GeoZS
Geological Survey
of Slovenia

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MONITORING OF MICRO-ORGANIC POLLUTANTS IN GROUNDWATER BY MEANS OF PASSIVE SAMPLING: CASE STUDY DRAVSKO POLJE, SLOVENIA

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Sesion 5.04. Emerging contaminants and risk

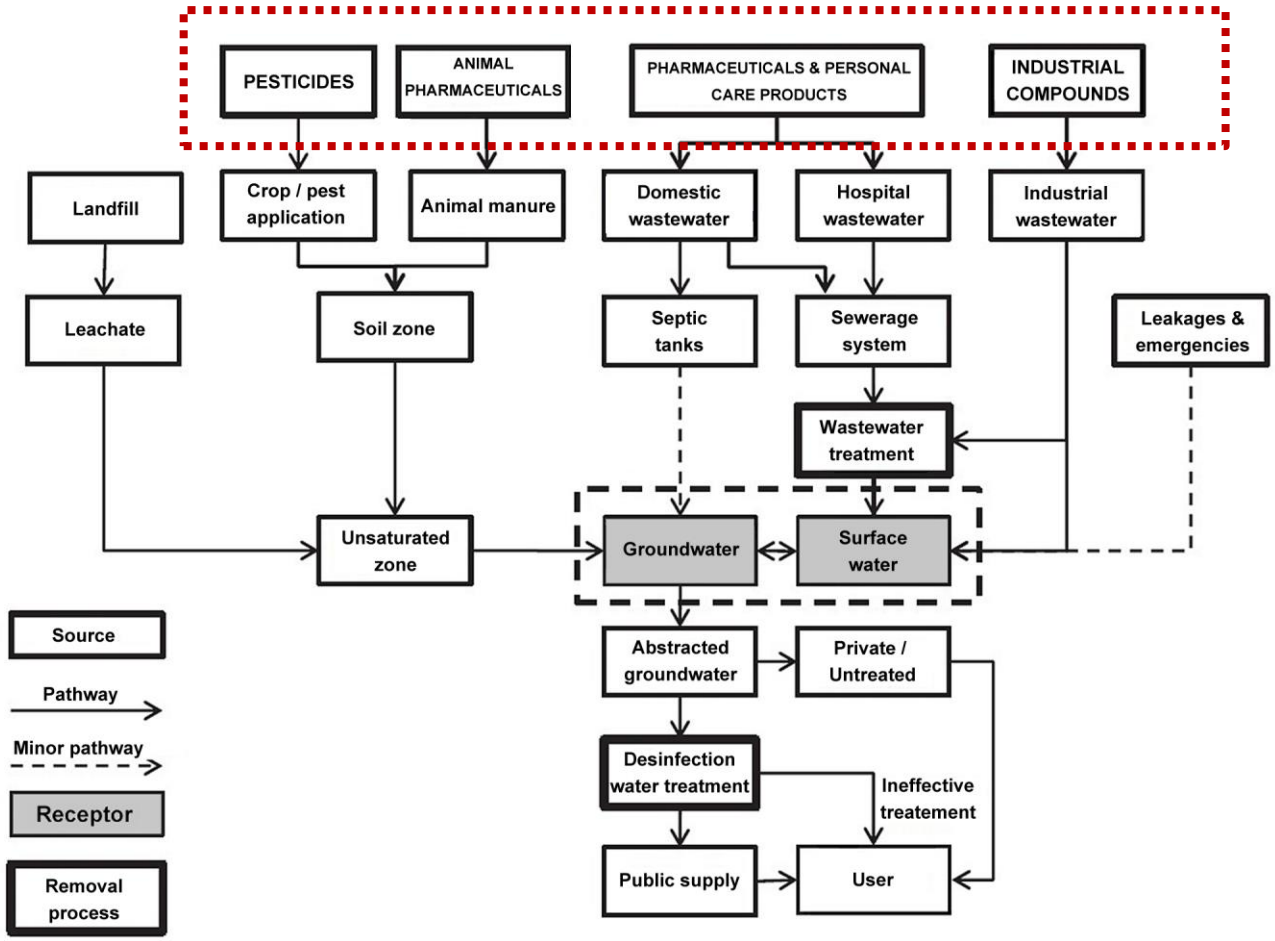
- **INTRODUCTION**
- **MICRO-ORGANIC POLLUTANTS**
- **PASSIVE SAMPLERS**
- **RESEARCH OF AQUIFER**
  - Study area
  - Methodology
- **RESULTS**
- **CONCLUSIONS**

INTRODUCTION

- ***Micro-organic pollutants in groundwater:***
  - anthropogenic origin
  - result of the activities of the urban environment and agriculture
  - pharmaceutcals, hormones, substances in personal care products, pesticides, veterinary products, industrial compounds, etc.

  - ***PESTICIDES***
    - use in agriculture, households, industry
  - ***DOMESTICAL (URBAN) COMPOUNDS***
    - Pharmaceuticals, flavors, food aditives, fragnances, etc.
  - ***INDUSTRIAL COMPOUNDS***
    - solvents, esters, aromatic and polyaromatic hydrocarbons, resins, plasticizers, etc.

INTRODUCTION



Source: (Stuart et al., 2012)

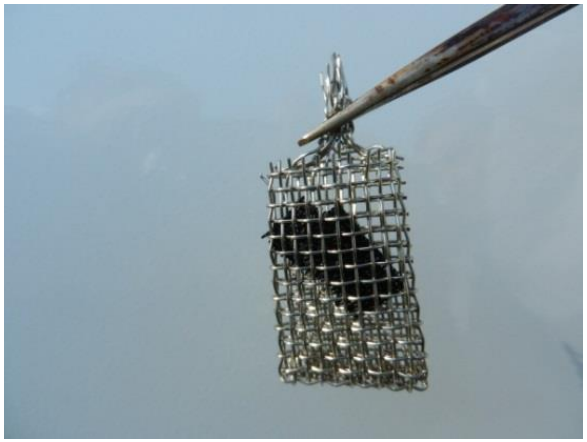
OBJECTIVES

- Determination of the presence of micro-organic pollutants in groundwater by means of passive sampling
- Identify pollutants of anthropogenic origin
- Development of sampling methods for the identification of organic compounds (passive samplers)



PASSIVE SAMPLERS

- Passive samplers – tool for qualitative monitoring which gave us information about probability of occurrence of different pollutants
- Less sensitive to extreme variations
- Long sampling period, which covers the concentrations of pollutants over time

