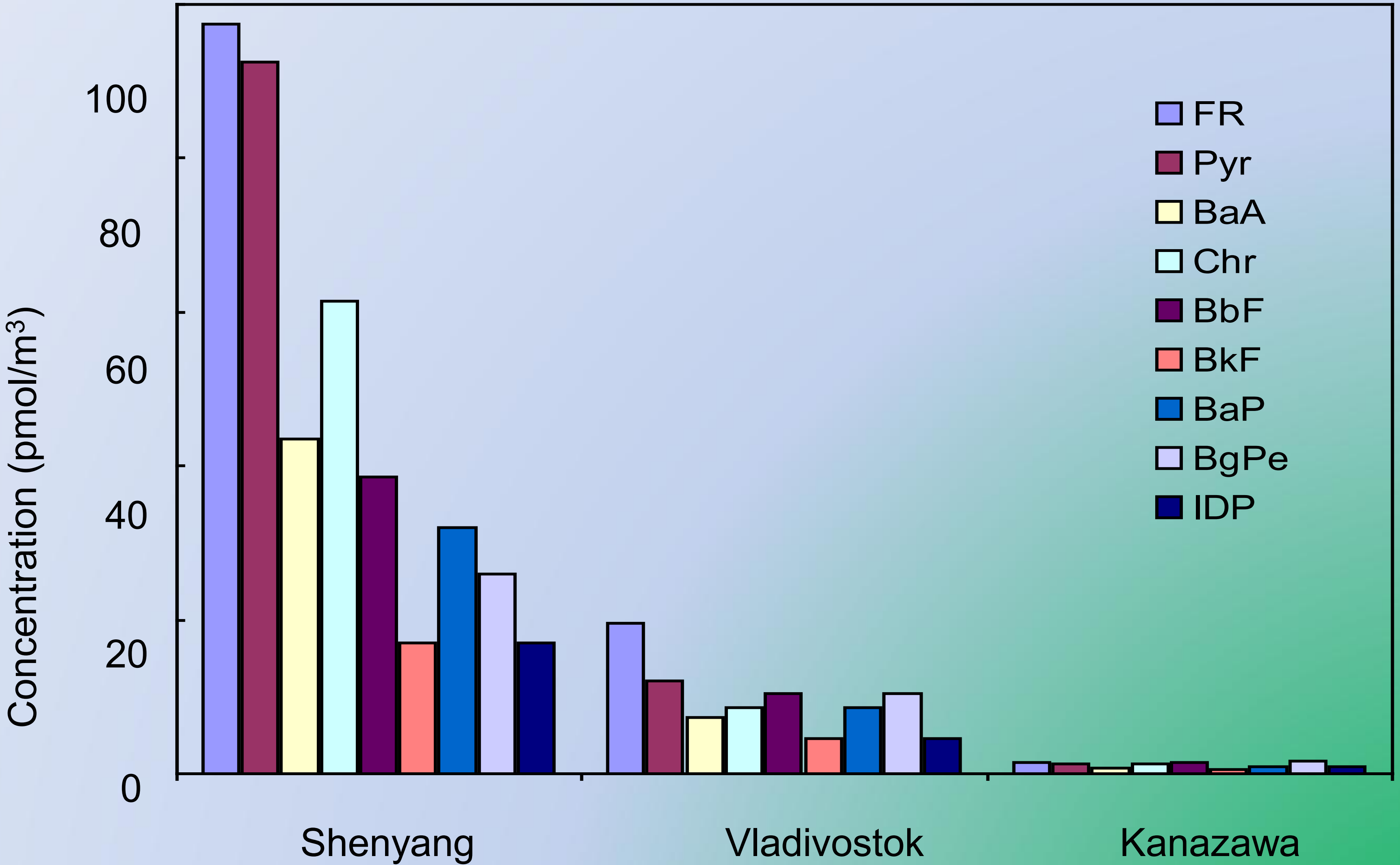
Benzo(*k*)fluoranthene



Naphthalene

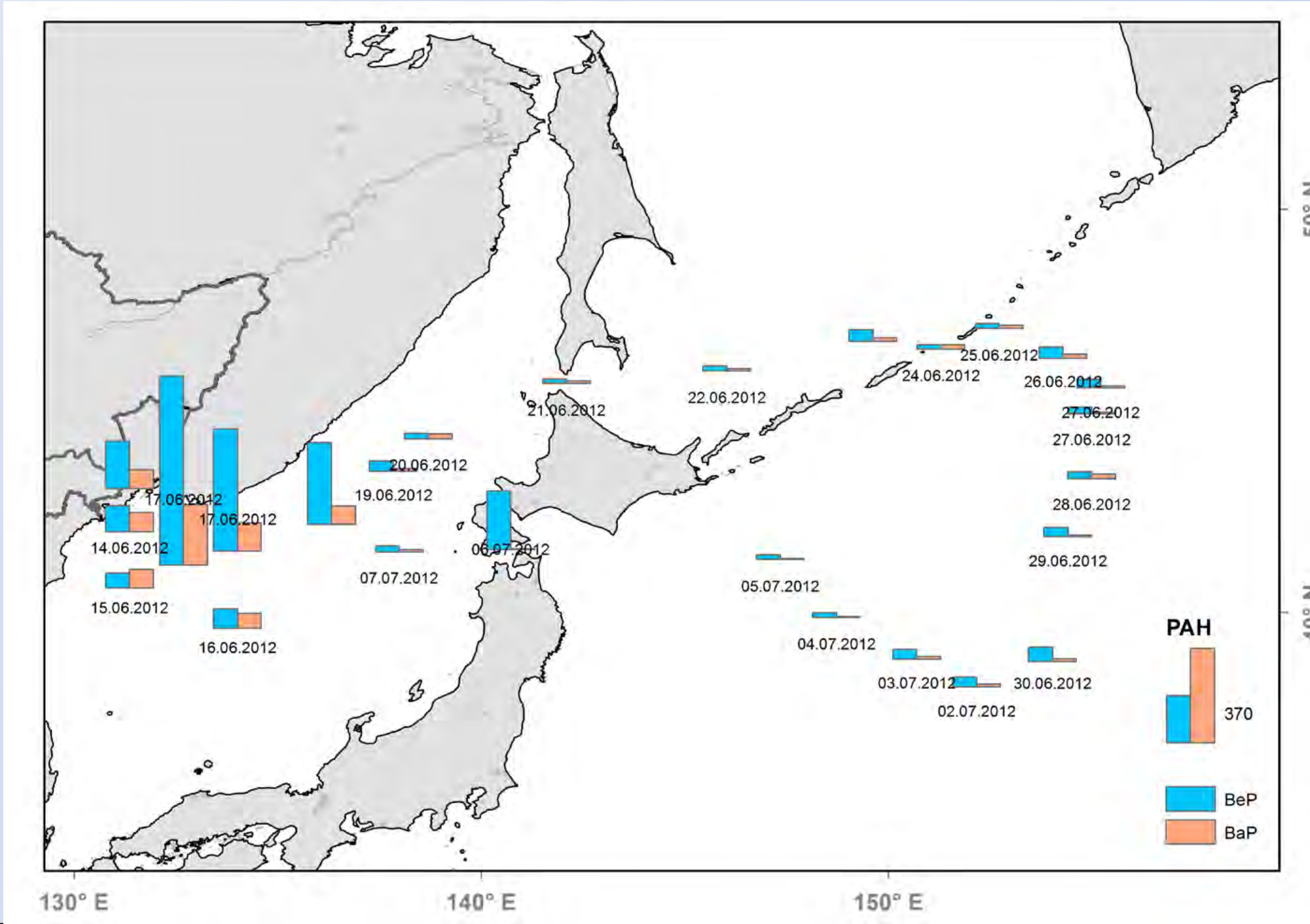
Seasonal variations of aerosol dinitropyrenes
Tang et.al., 2002



