UNIVERSITÉ DE BORDEAUX

THE MALIN FALKENMARK SEMINAR: EMERGING POLLUTANTS IN WATER RESOURCES
STOCKHOLM, SWEDEN, 5 SEPTEMBER 2010

EMERGING POLLUTANTS IN RIVERS OF EASTERN UKRAINE: MONITORING, ENVIRONMENTAL RISK ASSESSMENT AND SOCIO-ECONOMIC ISSUES

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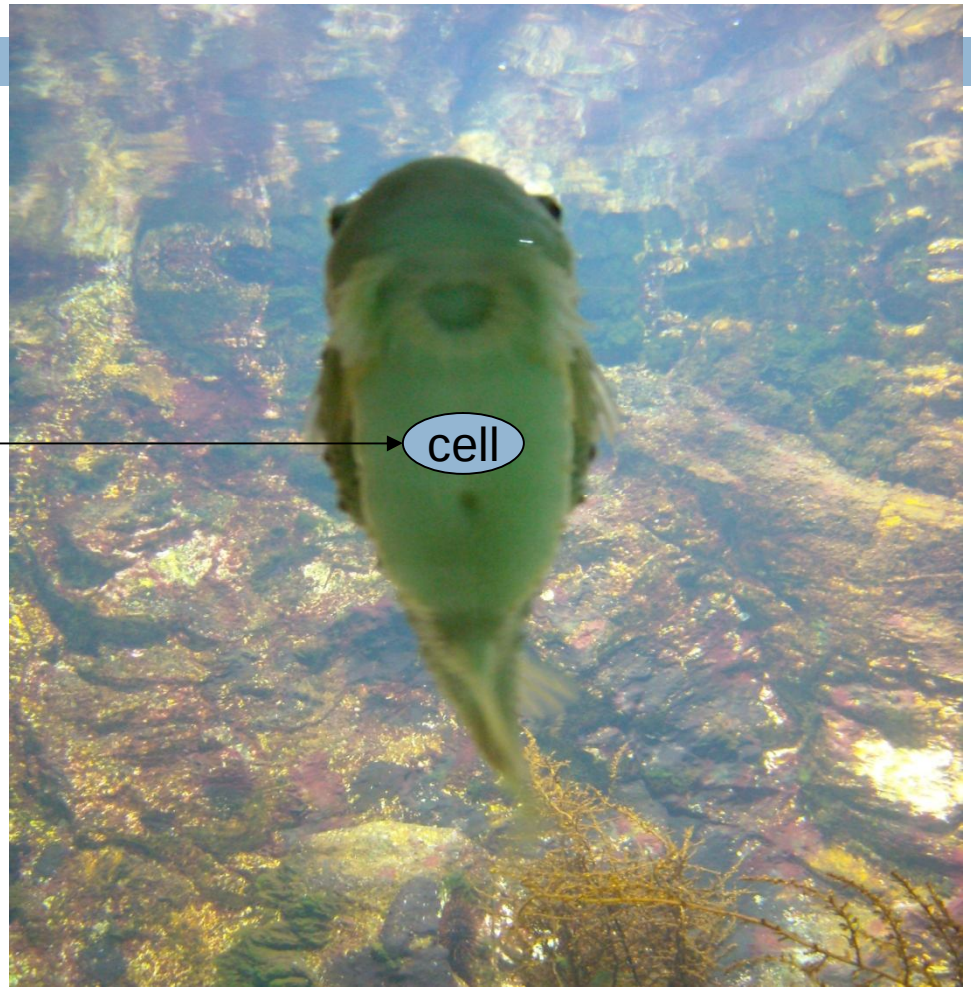
EMERGING POLLUTANTS

- *Emergent (emerging) contaminants (pollutants)* are non-regulated or very partly regulated and mostly non incorporated in the relevant environmental legislation, but they have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects (Kuster et al, 2006; Hanicke et al, 2007).
- Most *emerging pollutants* are man-made organic and nonorganic chemicals introduced into the environment by anthropogenic inputs (Zhang et al, 2008).
- Increasing standards of living, economic changes and human population growth lead to increased usage of various chemicals in households, office, industries, agriculture.
- More new pollutants will be found in nearest future with further development of analytical methods.

BIOACCUMULATION

Cu, Ni, Zn, Pb, Co, Cd, Cr …
+
PPs



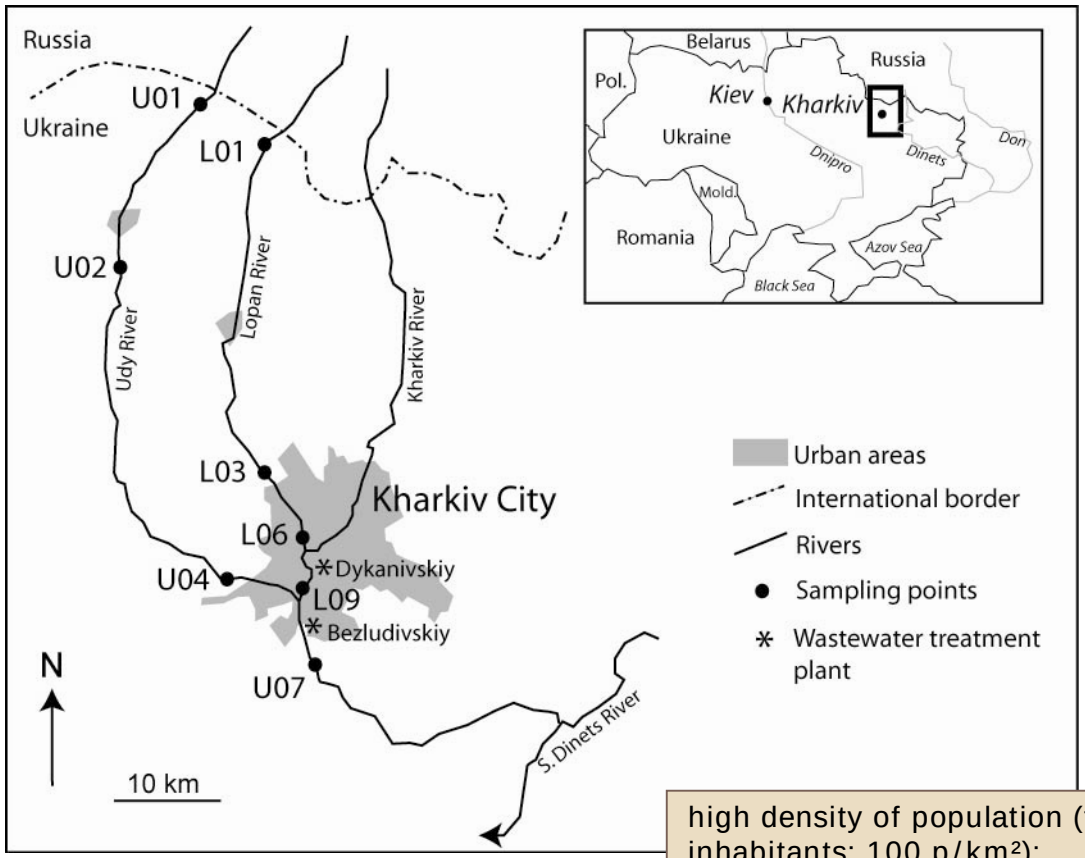
OBJECTIVES

- What trace metals and pharmaceuticals are present in the two transboundary rivers of Eastern Ukraine?
- Which technologies for the identification of emerging pollutants are efficient for the pilot water monitoring?
- Are there any environmental and health risks caused by the presence of emerging pollutants in surface waters of Ukraine?
- What relation between socio-economic indicators and emerging pollutants in water?
- How the water quality data can be use for the socio-economic studies?
- What strategy can be proposed for the development of the water monitoring system taking into account emerging pollutants issues?