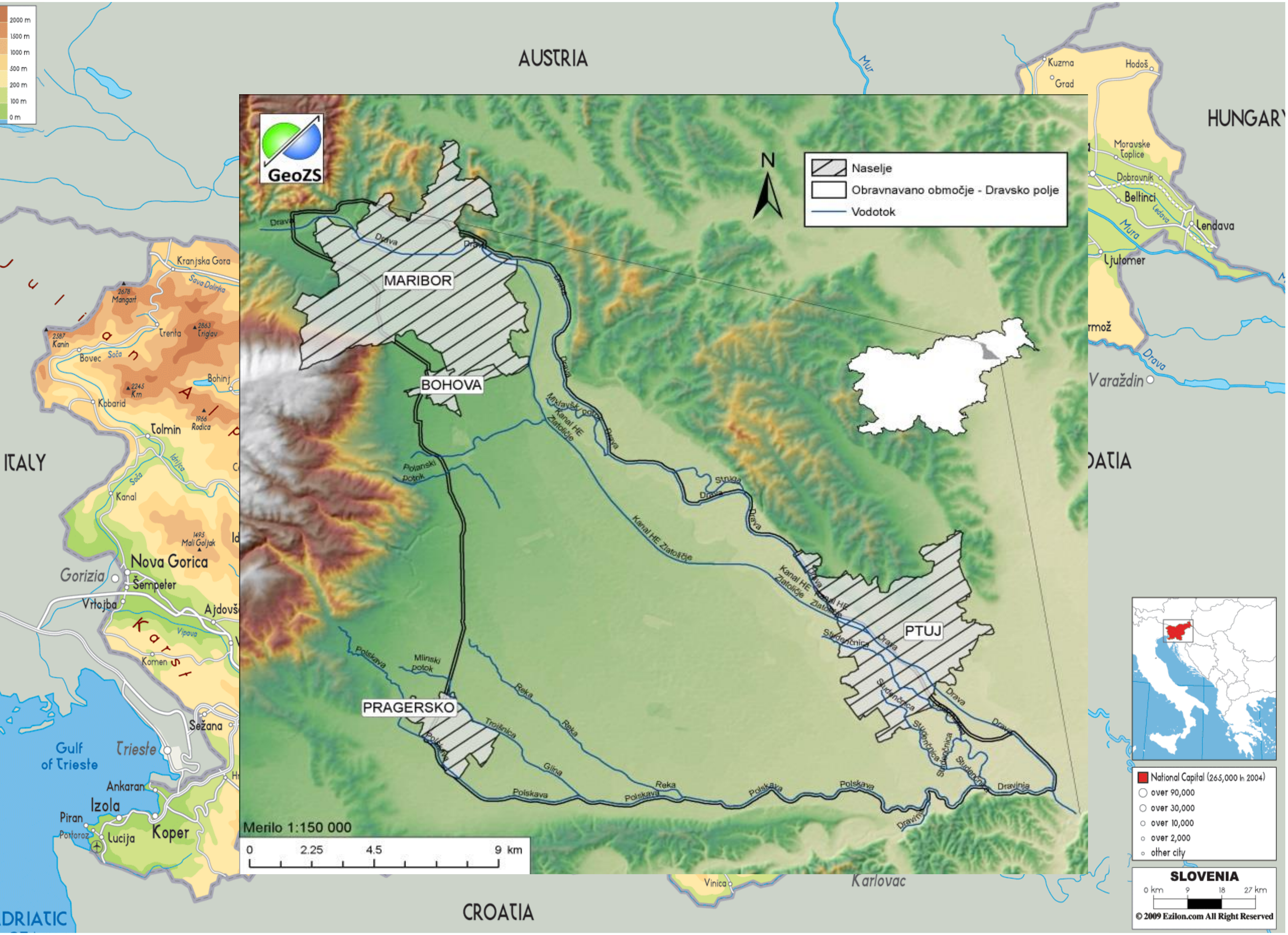


PASSIVE SAMPLERS

ADVANTAGES:

- A large spectrum of pollutants
- Low cost
- Easy to handle
- Average concentrations over a specified period

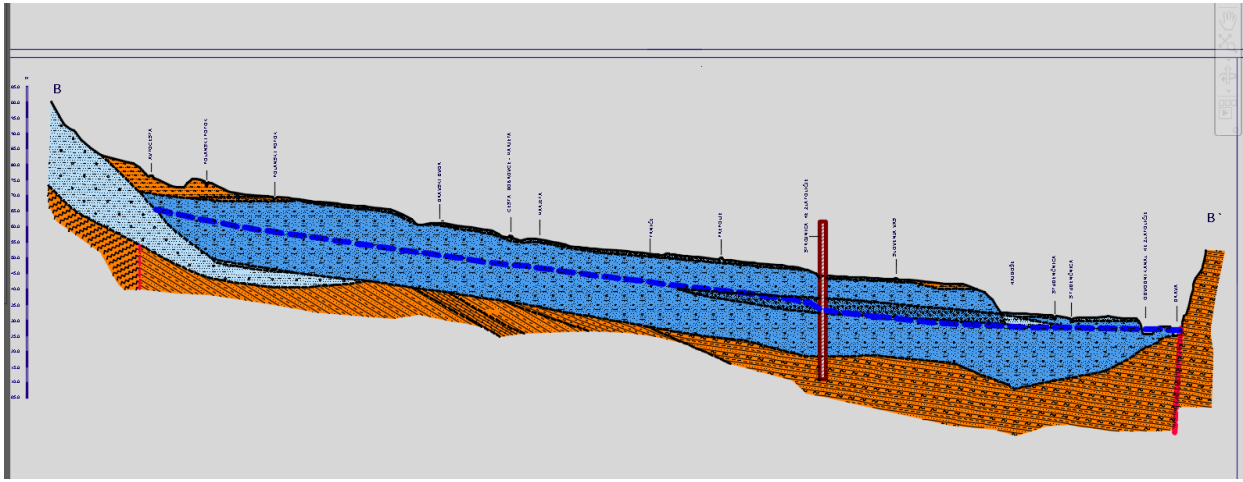
- Passive samplers – insert the sorbent into the borehole for a limited time and analyze the adsorbed compounds
- The results are evaluated according to the probability of identification and potential relevance according to the signal intensity
- Qualitative monitoring is the basis for targeted quantitative monitoring