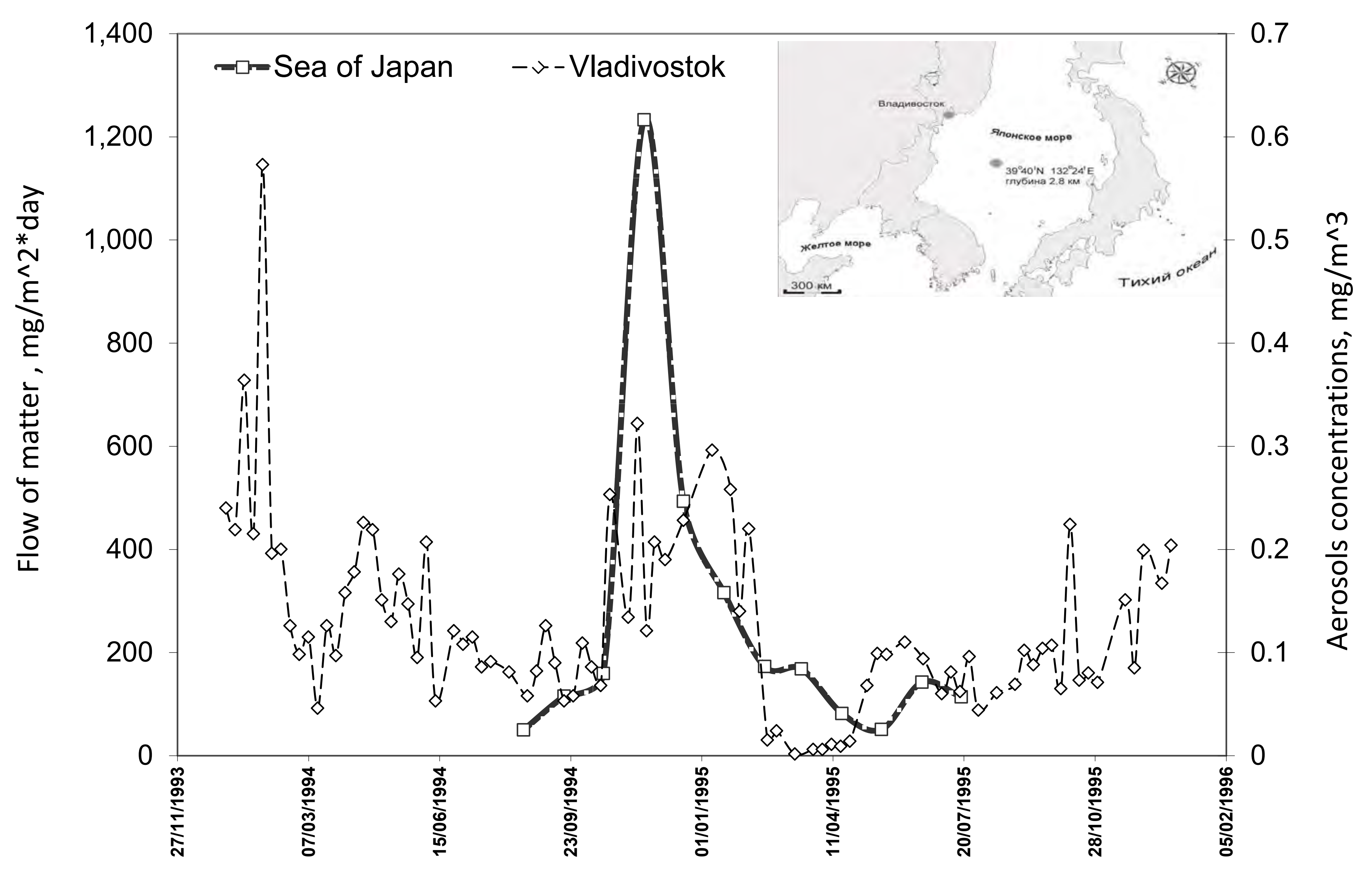


Atmospheric Concentrations of PAHs in Three Cities
Tang et.al., 2004

BeP and BaP in the particulate matter of sea water, Pg/L (2012)