WATER MONITORING IN EASTERN UKRAINE

- The water quality of surface water in Ukraine does not meet national water quality standards and classified as 'polluted' or 'extremely polluted'– uncontrolled wastewater discharge is one of the reason (National Report on the Drinking Water Quality in Ukraine, 2009)
- Ukraine still use the old Soviet system of water monitoring and water quality standards
- The monitoring of trace elements, emerging pollutants and others in Ukraine is yet insufficient (lack of equipment and financing for research laboratories and environmental control authorities)
- International legislation on the regulation of transboundary watersheds is underdeveloped and has poor practical implementation in some cases
- Environmental information and data on water quality are publishing in some national reports (National Report on Environmental Status; National Report on the Drinking Water Quality), but very limited, unavailable to the major part of the society and coming with significant delay (2-3 years)

THE STUDY AREA – the Kharkiv region (Eastern Ukraine)



high density of population (total 2,8 mln. inhabitants; 100 p/km²);
urban (78%) and rural (22%) settlements;
industry (engineering and chemical industries, food production) and agriculture;
water scarce region (3,41 km³ per year);

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METHODS

1. **Standard sampling** of the water– to obtain data on major ions and dissolved metals and its correlation with labile forms;
2. **Passive sampling** – to get information on the presence of labile forms of trace metals (DGT) and pharmaceuticals (POCIS) as the most toxic for living organisms in rivers;
3. **Sediments analysis** – to add data on the deposition of metals in the sediments as potential source of secondary pollution of water;
4. **Statistical tools** – to analyze the origin, behavior and variations of trace metals and pharmaceuticals in water; determine the zones of pollution; process regional social and economic indicators;
5. **Mathematical modelling** – to process the environmental, social and economic data of water pollution by emergent pollutants

THE MONITORING (2008-2010) – grab method or passive technique?

- **Grab method** – ions, dissolved metals, sediments

- **Passive technique** – labile metals (diffusive gradient in the thin film – DGT) and pharmaceuticals (polar organic chemical integrated sampler – POSIC) in the water

DGT (diffusive gradient in the thin film)

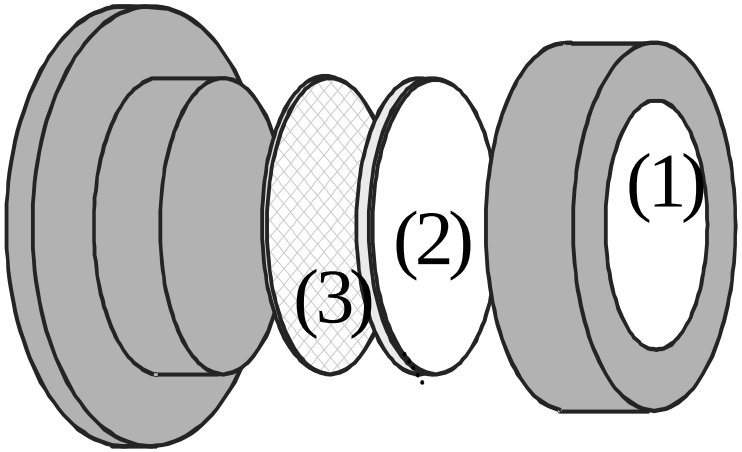


Figure 1. The Diffusive Gradient in Thin film devices (DGT) include the probe plastic housing (1) filter (2) diffusive gel and (3) resin gel layers