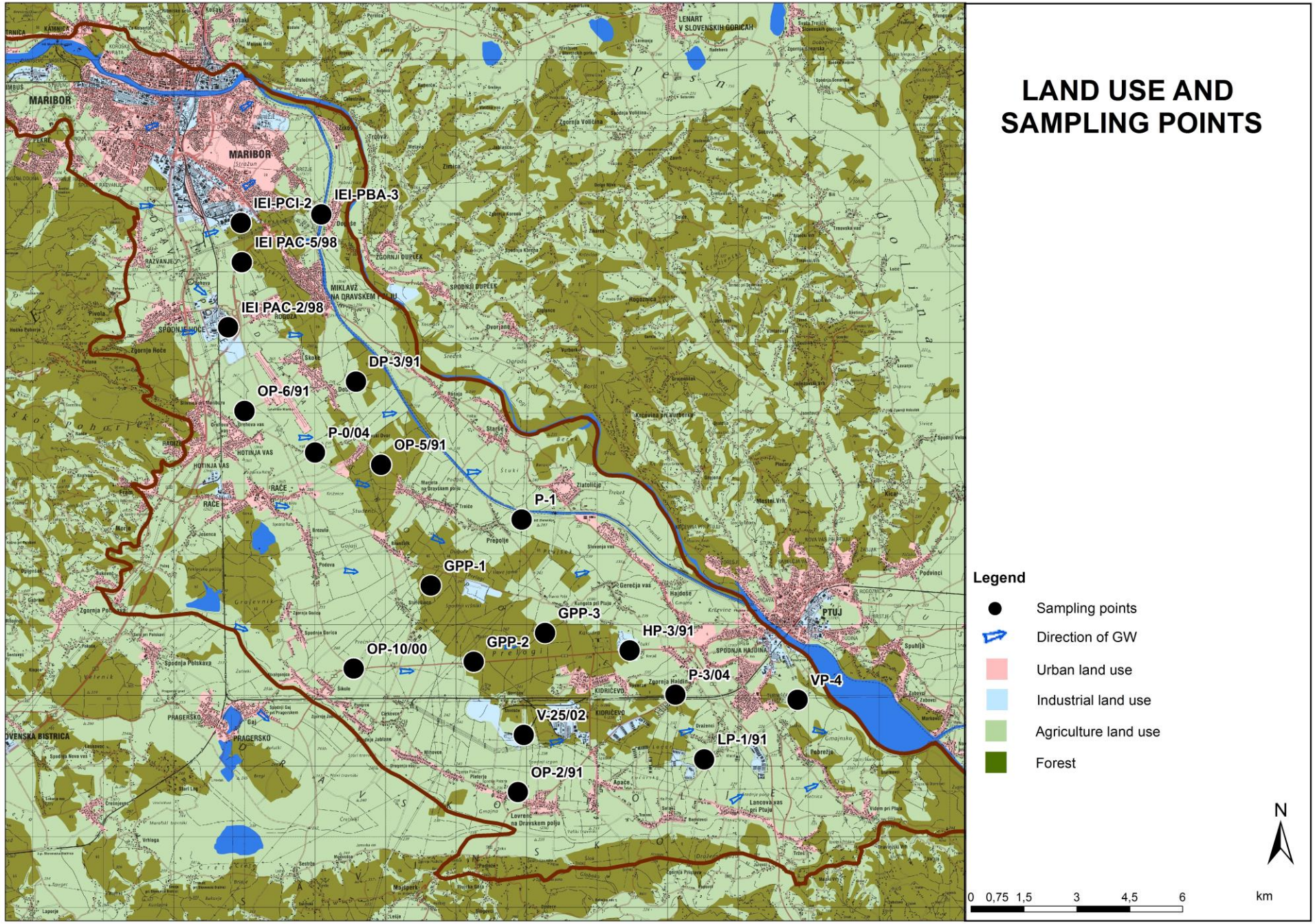


AUSTRIA
HUNGARY
ITALY
CROATIA
Naselje
Obravnavano območje - Dravsko polje
Vodotok
N
GeoZS
MARIBOR
BOHOVA
PRAGERSKO
PTUJ
Drava
Polskava
Reka
Studenčnica
Dravinja
Kanal HE Zlatoličje
Polanski potok
Mlinski potok
Merilo 1:150 000
0 2.25 4.5 9 km
SLOVENIA
0 km 9 18 27 km
© 2009 Ezilon.com All Right Reserved
National Capital (265,000 in 2004)
over 90,000
over 30,000
over 10,000
over 2,000
other city
Nova Gorica
Koper
Izola
Piran
Gulf of Trieste
Trieste
Lendava
Beltinci
Ljutomer
Varaždin
Karlovac

STUDY AREA

- Quaternary unconfined intergranular aquifer
- Hydraulic conductivity of the gravel is estimated between 10^{-2} in 10^{-4} m/s
- Average yearly rainfall between 1200 and 1300 mm
- Moderate continental climate with a mean annual temperature between 8 and 10°C.




LAND USE AND SAMPLING POINTS
IEI-PCI-2
IEI-PBA-3
IEI PAC-5/98
IEI PAC-2/98
DP-3/91
OP-6/91
P-0/04
OP-5/91
P-1
GPP-1
GPP-3
GPP-2
HP-3/91
OP-10/00
P-3/04
VP-4
V-25/02
LP-1/91
OP-2/91
MARIBOR
PTUJ
Legend
Sampling points
Direction of GW
Urban land use
Industrial land use
Agriculture land use
Forest
N
0 0,75 1,5 3 4,5 6
km

METHODS - sampling

- SAMPLING:
  - Active carbon fibers insert into stainless steel mesh
  - 19 sampling points

    - 4 series (2013-2015)
  - QC (blank samples exposed to air)
  - In-situ measurements (T, EC, pH)

METHODS - analysis

- **Analysis** (VO-KA, Drinking Water and Sewege System Public Utility)

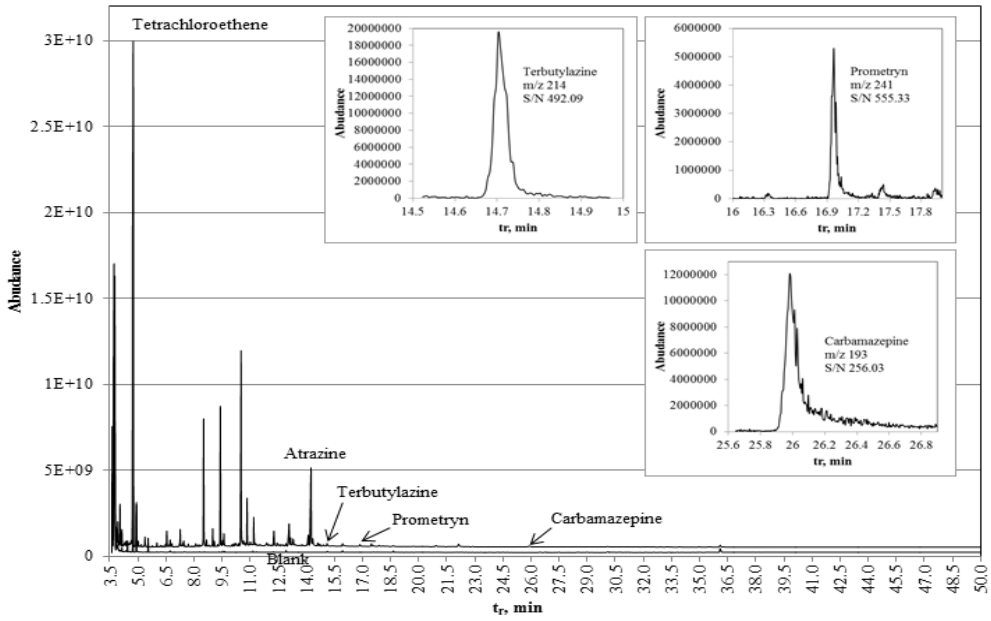
- Adsorbed material was eluted from the active carbon and the extract was further analyzed with GC-MS.

- For the interpretation of chromatograms the AMDIS deconvolution was used. The deconvolution was covered by GC-MS library with retention times for 921 organic contaminants from Agilent USA, and also the NIST 2008 library of mass spectra.

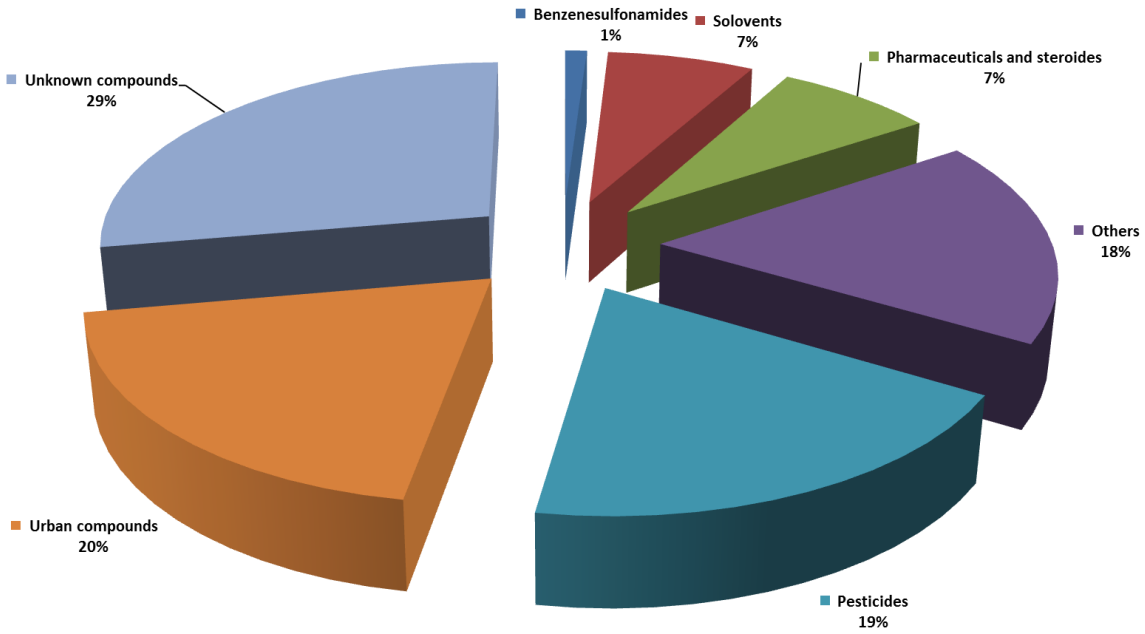
METHODS - analysis

- The results are evaluated according to the probability of identifying and potential relevance of signal intensity.