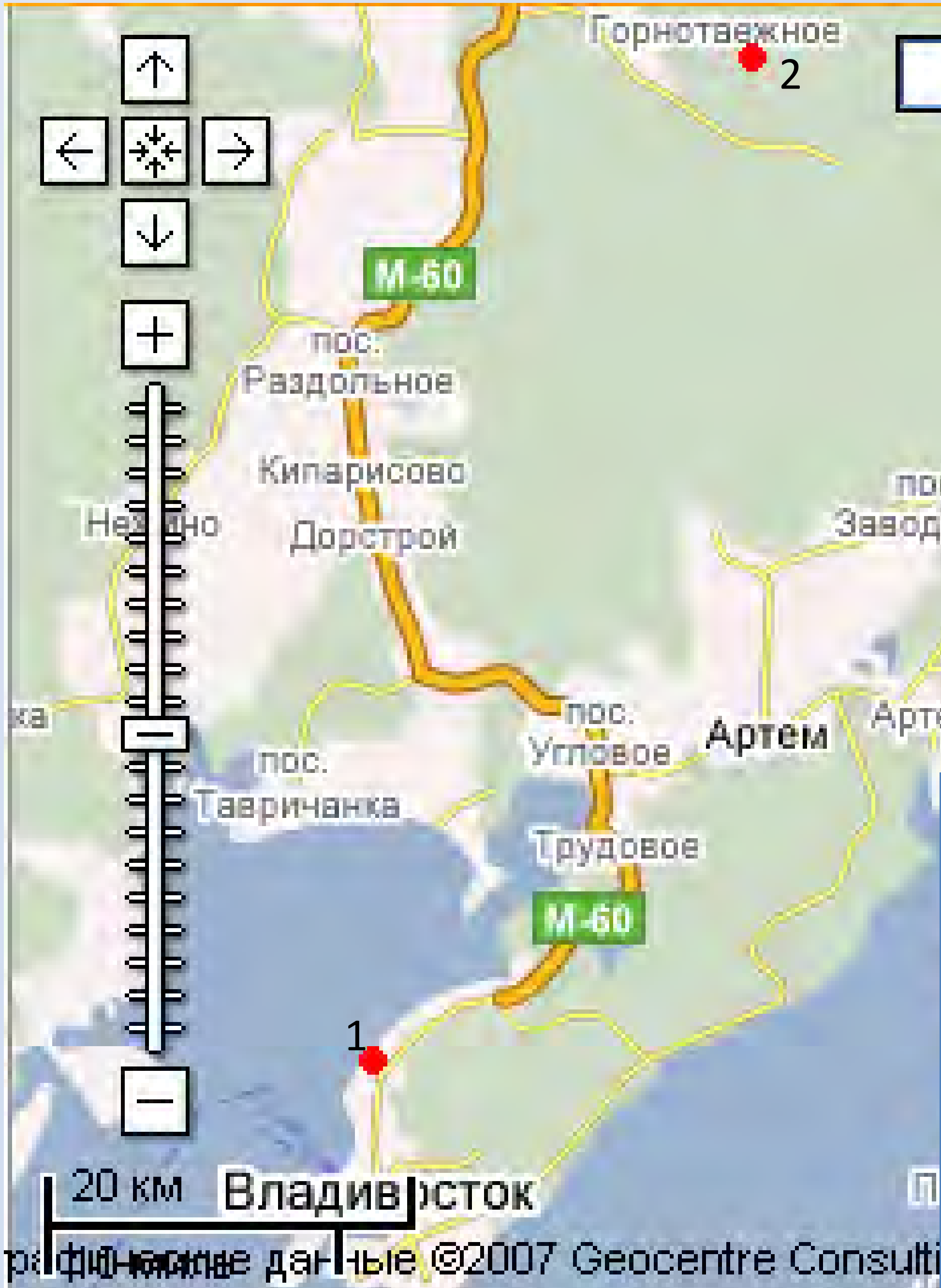


Interelation between aerosol concentration in atmosphere and particulate flow in deep water trap



Local atmospheric transboundary transport

Location of aerosol sampling station in 2006-2007



Местоположение:

1. г. Владивосток (район ж/д ост. Чайка)
2. п. Горнотаежное

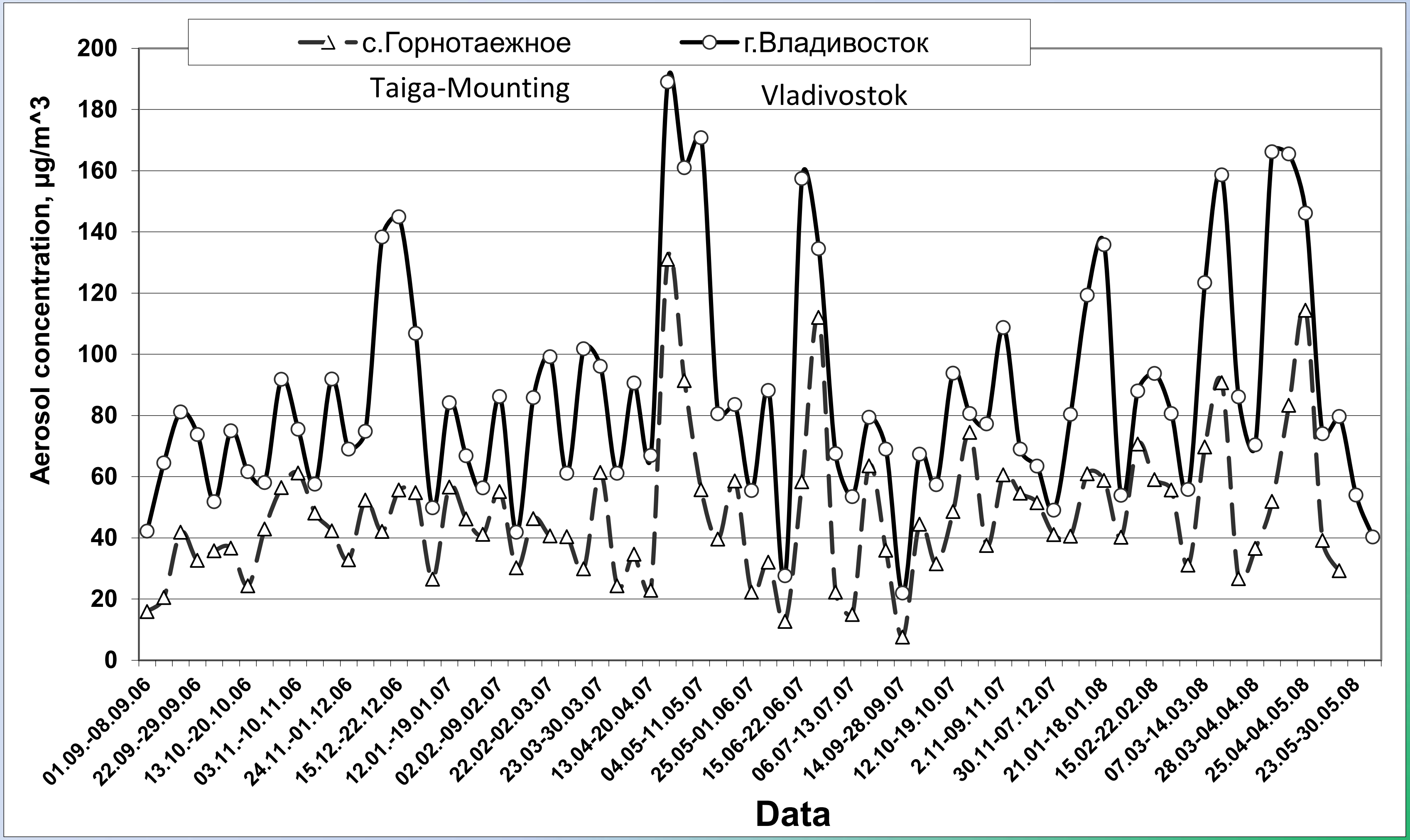
пробоотборники воздуха высокого объема (фирма Kimoto, Japan)