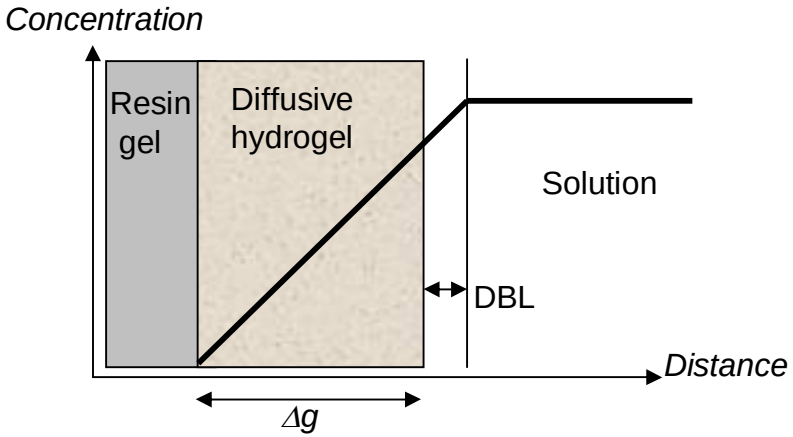
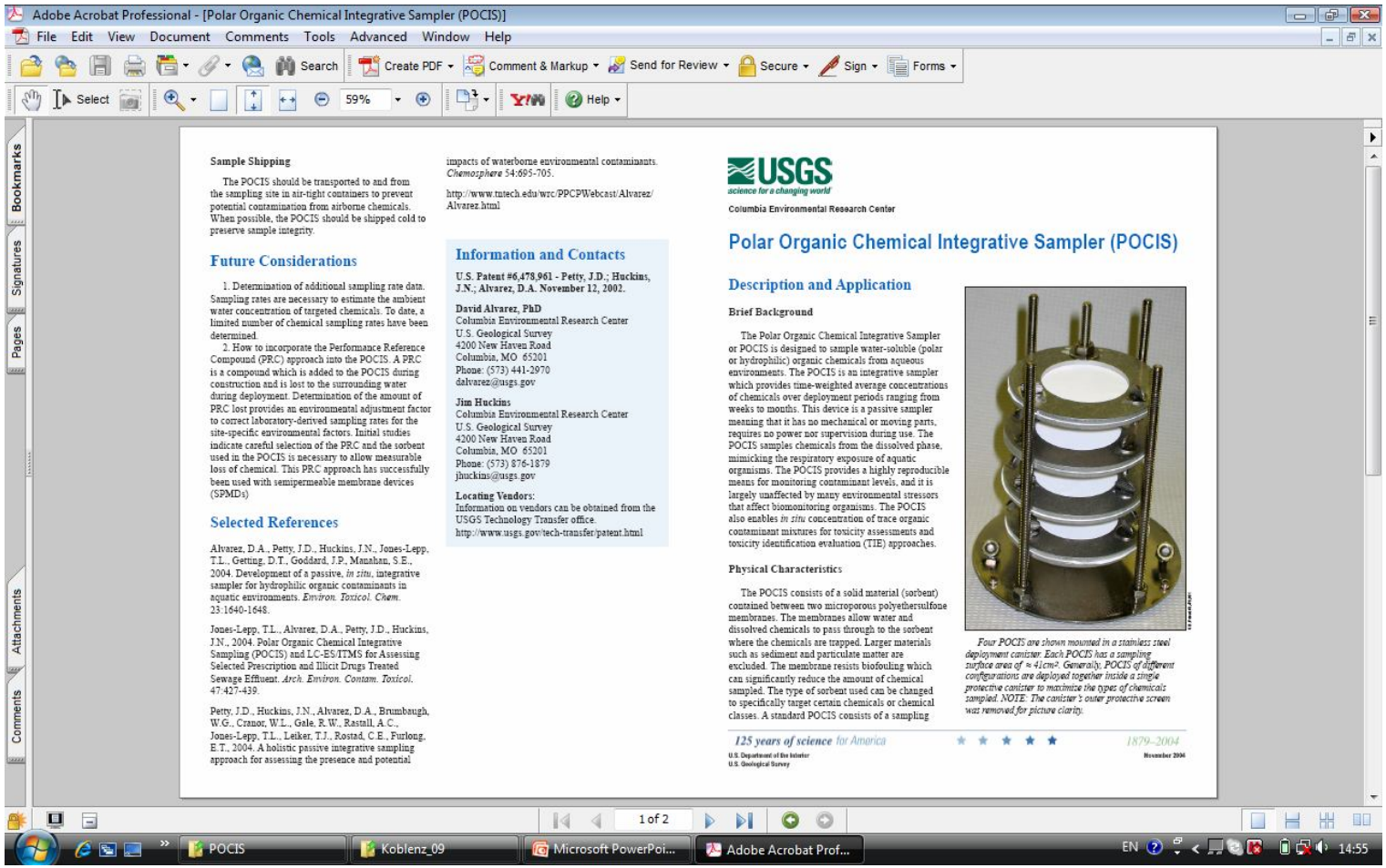


Figure 2. Principle for mercury accumulation and measurement with the DGT device. *DBL*: diffusive water boundary layer at the sampling surface of the device.

Polar Organic Chemical Integrative Sampler (POCIS)



THE MONITORING – IN THE FIELD (2008-2010) – not so easy in winter

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THE MONITORING – IN THE FIELD (2008-2010) – ….not so easy in summer

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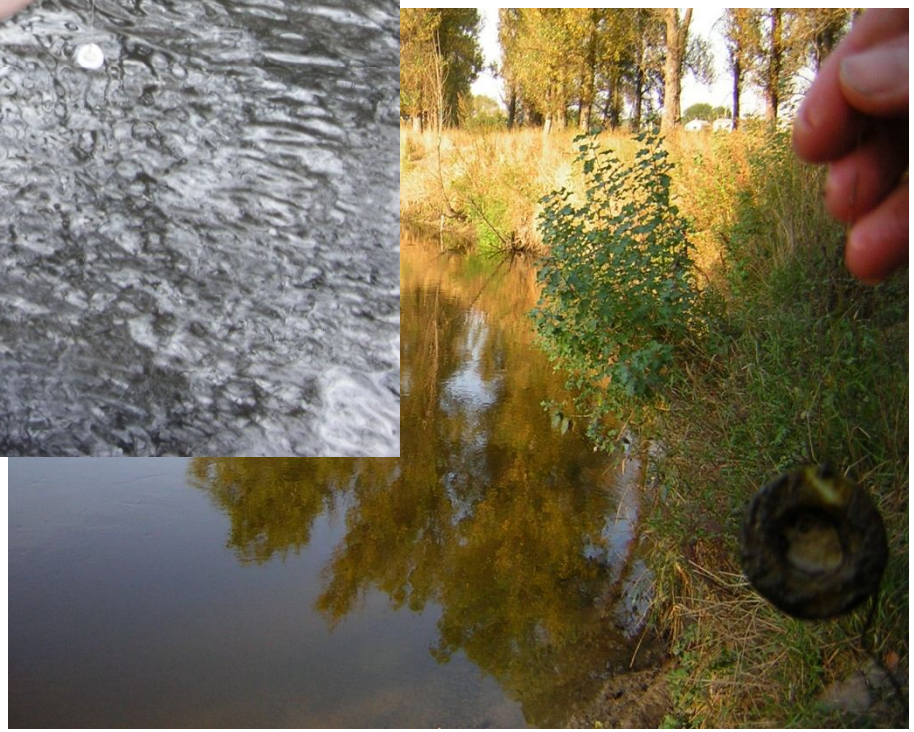
THE MONITORING (2008-2009) – limitation of the passive technique