- Evaluation was integration of mass fragment of compound and mass fragment of caffeine–D10 as internal standard.



RESULTS



- **382 micro-organic pollutants**

- ***7 groups:***
  - Unknown compounds
  - Urban compounds
  - Pesticides
  - Others
  - Pharmaceuticals and steroides
  - Solvents
  - Benzenesulphonamides

		tr	NAME	CAS NUMBER	*USAGE*
PESTICIDES	ti	14,2	Atrazine	1912-24-9	*herbicide*
	ti	13,4	Chloridazon methyl desphenyl	17254-80-7	*degradation product of the herbicide*
	ci	13	Desethylatrazine	6190-65-4	*degradation product of herbicide atrazine*
	ci	13,2	Desethylterbuthylazine	30125-63-4	*degradation product of herbicide terbuthylazine*
	ti	4,7	Dimethyl oxalate	553-90-2	*degradation of halogenated pesticides*
	ci	17,2	Ethofumesate	26225-79-6	*herbicide*
	ti	17,7	Metalochlor	51218-45-2	*herbicide*
	ci	24,7	Metalochlor-M m/z 162,282	-	*degradation product of herbicide matalochlor*
	ci	14,1	Propazine	139-40-2	*herbicide*
	ti	13,9	Simazine	122-34-9	*herbicide*
	ci	14,4	Terbuthylazine	5915-41-3	*herbicide*
	ci		Unknown compound m/z 176, 252	-	*degradation product of herbicide*
SOLVENTS	ti	11,1	Tetraethylene glycol dimethyl eth	143-24-8	*solvent*
	ti	6,5	1-(2-Methoxypropoxy)-2-propanc	13429-07-7	*solvent*
	ti	6,4	2-(2-methoxypropoxy)propan-1-c	13588-28-8	*solvent*
	ti	4,3	Acetamide	60-35-5	solvent , a plasticizer, a chemical intermediate
	ti	6	Benzaldehyde	100-52-7	*chemical intermediates, solvent, bee repellents*
	ti	7,1	Diethyldiglycol	112-36-7	*solvent*
	ti	4,5	Dimethyl sulfoxide	67-68-5	*solvent, chemical intermediate*
	ti	7,1	Nitrosomorpholine	59-89-2	*solvent, chemical intermediate*
	ti	4,5	Tetrachloroethylene	127-18-4	*dry cleaning, degreasing, industrial solvent*
	ti	3,9	Trichloroethylene	79-01-6	*dry cleaning, degreasing, industrial solvent*
PHARMACEUTICALS	ti	17,2	5-Methoxygramine	16620-52-3	*Pharmaceutical Intermediates*
	ti	13	5-Methoxytryptamine	608-07-1	*Pharmaceutical Intermediates*
	ci	25,7	Carbamazepine	298-46-4	*drug*
	ti	9,7	Triacetin	102-76-1	solvent , Cosmetics , Pharmaceuticals
URBAN COMPOUNDS	ti	9,3	2,4-dimethyl-2H-benzotriazole	-	*degradation product of fungicides, drugs, UV absorbers, corrosion inhib*
	ti	4,6	2-Hexanol	626-93-7	*flavors, fragrances*
	c.i.	8,4	2-methyl-2H-benzotriazole	16584-00-2	*degradation product of fungicides, drugs, UV absorbers, corrosion inhib*
	ti	6,7	Benzylalcohol	100-51-6	*cosmetics, chemicals intermediate*
	ti	22,2	Butyl hexadecanoate	111-06-8	*cosmetics, food additives*
	ti	10,4	Dodecanal	112-54-9	*cosmetics*
	ti	12,3	Dodecyl acetate	112-66-3	natural compound
	ti	9,4	Indole	120-72-9	*cosmetics, chemicals intermediate*
	ti	26,7	Isobutyl stearate	646-13-9	cosmetics, food additives
	ti	7,6	Methyl octanoate	111-11-5	*chemical intermediate, fragrances, naravna spojina*
	ti	16,8	Methyl palmitate	112-39-0	*chemical intermediate*
	ti	17,6	Palmitic acid	57-10-3	*emulsions, polymer coatings, food*
	ti	8,3	p-cymen-8-ol	1197-01-9	*natural compound, digestion of the plant material, flavors*
	ti	21,6	Stearic Acid	57-11-4	*chemical intermediate, cosmetics , pharmaceuticals*
	ti	11,2	Tridecanal	10486-19-8	*natural compound, cosmetics*
OTHERS	ti	7,2	2,2-dihydroxyacetophenone	1075-06-5	*chemical intermediate*
	ti	7,2	2-Methylphenol	95-48-7	*disinfection, solvent, chemical intermediate*
	ti	7,4	2-butenylbenzene	1560-06-1	*petroleum products*
	ci	6,1	Phenol	108-95-2	*disinfection and chemical intermediate*
	ti	11,1	Tetrahydro-8-hydroxy-4-oxoquinoline-2-carboxylic acid	4886-42-4	-
	ti	9,4	Undecanal	112-44-7	*cosmetics, natural compound*