Скорость прокачки воздуха 700 л/мин

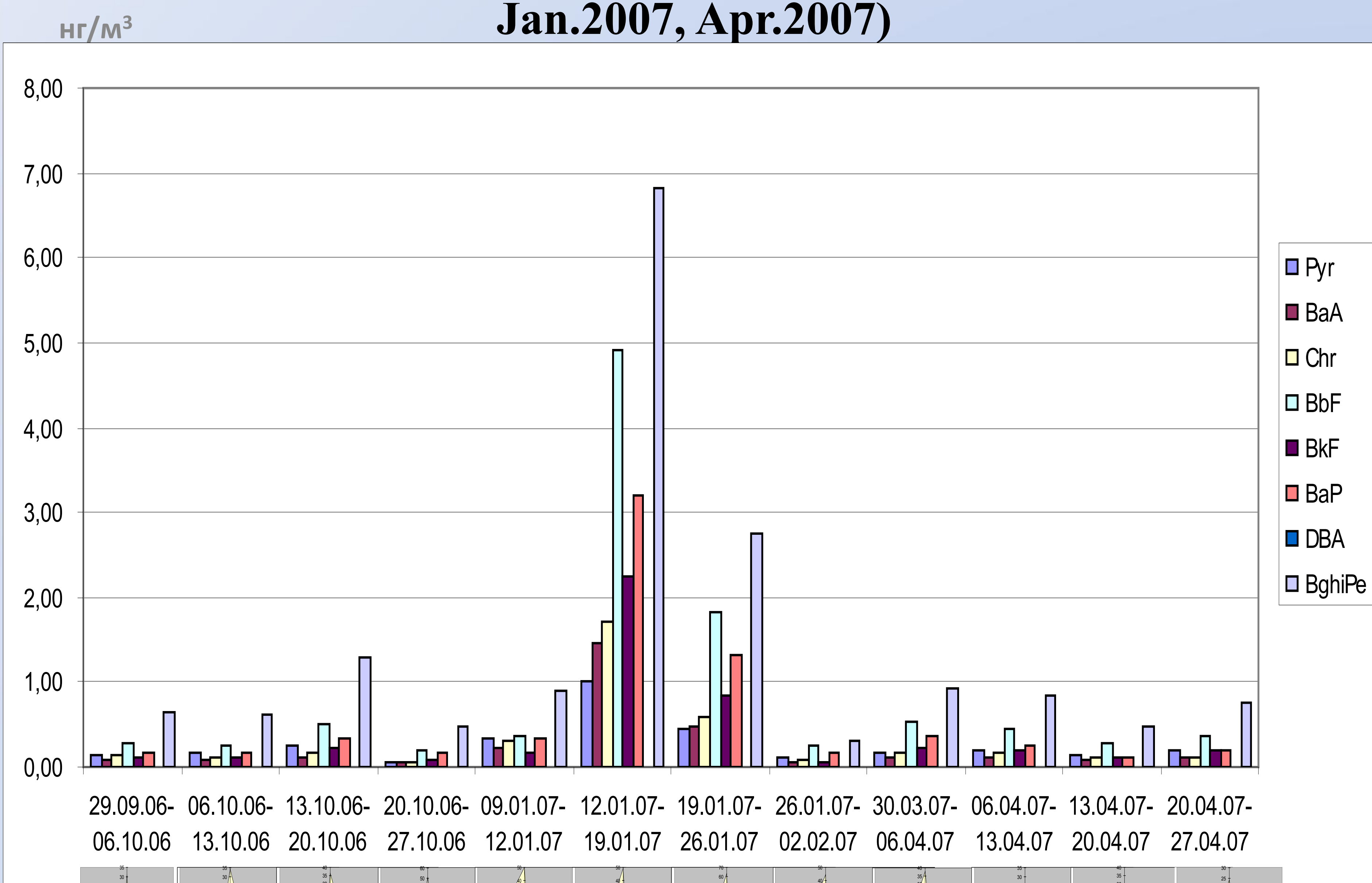
Фильтр : кварцево-волокнистые фильтры

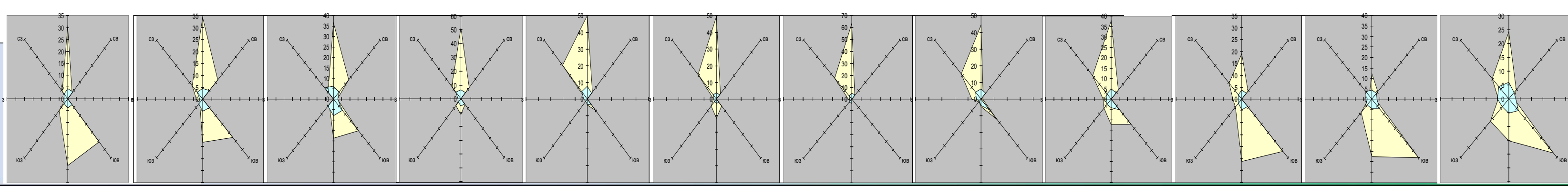
Период : октябрь 2006, январь, апрель 2007 (смена фильтров каждую неделю)

Aerosol concentration in background taiga-mounting St. and Vladivostok, 2006-2008.