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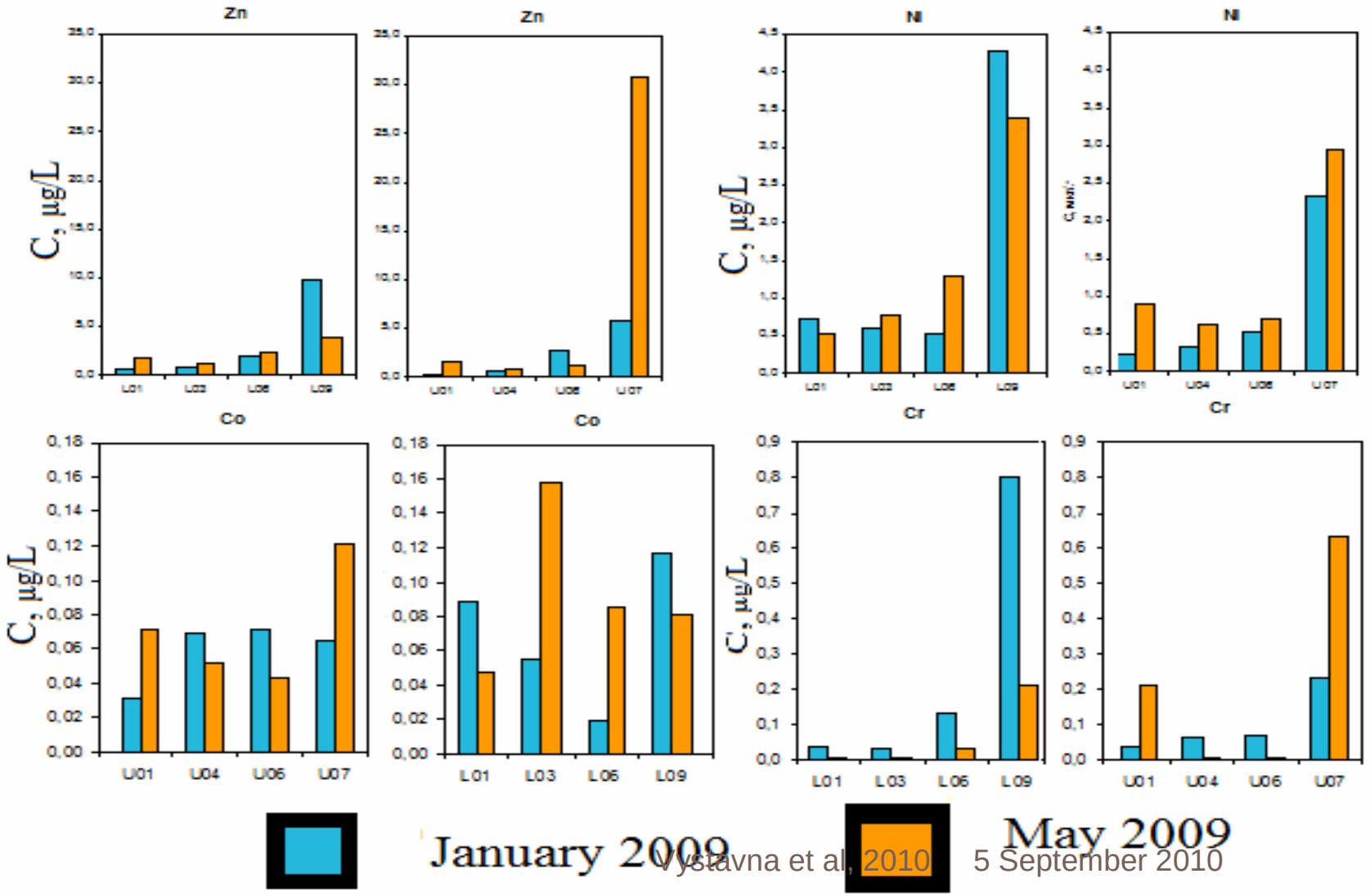
TRACE METALS IN WATER AND SEDIMENTS OF UDY AND LOPAN RIVERS

- Priority trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn)
- Urban tracer (Ag)
- and potentially toxic elements - Co, Mo, V and Th

TWO GROUPS OF ELEMENTS

- (1) Anthropogenic components (associates with anthropogenic sources) – Ag, Cd, Cr, Cu, Hg, Ni, Pb and Zn - form geochemical anomalies in the urban area
- (2) Natural regional components – Co, V, As and Mo - presents in low range concentration and mostly links to the regional geological baseline.

RESULT 1. LABILE METALS CONCENTRATION (µg/L) MEASURED WITH THE DGT METHOD IN THE LOPAN AND THE UDY RIVERS



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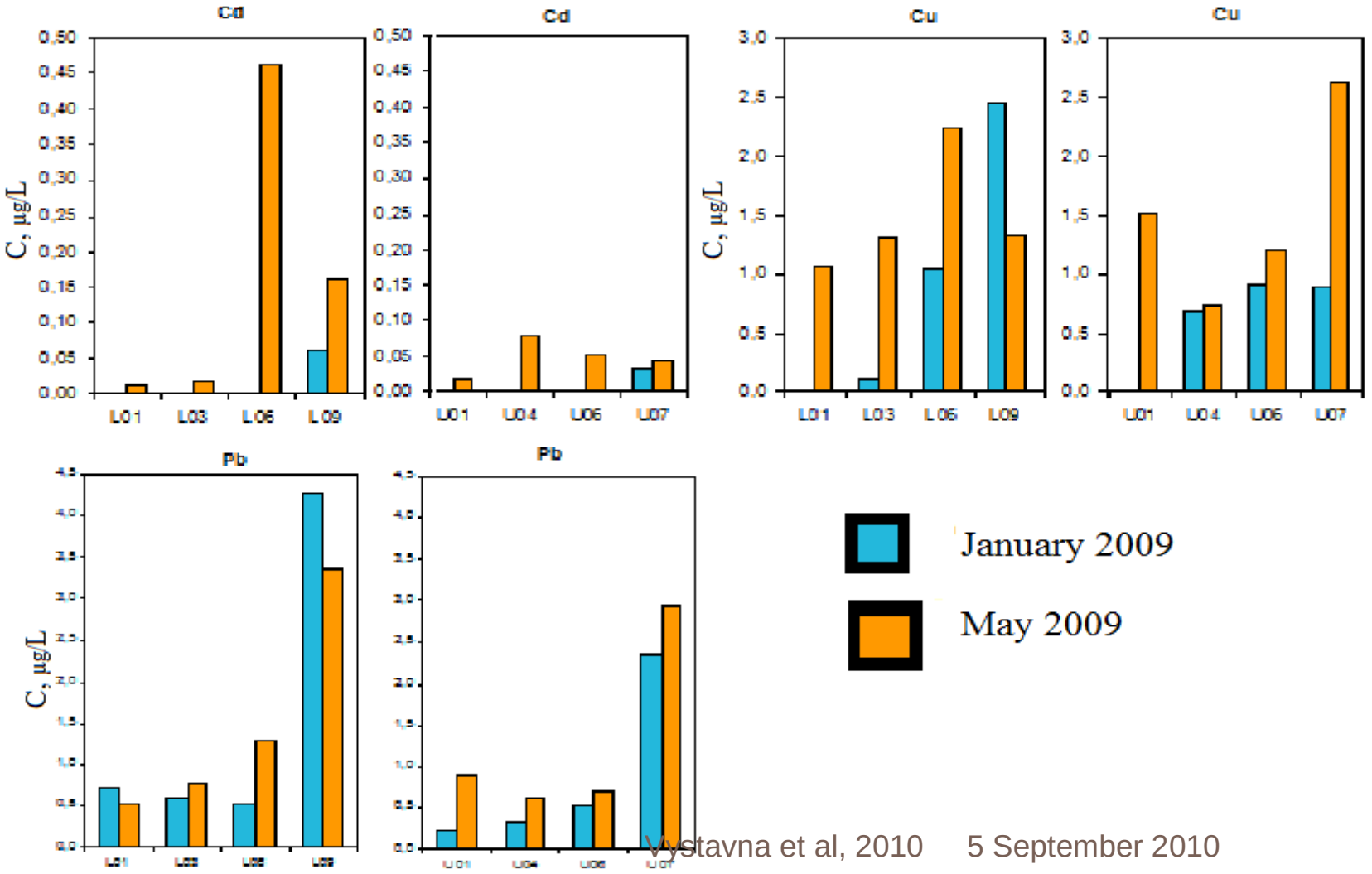