47 selected compounds

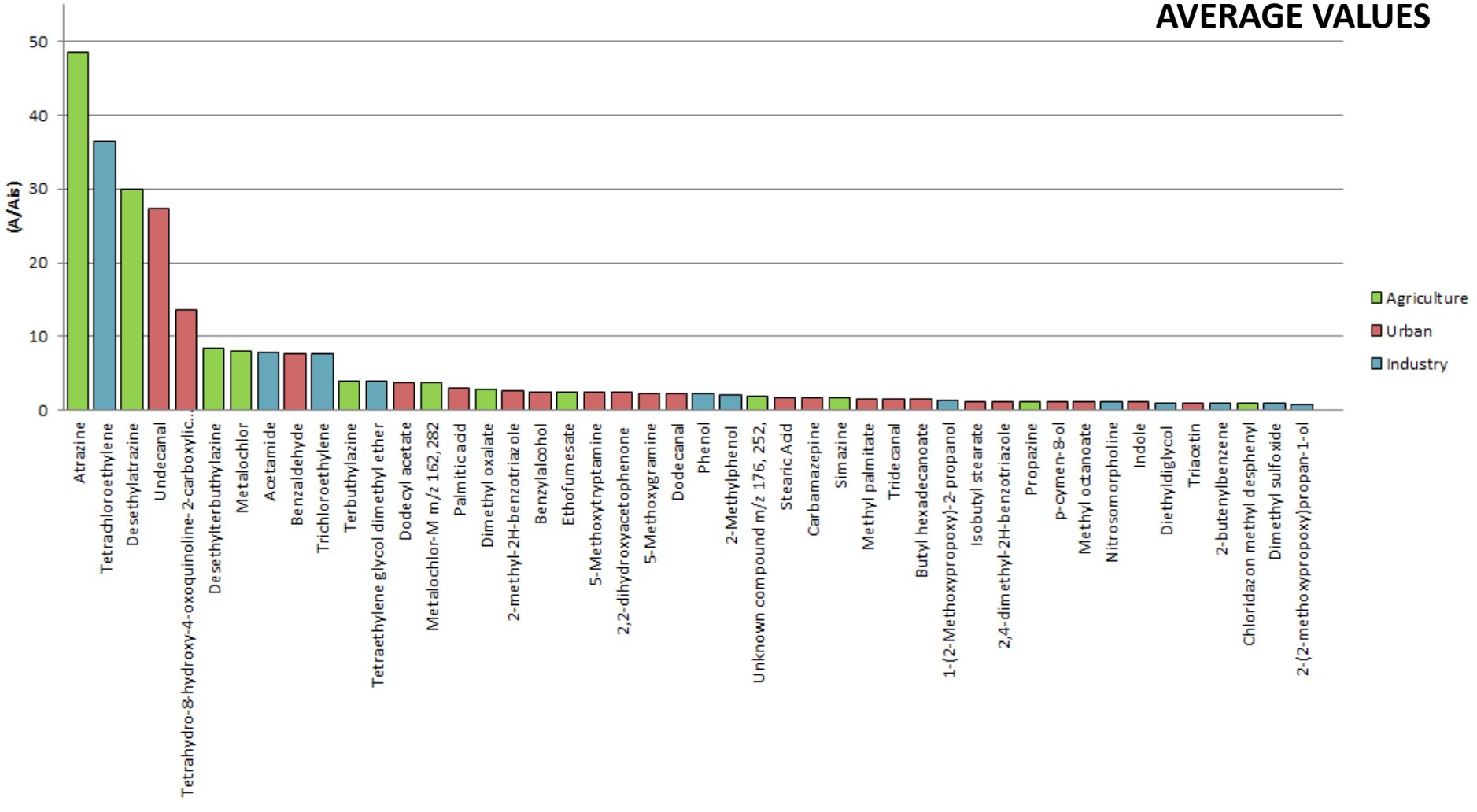
70 YEARS GeoZS Geološki zavod Slovenije

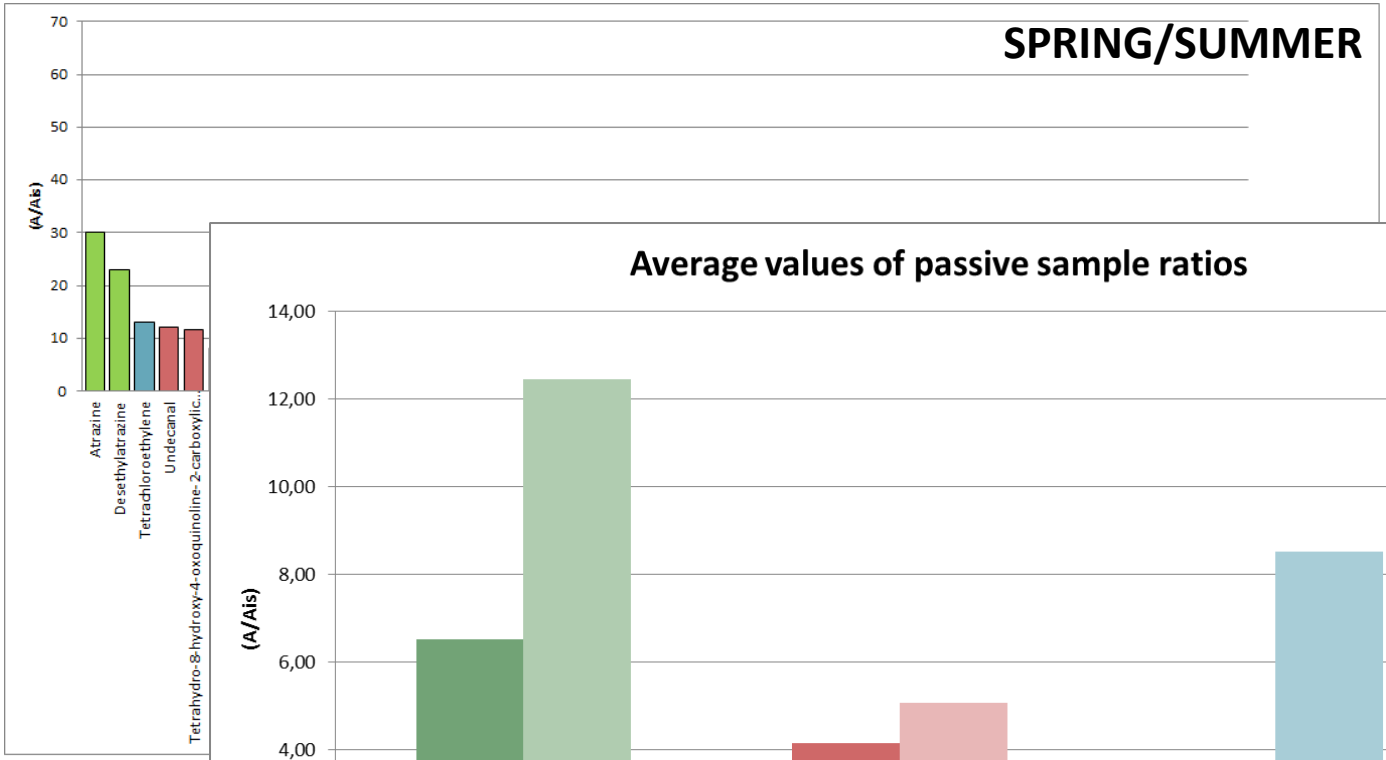
		tr, min	NAME	CAS NUMBER	*USAGE*
AGRICULTURAL	ci	14,2	Atrazine	1912-24-9	*herbicide*
	ci	13	Desethylatrazine	6190-65-4	*degradation product of herbicide atrazine*
	ci	13,2	Desethylterbuthylazine	30125-63-4	*degradation product of herbicide terbuthylazine*
	ti	4,7	Dimethyl oxalate	553-90-2	*degradation of halogenated pesticides*
	ti	17,2	Ethofumesate	26225-79-6	*herbicide*
	ci	17,7	Metalochlor	51218-45-2	*herbicide*
	ti	24,7	Metalochlor-M m/z 162,282	-	*degradation product of herbicide matalochlor*
	ti	13,4	Chloridazon methyl desphenyl	17254-80-7	*degradation product of the herbicide*
	ti		neznana spojina m/z 176, 252,	-	*degradation product of herbicide*
	ci	14,1	Propazine	139-40-2	*herbicide*
	ci	13,9	Simazine	122-34-9	*herbicide*
	ci	14,4	Terbuthylazine	5915-41-3	*herbicide*
URBAN	ti	7,2	2,2-dihydroxyacetophenone	1075-06-5	*chemical intermediate*
	ti	9,3	2,4-dimethyl-2H-benzotriazole	-	*degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors*
	ti	4,6	2-Hexanol	626-93-7	*flavors, fragrances*
	c.i.	8,4	2-methyl-2H-benzotriazole	16584-00-2	*degradation product of fungicides, drugs, UV absorbers, corrosion inhibitors*
	ti	17,2	5-Methoxygramine	16620-52-3	*Pharmaceutical Intermediates*
	ti	13	5-Methoxytryptamine	608-07-1	*Pharmaceutical Intermediates*
	ti	6	Benzaldehyde	100-52-7	*chemical intermediates, solvent, bee repellents*
	ti	6,7	Benzylalcohol	100-51-6	*cosmetics, chemicals intermediate*
	ti	22,2	Butyl hexadecanoate	111-06-8	*cosmetics, food additives*
	ci	25,7	Carbamazepine	298-46-4	*drug*
	ti	12,3	Dodecyl acetate	112-66-3	natural compound
	ti	10,4	Dodecanal	112-54-9	*cosmetics*
	ti	26,7	Isobutyl stearate	646-13-9	cosmetics, food additives
	ti	9,4	Indole	120-72-9	*cosmetics, chemicals intermediate*
	ti	7,6	Methyl octanoate	111-11-5	*chemical intermediate, fragrances, naravna spojina*
	ti	16,8	Methyl palmitate	112-39-0	*chemical intermediate*
	ti	17,6	Palmitic acid	57-10-3	*emulsions, polymer coatings, food*
	ti	8,3	p-cymen-8-ol	1197-01-9	*natural compound, digestion of the plant material, flavors*
	ti	21,6	Stearic Acid	57-11-4	*chemical intermediate, cosmetics , pharmaceuticals*
	ti	11,1	Tetrahydro-8-hydroxy-4-oxoquinoline-2-carboxylic acid	4886-42-4	-
	ti	9,7	Triacetin	102-76-1	solvent , Cosmetics , Pharmaceuticals
	ti	11,2	Tridecanal	10486-19-8	*natural compound, cosmetics*
	ti	9,4	Undecanal	112-44-7	*cosmetics, natural compound*
INDUSTRIAL	ti	6,5	1-(2-Methoxypropoxy)-2-propanol	13429-07-7	*solvent*
	ti	6,4	2-(2-methoxypropoxy)propan-1-ol	13588-28-8	*solvent*
	ti	7,4	2-butenylbenzene	1560-06-1	*petroleum products*
	ti	7,2	2-Methylphenol	95-48-7	*disinfection, solvent, chemical intermediate*
	ti	4,3	Acetamide	60-35-5	solvent , a plasticizer, a chemical intermediate
	ti	7,1	Diethyldiglycol	112-36-7	*solvent*
	ti	4,5	Dimethyl sulfoxide	67-68-5	*solvent, chemical intermediate*
	ci	6,1	Phenol	108-95-2	*disinfection and chemical intermediate*
	ti	7,1	Nitrosomorpholine	59-89-2	*solvent, chemical intermediate*
	ti	4,5	Tetrachloroethylene	127-18-4	*dry cleaning, degreasing, industrial solvent*
	ti	11,1	Tetraethylene glycol dimethyl ether	143-24-8	*solvent*
	ti	3,9	Trichloroethylene	79-01-6	*dry cleaning, degreasing, industrial solvent*