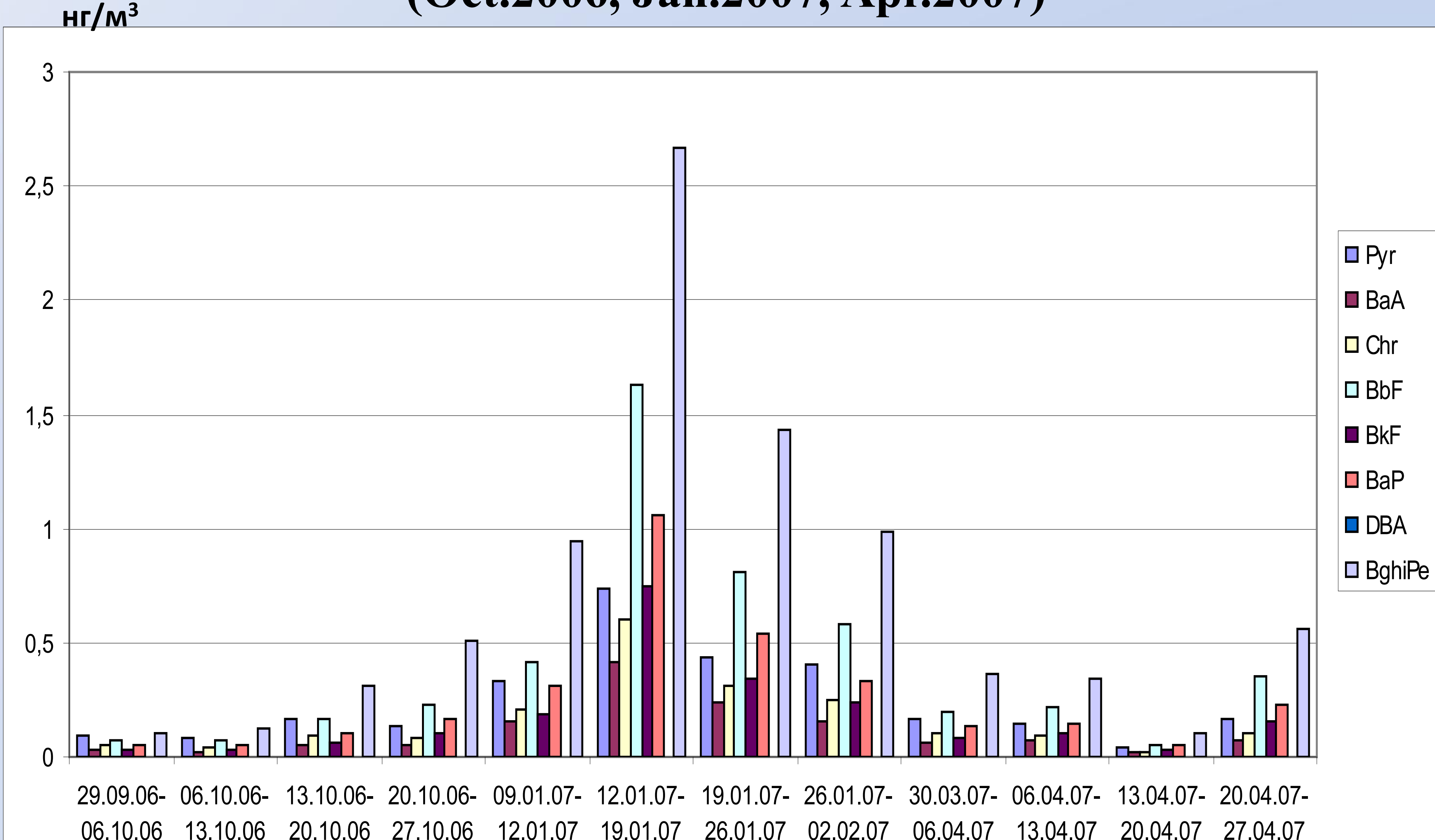


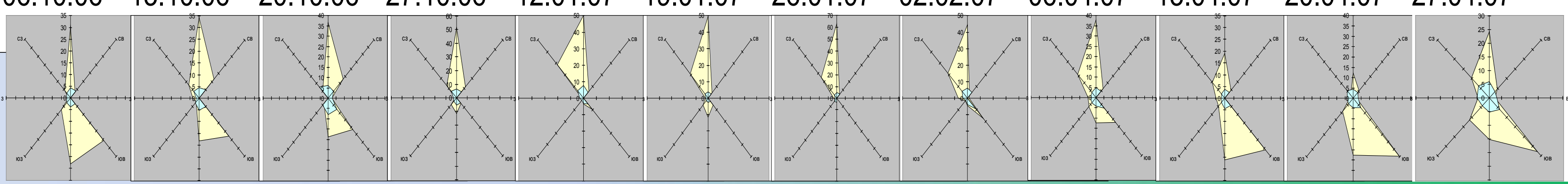
Concentration of PAH in atmosphere over Vladivostok (Oct.2006, Jan.2007, Apr.2007)



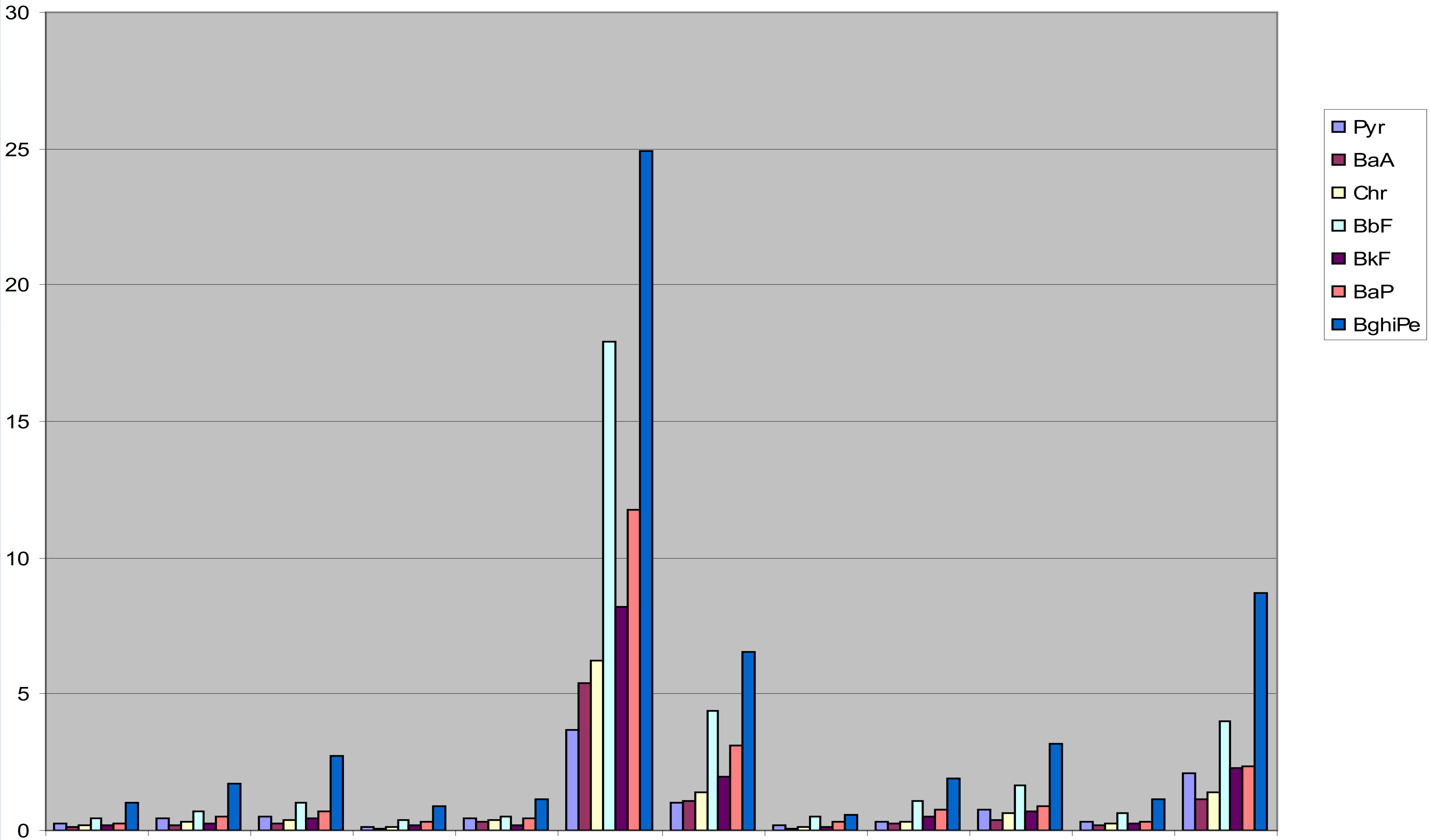


Concentration of PAH in atmosphere over taiga-mounting St. (Oct.2006, Jan.2007, Apr.2007)