RESULT 2. HEALTH RISK ASSESSMENT OF THE SEDIMENTS (mg/kg) IN THE LOPAN AND UDY RIVERS

	Cd	Cr	Cu	Pb	Ni	Zn	Zs	Health risk* Saet 1990
Lopan River								
Upstream city	0,32	44	15,6	19,9	21,1	59,8	11	Moderate
City Centre	0,56	25,7	60,4	54,4	31,7	136	29	Significant
Urban WWTP	6,45	219	97,9	46,6	31,8	291	235	Very high
Udy River								
Upstream city	0,06	11,4	3,1	5,8	3,9	8,3	2	Moderate
City centre	0,72	54,2	21,5	19,8	18,9	91,7	30	Significant
Urban WWTP	3,42	114	101	13,1	13,5	76,5	118	Dangerous
Background concentrations, mg/kg								
Regional baseline	0,5	70	27	20	38	70		
World average concentration in soils	0,3	80	25	20	70	0,0004		

RESULT 3. SEASONAL VARIATION - CORRELATIONS OF PAIRED METAL ELEMENTS IN THE LOPAN AND THE UDY RIVERS (BY PEARSON'S COEFFICIENT)

Summer / Winter	Cd	Co	Cr	Cu	Ni	Pb	Zn
Cd	1	-0,25	0,06	0,21	0,29	0,13	-0,34
Co	0,67	1	0,26	-0,21	-0,13	0,42	0,65
Cr	**0,96**	0,65	1	0,05	0,31	**0,90**	0,79
Cu	**0,87**	0,49	**0,94**	1	0,56	0,25	-0,34
Ni	**0,99**	0,71	**0,96**	**0,87**	1	0,23	-0,17
Pb	**0,93**	0,45	**0,89**	0,77	**0,91**	1	0,74
Zn	**0,99**	0,61	**0,96**	**0,91**	**0,99**	0,91	1