47 indicators of different source of pollution

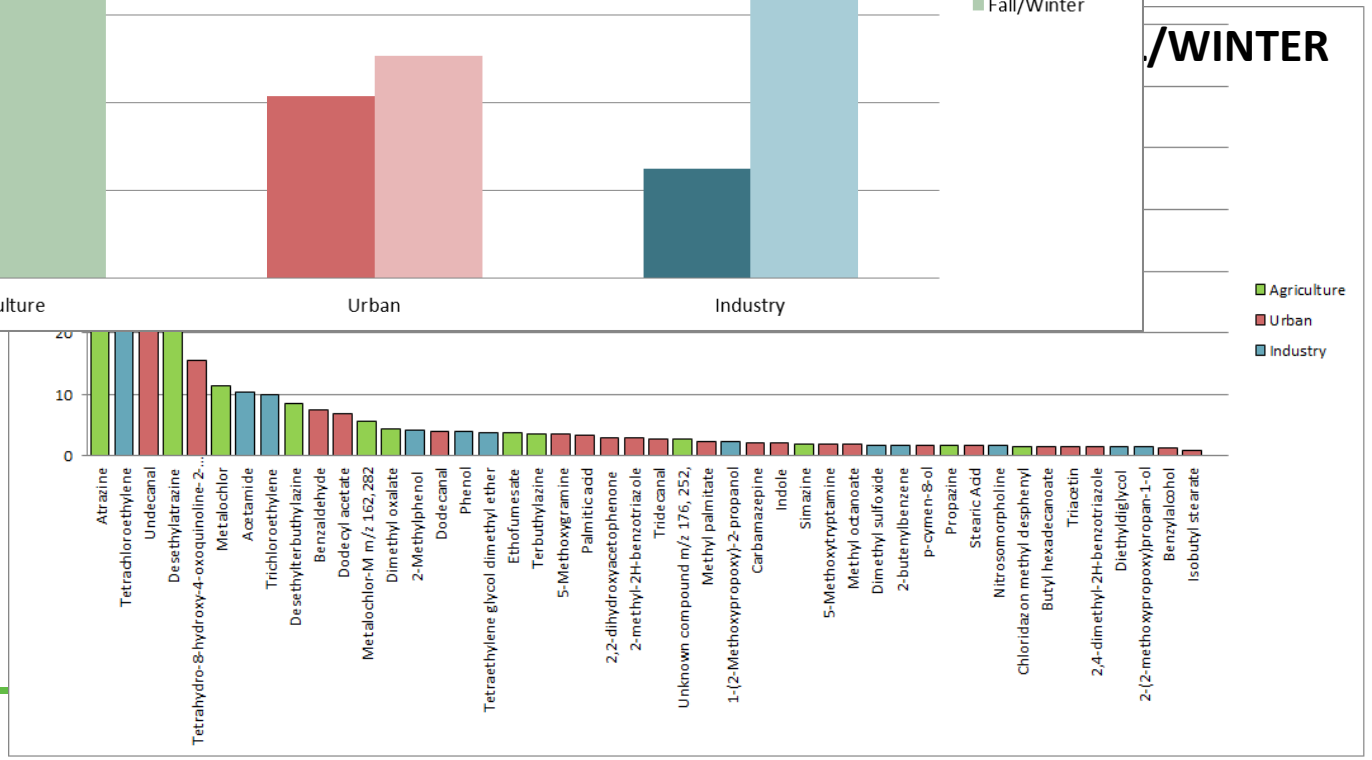
70 YEARS GeoZS Geološki zavod Slovenije

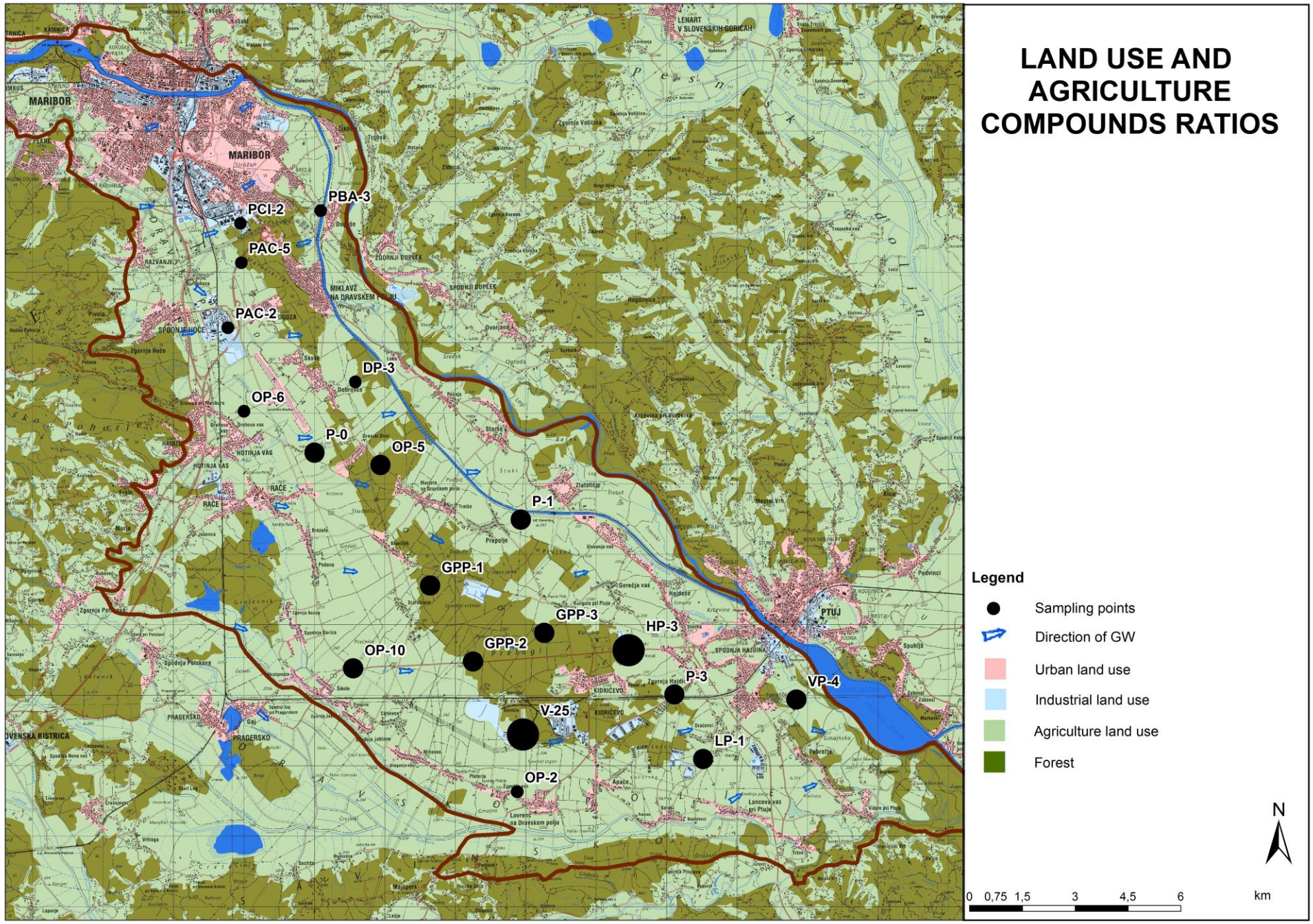
AVERAGE VALUES

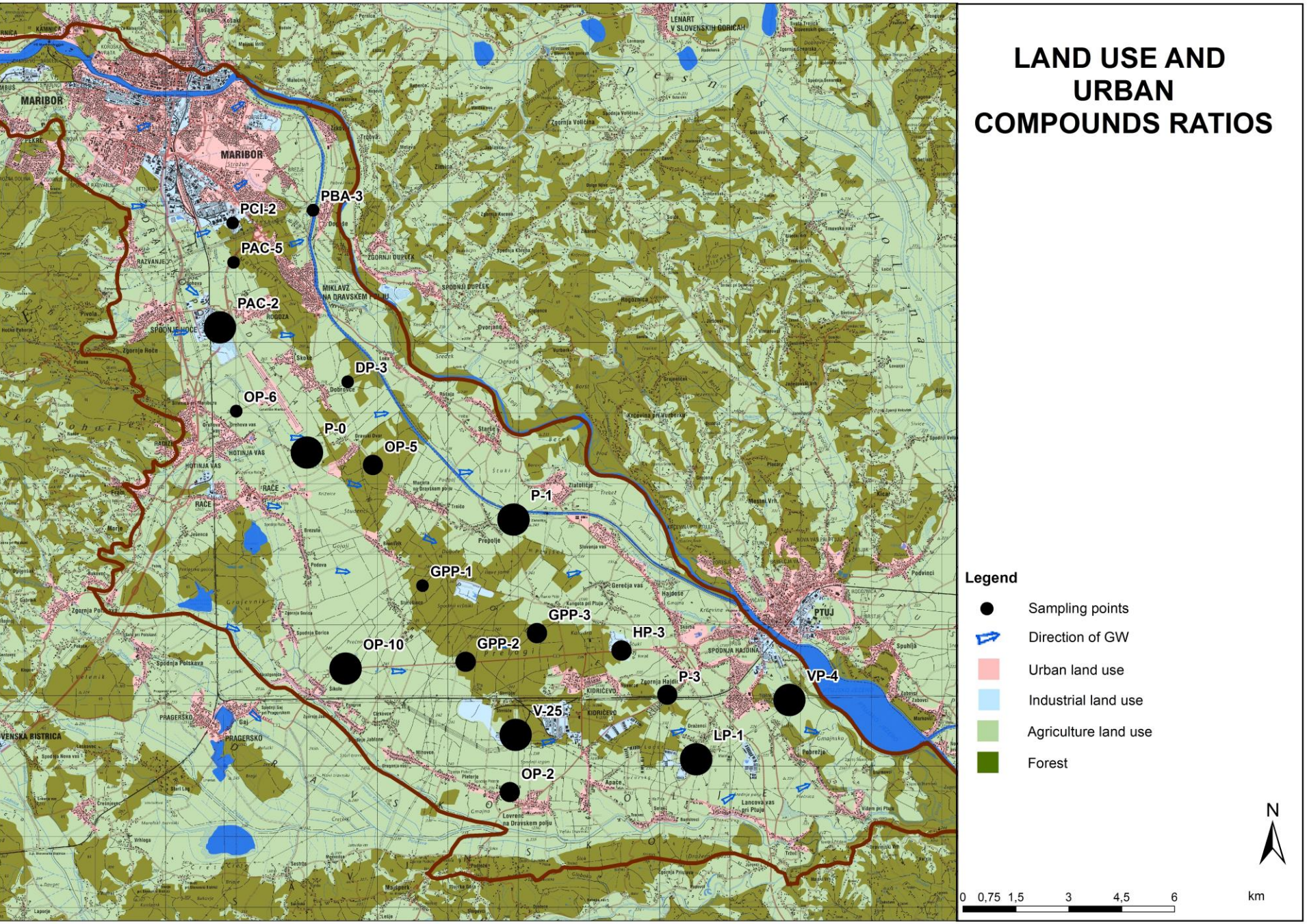


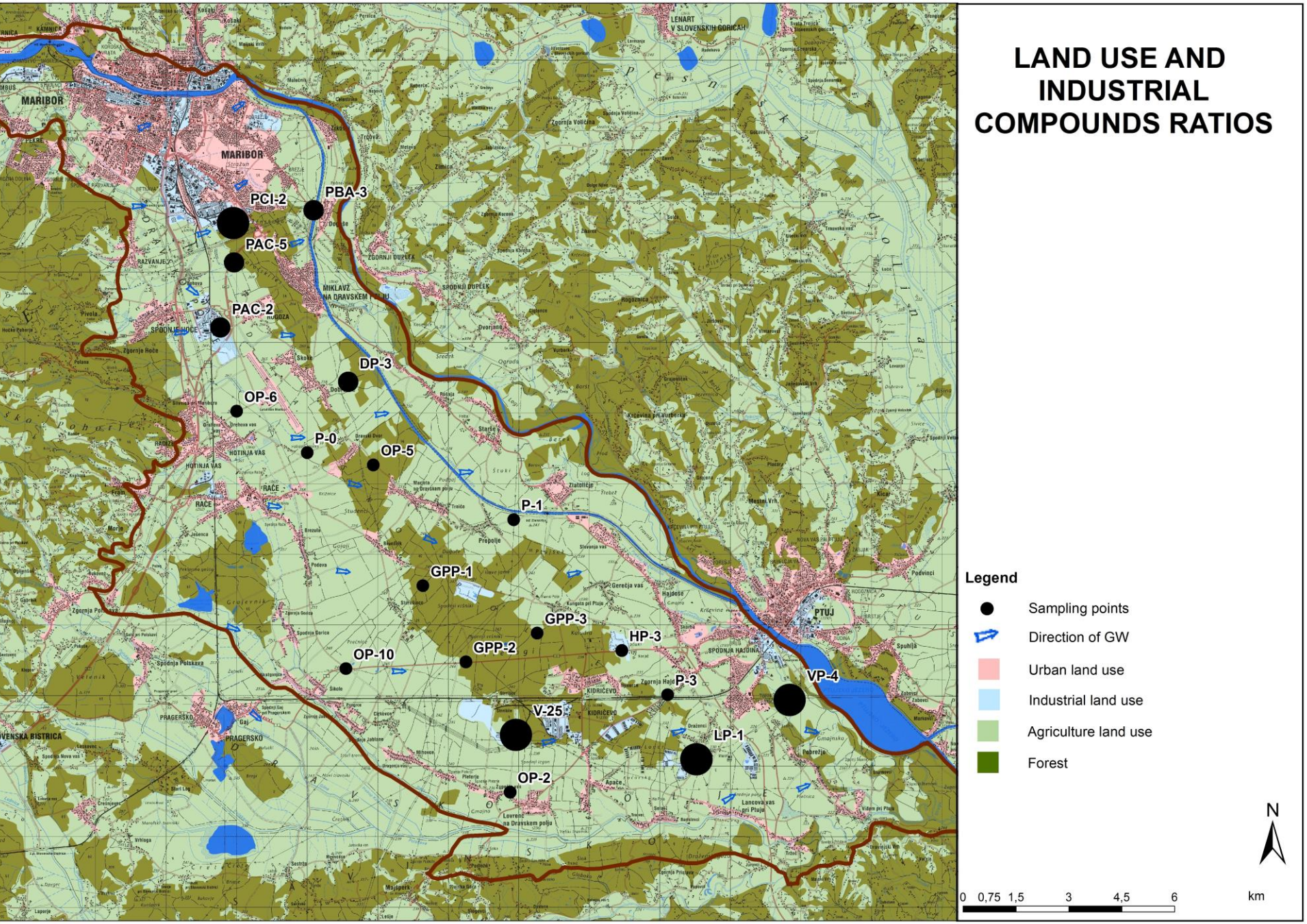

SPRING/SUMMER
(A/Ais)
70
60
50
40
30
20
10
0
Atrazine
Desethylatrazine
Tetrachloroethylene
Undecanal
Tetrahydro-8-hydroxy-4-oxoquinoline-2-carboxylic...

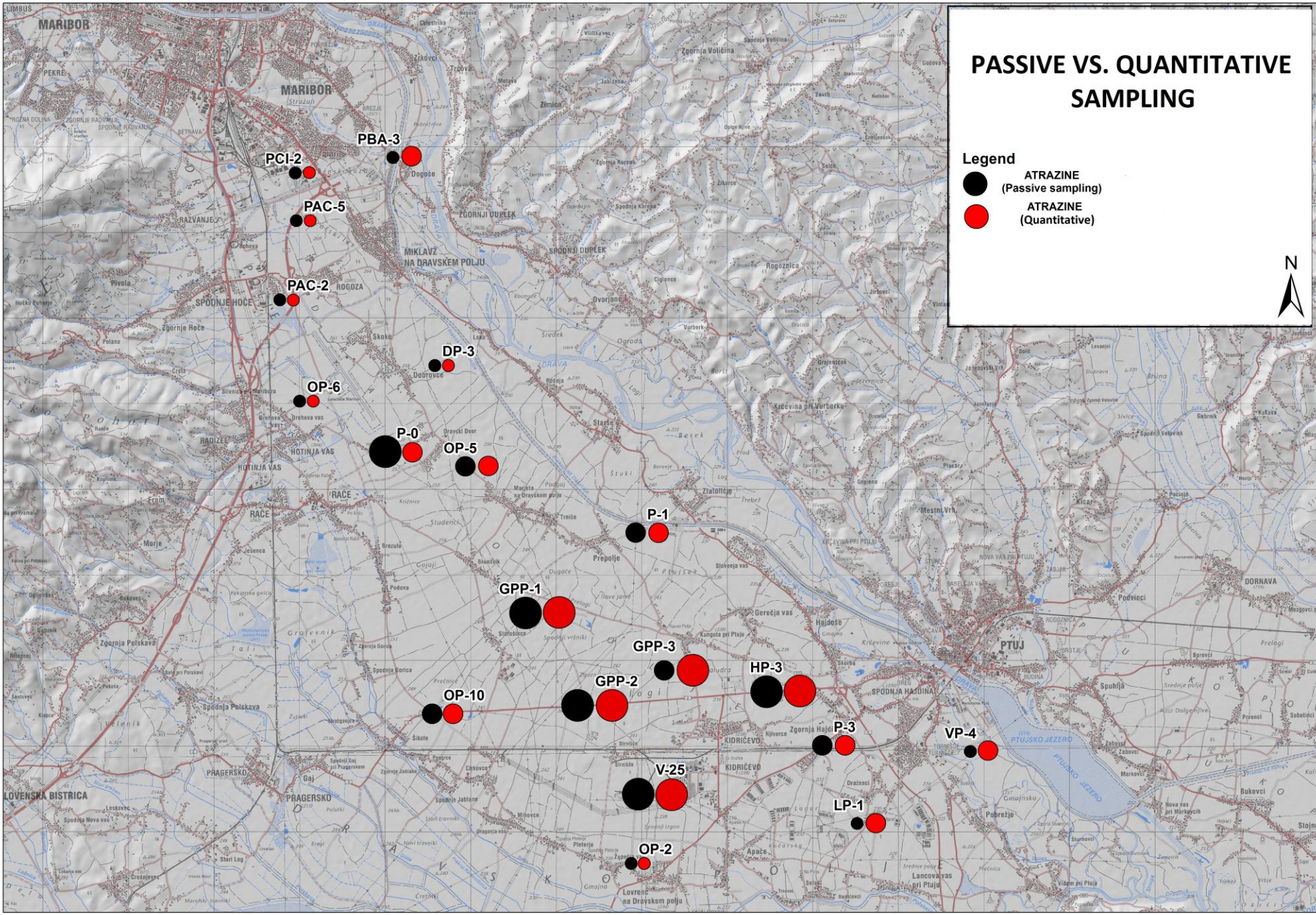
Average values of passive sample ratios
(A/Ais)