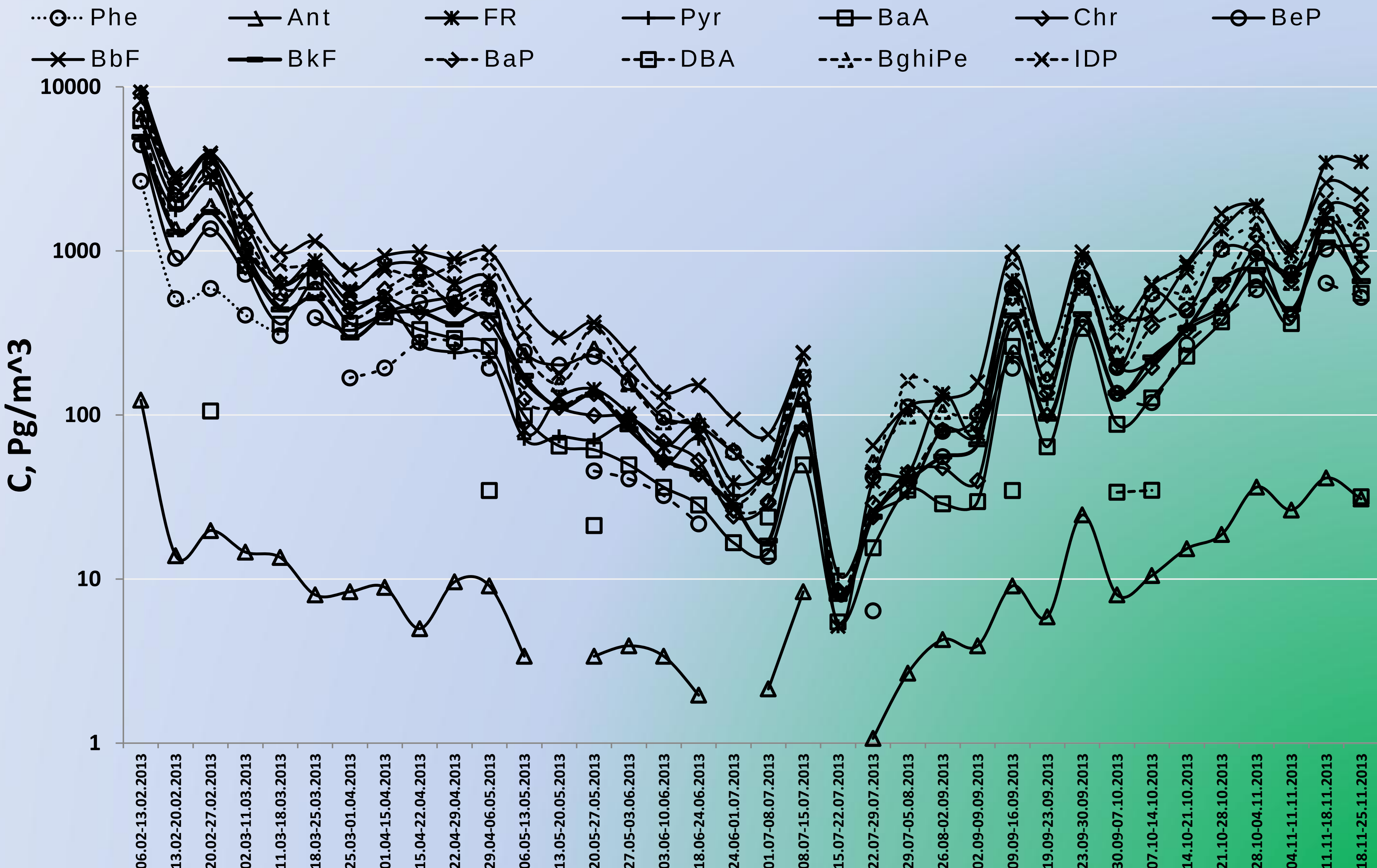


Fluxes of PAH on the sea surface of the Peter the Great, kg/day

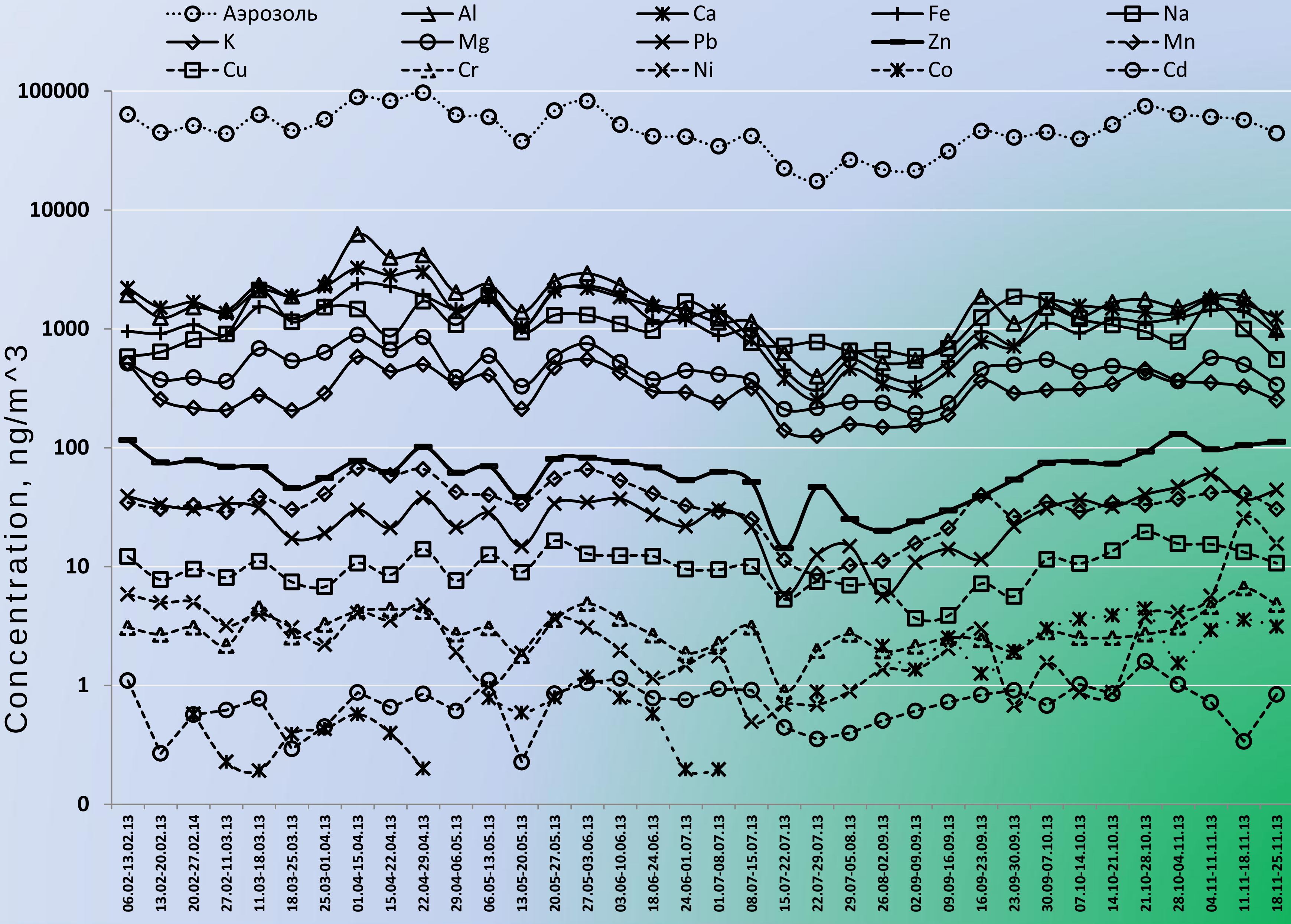


	29.09.06-06.10.06	06.10.06-13.10.06	13.10.06-20.10.06	20.10.06-27.10.06	09.01.07-12.01.07	12.01.07-19.01.07	19.01.07-26.01.07	26.01.07-02.02.07	30.03.07-06.04.07	06.04.07-13.04.07	13.04.07-20.04.07	20.04.07-27.04.07
Σ, кг	**2,54**	**4,17**	**6,01**	**2,06**	**3,35**	**78,10**	**19,54**	**1,87**	**5,18**	**8,21**	**3,06**	**21,96**

PAH’s concentrations in the Vladivostok (2013)



Element concentrations in aerosols over the Vladivostok (2013)



Корреляция ПАУ с макро- и микроэлементами (Владивосток)

	Пыль	Pyr	BaA	Chr	BbF	BkF	BaP	BghiPe	Fe	Mn	Cu	Zn	Cd	Pb	Co	Ni	Ca	Mg
Пыль	**1,00**																	
Pyr	0,09	**1,00**																
BaA	0,08	**0,99**	**1,00**															
Chr	0,06	**0,99**	**1,00**	**1,00**														
BbF	0,09	**0,97**	**0,99**	**0,99**	**1,00**													
BkF	0,11	**0,97**	**0,99**	**0,99**	**1,00**	**1,00**												
BaP	0,07	**0,97**	**0,99**	**0,99**	**1,00**	**1,00**	**1,00**											
BghiPe	0,09	**0,98**	**0,99**	**0,99**	**1,00**	**1,00**	**1,00**	**1,00**										