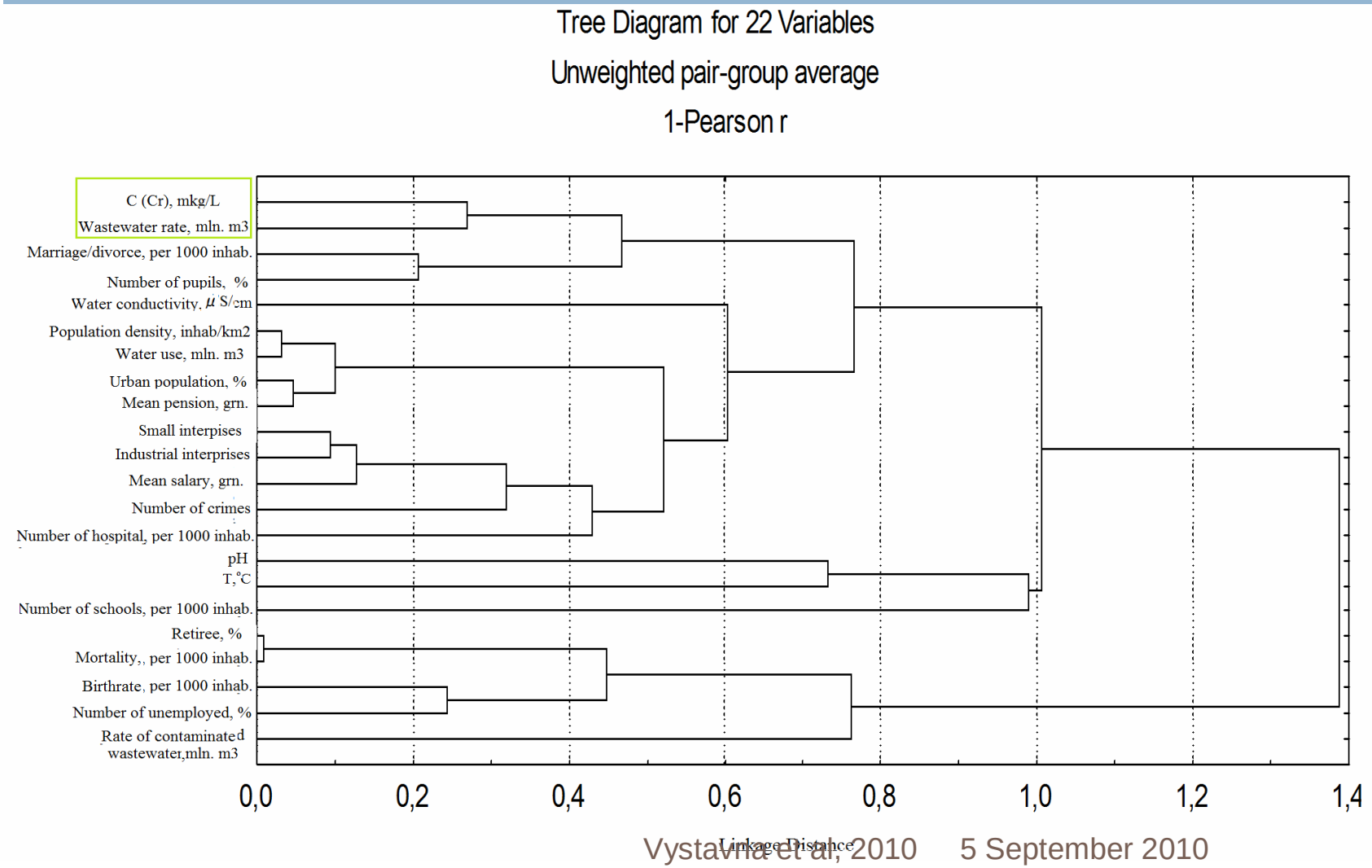
winter **summer**

RESULT 4. SOCIO-ECONOMIC DIFFERENCES OF THE REGIONS

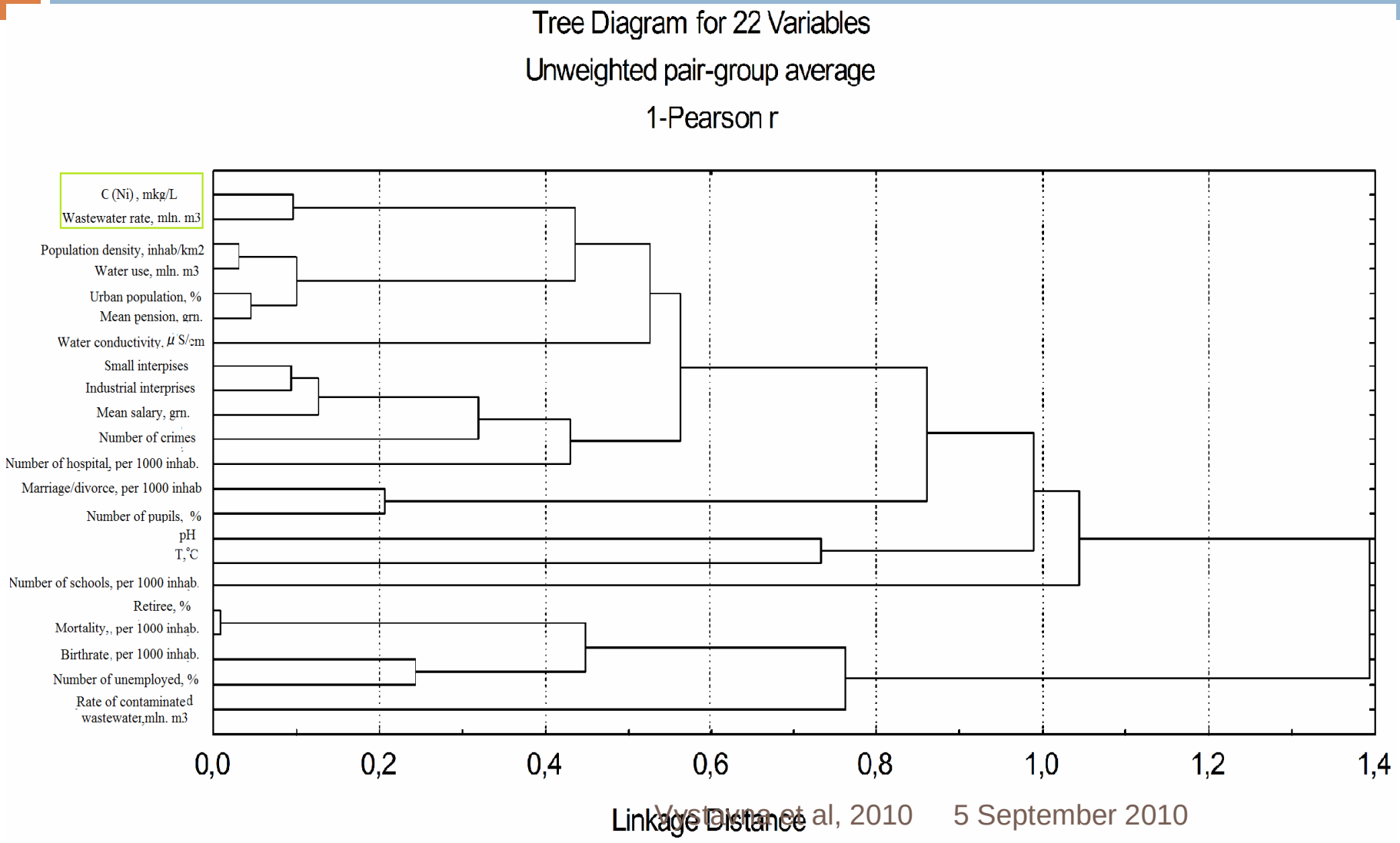
http://khrda.gov.ua/uk/article/view/id/9/
http://uprstat.kharkov.ukrtel.net/ua/stat/stat_inf.html

Region	Belgorod	Zolochiv	Derkachy	Kharkiv city (urban)
Population density (inhabitants per km²)	56	33	110	4674
Urban population (%)	66	43	71	100
Retired population (%)	nd	34	29	21
Mortality rate per 1000 persons	14.7	23.3	19.8	17.6
Major diseases	Respiratory ; aftereffect of pregnancy and birth	Musculoskeletal system; endocrine and blood system	Musculoskeletal system; endocrine and blood system	Musculoskeletal system; endocrine and blood system
Congenital diseases*	nd	2 (skin)	1 (respiratory)	3 (respiratory; blood)
Congenital anomalies*	nd	1	2	3

RESULT 5. CLUSTER ANALYSIS OF SOCIO-ECONOMICAL INDICATORS AND CONCENTRATIONS OF LABILE FORMS OF CHROMIUM



RESULT 6. CLUSTER ANALYSIS OF SOCIO-ECONOMICAL INDICATORS AND CONCENTRATIONS OF LABILE FORMS OF NICKEL



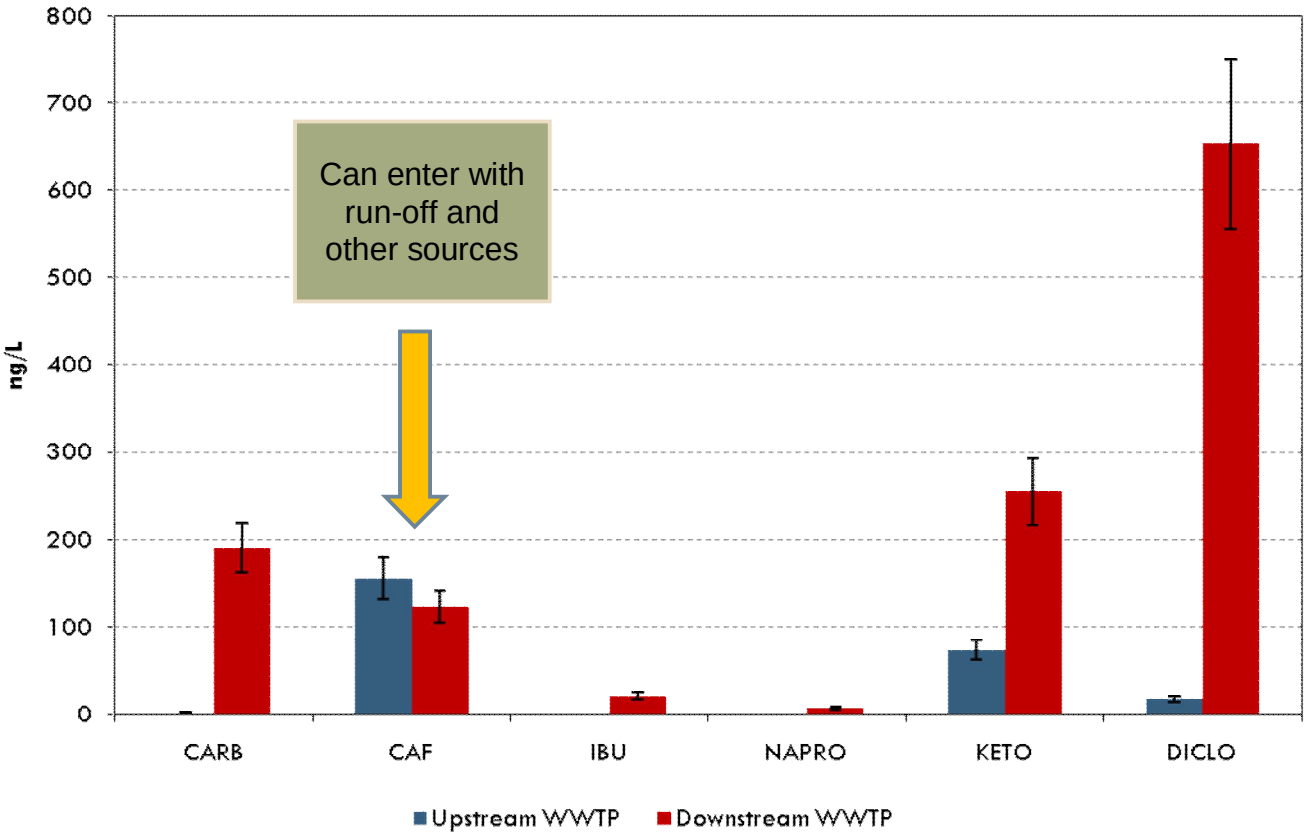
PHARMACEUTICALS:

- psychiatric drugs: alprazolam, amitriptylline, diazepam, doxepine, fluxetine, imipramine, nordiazepam, carbamazepine, bromazepam;
- analgesics: aspirin, paracetamol;
- broncholidator: clenbuterol, salbutamol, terbutaline;
- non-steroidal anti-inflammatory drugs: diclofenac, ibuprofen, ketofen, naproxen;
- lipid regulator: gemfibrozil;
- stimulants: caffeine, theophylline.

RESULT 1: OCCURRENCE OF PHARMACEUTICALS IN LOPAN AND UDY RIVERS

Pharmaceutical	August 2008				January 2009			
	Udy River		Lopan River		Udy River		Lopan River	
	Up	Down	Up	Down	Up	Down	Up	Down
	ng/POCIS	ng /POCIS	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS	ng/POCIS
Psychiatric drugs								
Carbamazepine	<	197	10	1	4	275	5	12
Diazepam	<	6	<	<	<	2	<	<
Amitriptylline	<	15	<	<	<	<	<	<
Analgesics								
Paracetamol	1	<	<	<	1	4	8	36
Stimulants								
Caffeine	4	14	27	<	418	305	42	461
Theophylline	<	6	7	<	42	112	23	128
Non-steroidal anti-inflammatory drugs								
Ibuprofen	<	19	<	<	<	7	3	61
Naproxen	<	5	<	<	1	37	<	2
Ketoprofen	6	18	61	5	51	165	11	<
Diclofenac	<	149	11	3	14	486	6	23

Concentrations of PPs in the Udy River



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RESULT 2: THE SEASONAL VARIATION OF PHARMACEUTICALS

Caffeine and carbamazepine – wastewaters markers???

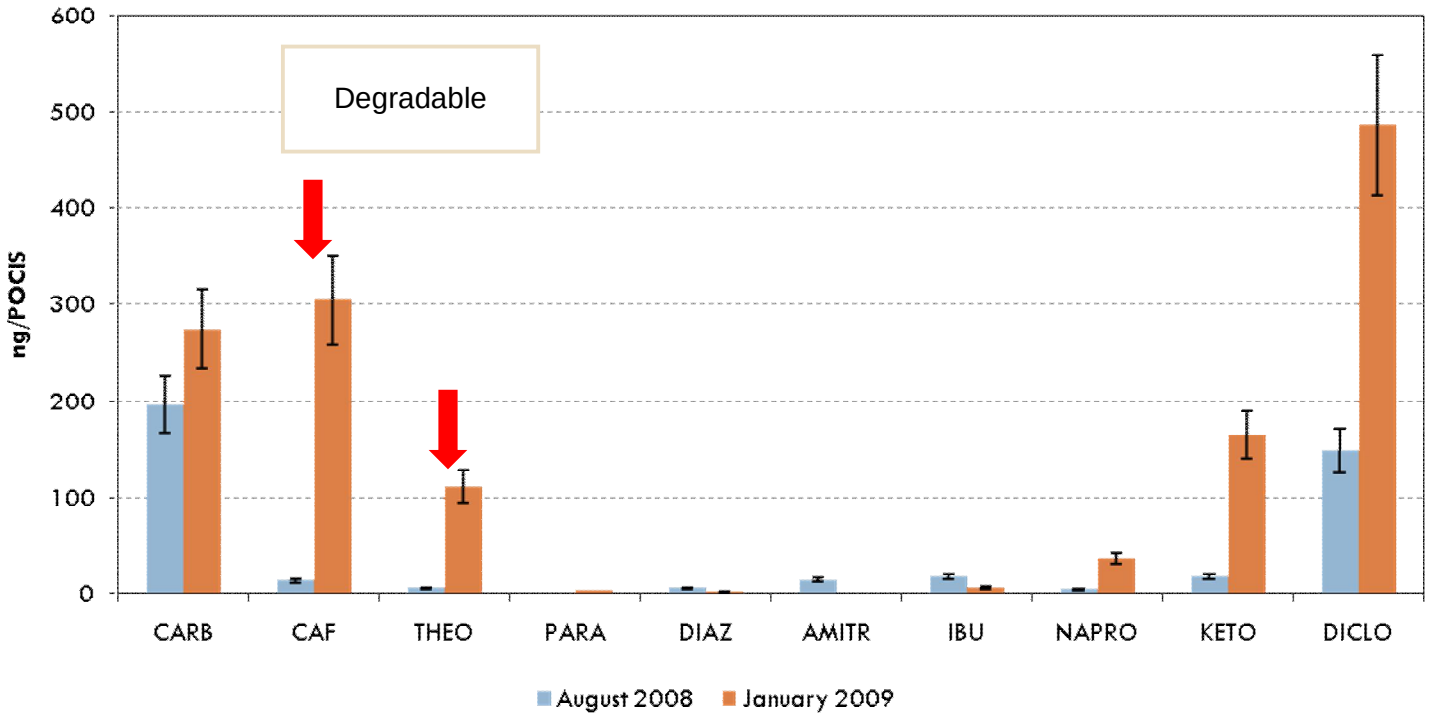


Fig. The accumulation of selected pharmaceuticals in the Udy River downstream of WWTP, ng/POCIS

RESULT 3: ENVIRONMENTAL AND HEALTH RISKS

PP	Our max, ng/L	MacLeod et al., 2007 (Canada) ng/L	Togola and Budzinski, 2007 (France) ng/L	Bartelt-Hunt et al., 2009 (USA) ng/L	Ecotoxic data (lowest value of the pharmaceutical in nature water)*			
					ng/L	Toxicological endpoint	Species	Country
DICLO	653	52	609	na	500	NOEC - 21 days (histopathological alteration)	*Fish*	Sweden
KETO	255	15	81	na	na			
IBU	21	na	12	na	10	LOEC (behavior)	*Crustaceans*	Italy
NAPRO	7	17	53	na	330,000	EC_{50} - 7 days (growth inhibition)	*Rotifers*	Japan
CAF	182	na	16	980	na			
CARB	**191**	30	250	296	10	LOEC (behavior)	*Crustaceans*	Sweden

* from the paper Santos et al, 2010
NOEC – No observed effect concentration
LOEC – Lowest observed effect concentration
EC50 – Half maximal effect concentration

RESULT 4. MASS-BALANCE MODELLING OF DRUGS CONSUMPTION – APPLIED MODEL

$$M_c = (Q_{uw} (C_{wu}-C_u)) / (K_1 (1-K_2))$$

M_c - drug consumption rate in a studied settlement, which is served by sewage system, (g d^{-1});

K_1 – drug excretion rate (a part of a pharmaceutical component which enters a sewerage system in unchanged form with human excretion), (g g^{-1}).

K_2 – the efficiency of wastewater treatment processes, that was estimated a part of a pharmaceuticals what are removed during the treatment, (g g^{-1})

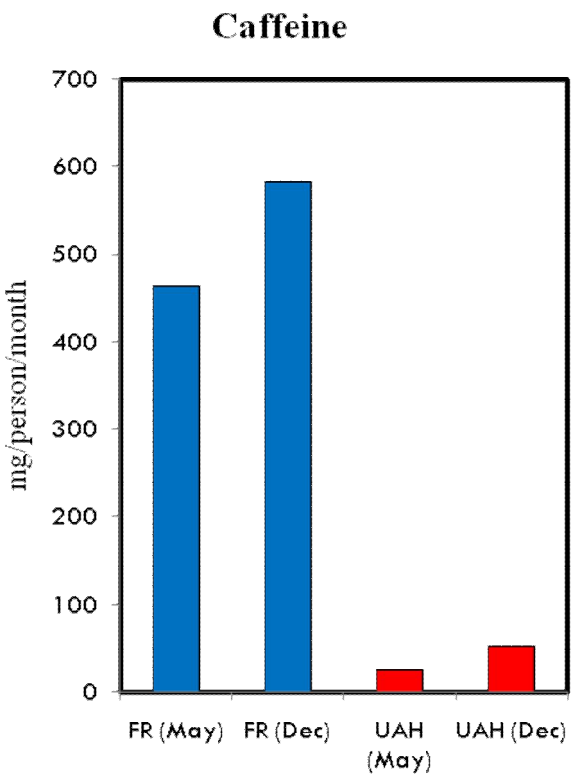
C_u – the concentration of the pharmaceuticals in the upstream part, (g m^{-3});

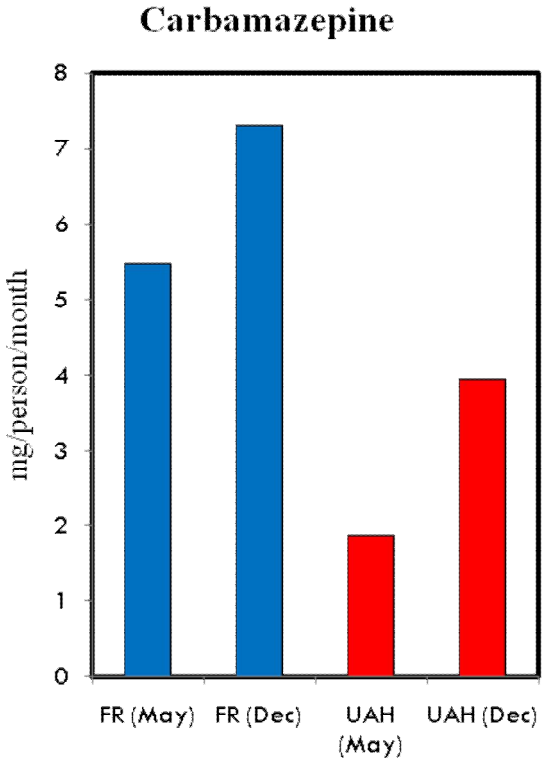
The daily drug consumption rate per person (D) was estimated as:

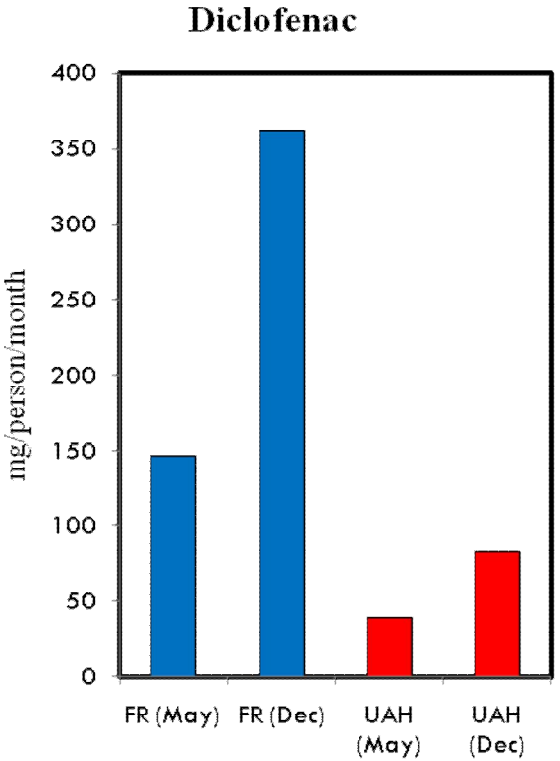
$$D = M_c/P$$

- Where P – is the number of people using the sewage system, inhabitants

RESULT 4. MASS-BALANCE MODELLING OF SOME DRUGS CONSUMPTION – COMPARISON WITH FRANCE







RESULT 4. MASS-BALANCE MODELLING OF SOME DRUGS CONSUMPTION – DATA VERIFICATION

PP	Fact (France, 2006)*	Calculated (France, 2009)
Carbamazepine	0.3	0.1
Diclofenac	4.3	0.3

*Coetsier at al, 2009

GENERAL CONCLUSIONS

- Emerging pollutants (trace metals and pharmaceuticals) are present in the urban and rural watershed regions and they have temporal, spatial and seasonal variations
- The highest accumulation of studied emerging pollutants was observed in the urban area downstream of WWTP
- Emerging pollutants monitoring is more efficient with the combination of grab and passive sampling techniques
- Presence of trace metals and some of pharmaceuticals (diclofenac, carbamazepine and ibuprofen) was at the dangerous level for the human health and ecosystem
- Socio-economic processes impact on the accumulation of the emerging pollutants in water

DISCUSSIONS

- The monitoring tool and system should be improved – ‘strategic monitoring’?
- Additional water quality standards should be applied – ‘development of the analytical chemistry and monitoring tools’?
- Preventive and protective measures are necessary to decrease the risk for the human health and ecosystem - ‘biotechnology’?
- Use of the water monitoring data in the socio-economic research and in other investigation – ‘drug and illicit drug consumption, drug market and etc’?

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THANK YOU FOR THE ATTENTION! QUESTIONS ARE WELCOME

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STOCKHOLM - WORLD WATER WEEK