Fe	0,52	-0,27	-0,26	-0,26	-0,26	-0,24	-0,29	-0,25	**1,00**									
Mn	**0,65**	-0,18	-0,17	-0,18	-0,17	-0,15	-0,19	-0,17	**0,96**	**1,00**								
Cu	**0,64**	0,25	0,23	0,23	0,23	0,24	0,19	0,24	0,56	0,53	**1,00**							
Zn	0,16	**0,79**	**0,82**	**0,82**	**0,81**	**0,80**	**0,79**	**0,79**	0,18	0,26	0,32	**1,00**						
Cd	0,27	**0,90**	**0,92**	**0,92**	**0,91**	**0,92**	**0,90**	**0,91**	0,05	0,11	0,50	0,88	**1,00**					
Pb	0,06	**0,69**	**0,75**	**0,75**	**0,75**	**0,74**	**0,73**	**0,72**	0,00	0,04	0,28	0,90	0,80	**1,00**				
Co	**0,59**	-0,12	-0,10	-0,11	-0,08	-0,06	-0,11	-0,07	**0,96**	**0,94**	**0,66**	0,28	0,23	0,12	**1,00**			
Ni	0,52	0,17	0,14	0,14	0,11	0,12	0,08	0,10	**0,76**	**0,76**	**0,58**	0,44	0,32	0,24	**0,71**	**1,00**		
Ca	0,27	-0,30	-0,28	-0,28	-0,27	-0,26	-0,29	-0,27	**0,93**	**0,90**	0,32	0,21	-0,03	0,02	**0,88**	**0,64**	**1,00**	
Mg	0,11	-0,21	-0,19	-0,19	-0,19	-0,19	-0,21	-0,19	**0,85**	**0,82**	0,21	0,32	0,03	0,12	**0,79**	**0,60**	**0,97**	**1,00**

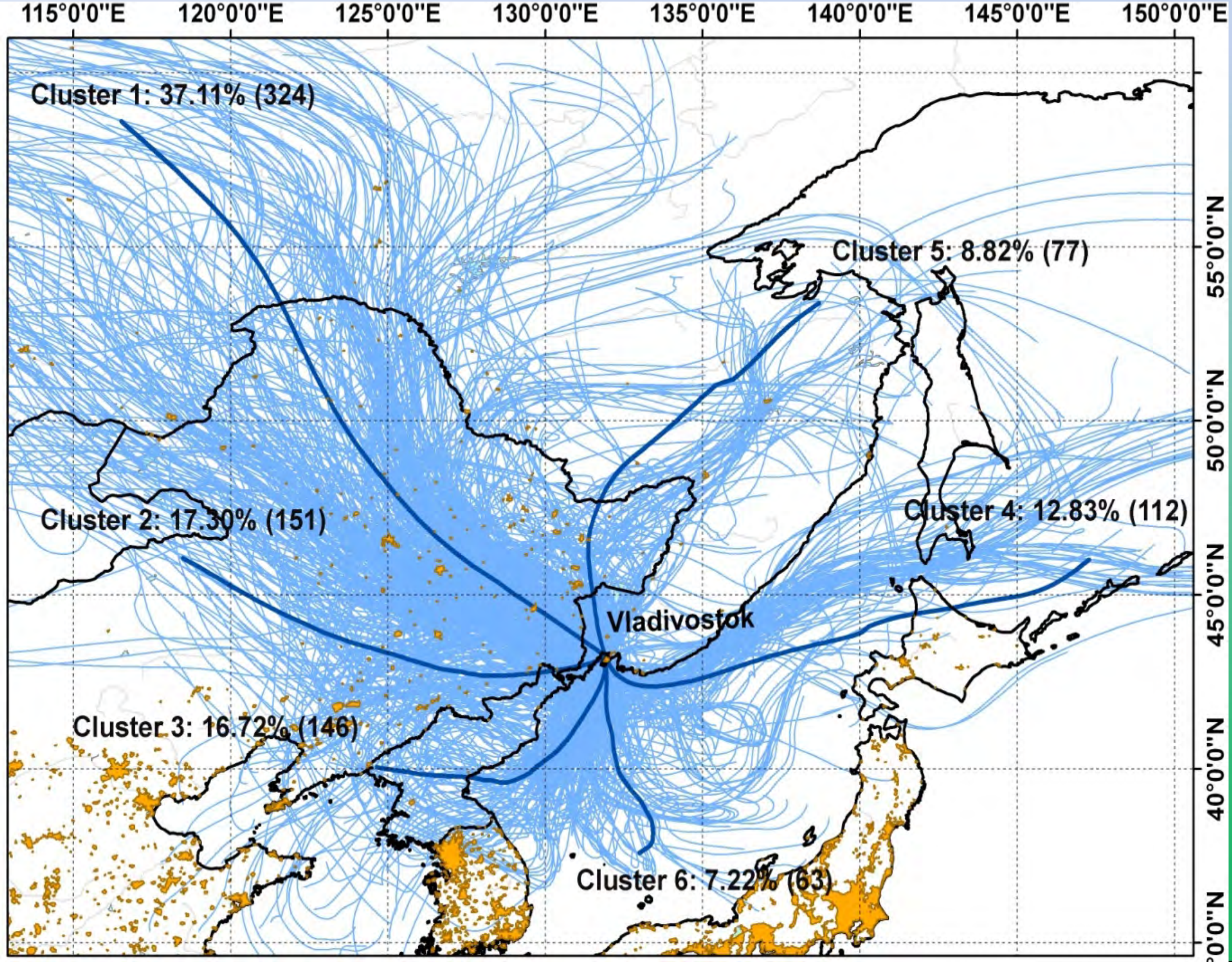
Корреляция ПАУ с макро- и микроэлементами (Горнатаежное)

	Пыль	Pyr	BaA	Chr	BbF	BkF	BaP	BghiPe	Fe	Mn	Cu	Zn	Cd	Pb	Co	Ni	Ca	Mg
Пыль	**1,00**																	
Pyr	0,16	**1,00**																
BaA	0,16	**0,99**	**1,00**															
Chr	0,16	**0,99**	**1,00**	**1,00**														
BbF	0,24	**0,97**	**0,99**	**0,99**	**1,00**													
BkF	0,25	**0,96**	**0,98**	**0,99**	**1,00**	**1,00**												
BaP	0,23	**0,97**	**0,99**	**0,99**	**1,00**	**1,00**	**1,00**											
BghiPe	0,22	**0,98**	**0,99**	**0,99**	**0,99**	**0,99**	**1,00**	**1,00**										
Fe	**0,96**	-0,03	-0,03	-0,04	0,04	0,05	0,03	0,02	**1,00**									
Mn	**0,97**	0,13	0,14	0,13	0,22	0,23	0,21	0,20	**0,96**	**1,00**								
Cu	0,55	0,33	0,36	0,36	0,43	0,44	0,41	0,37	0,49	**0,60**	**1,00**							
Zn	-0,01	0,34	0,30	0,33	0,31	0,30	0,27	0,28	-0,11	-0,09	0,23	**1,00**						
Cd	**0,64**	**0,67**	**0,70**	**0,71**	**0,76**	**0,77**	**0,75**	**0,72**	0,54	**0,68**	**0,68**	0,29	**1,00**					
Pb	0,49	0,52	0,56	0,55	**0,59**	**0,61**	**0,58**	0,55	0,46	0,57	**0,74**	0,30	**0,83**	**1,00**				
Co	**0,87**	0,12	0,13	0,12	0,19	0,20	0,17	0,15	**0,90**	**0,89**	**0,75**	0,06	**0,62**	**0,69**	**1,00**			
Ni	**0,64**	0,37	0,38	0,34	0,34	0,35	0,36	0,38	**0,60**	**0,60**	0,28	0,03	0,47	**0,59**	**0,62**	**1,00**		
Ca	**0,93**	-0,07	-0,09	-0,09	-0,02	-0,02	-0,04	-0,05	**0,95**	**0,88**	0,42	0,05	0,45	0,31	**0,83**	0,51	**1,00**	
Mg	**0,95**	0,03	0,00	0,01	0,07	0,08	0,06	0,05	**0,98**	**0,94**	0,50	0,07	0,57	0,49	**0,89**	**0,62**	**0,96**	**1,00**

- In 2006-07 Zn, Cd & Pb from pollution sources well correlated with PAHs in Vladivostok. In background taiga-mounting station this correlation was observed only for Cd.
- In 2013-14 PAHs well correlated with Zn, Pb & Ni.

- We analyzed the origin of incoming air masses to the sampling site by computing 72-h kinematic back-trajectories starting at 0, 3, 6, 9, 12, 15, 18 and 21 UTC each day. They were evaluated for the altitude of 100m using the Hybrid Single Particle Lagrangian Integrated Trajectory (Hysplit, version 4.9) model (Draxler and Rolph, 2003) with the GDAS1 (Global Data Assimilation System) global analysis meteorological data provided by NCEP (National Weather Service's National Center for Environmental Prediction) database as developed by the NOAA's Air Resources Laboratory (ARL) (Draxler 1999).
- It was shown that spatial error in location of trajectory points is about 20% of their traveled distance (Stohl, 1998). By using larger number of trajectories we can reduce influence of random spatial errors. We then used trajectory cluster analysis to obtain aggregate information about possible directions of aerosol transport (Dorling et al., 1992; Sirois and Bottenheim, 1995). K-means (MacQueen, 1967) is one of the simplest unsupervised learning algorithms that solve the well-known clustering problem. The most commonly used one is Euclidean distance and a clustering method based on it is implemented in NOAA Hysplit software package. Another way to measure distance is angular distance that is more appropriate if the most important trajectory parameter is its direction and not the wind speed (Sirois and Bottenheim, 1995).

6 clusters of air mass backward trajectories for Vladivostok. Thin lines are individual trajectories, dotted lines are cluster means. Industrial regions are marked by orange color.



The PAH's correlation with meteorological parameters in 2013.

	Phe	Ant	Flu	Pyr	BaA	Chr	BeP	BbF	BkF	BaP	BPe	IDP
H2O mixing ratio(max), g/(kg dry-air)	-0.55	-0.48	-0.60	-0.61	-0.56	-0.58	-0.56	-0.59	-0.57	-0.54	-0.56	-0.53
Sun Flux max, w/m^2	-0.57	-0.61	-0.68	-0.61	-0.51	-0.57	-0.59	-0.59	-0.55	-0.50	-0.59	-0.54

CONCLUSIONS

- Indicated results show that on formation of atmospheric aerosols near the Vladivostok largely influence global atmospheric transport, which was observed in winter-spring period. In these periods occur inputs of an atmospheric dust from east and central regions of an Asian continent. This global atmospheric transport gives inputs of macroelements from natural sources (clay, Earth's crust and soil).
- Coal fly ash is the main anthropogenic source for atmospheric environment near the Vladivostok, which can contribute to aerosol content up to 60-70 % of Pb and Co and up to 40 % of Ni and Zn.
- Atmospheric inputs with rain and snow transport elements mainly in dissolved form.
- Atmospheric inputs influence on chemical composition of seawater of coastal zone of Vladivostok.

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Thank you for attention