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
Agriculture
Urban
Industry
Spring/Summer
Fall/Winter


/WINTER
Agriculture
Urban
Industry
20
10
0
Atrazine
Tetrachloroethylene
Undecanal
Desethylatrazine
Tetrahydro-8-hydroxy-4-oxoquinoline-2-...
Metolachlor
Acetamide
Trichloroethylene
Desethylterbuthylazine
Benzaldehyde
Dodecyl acetate
Metalochlor-M m/z 162, 282
Dimethyl oxalate
2-Methylphenol
Dodecanal
Phenol
Tetraethylene glycol dimethyl ether
Ethofumesate
Terbuthylazine
5-Methoxygramine
Palmitic add
2,2-dihydroxyacetophenone
2-methyl-2H-benzotriazole
Tridecanal
Unknown compound m/z 176, 252,
Methyl palmitate
1-(2-Methoxypropoxy)-2-propanol
Carbamazepine
Indole
Simazine
5-Methoxytryptamine
Methyl octanoate
Dimethyl sulfoxide
2-butenylbenzene
p-cymen-8-ol
Propazine
Stearic Add
Nitrosomorpholine
Chloridazon methyl desphenyl
Butyl hexadecanoate
Triacetin
2,4-dimethyl-2H-benzotriazole
Diethyldiglycol
2-(2-methoxypropoxy)propan-1-ol
Benzylalcohol
Isobutyl stearate


LAND USE AND AGRICULTURE COMPOUNDS RATIOS
MARIBOR
PCI-2
PBA-3
PAC-5
PAC-2
DP-3
OP-6
P-0
OP-5
P-1
GPP-1
GPP-3
HP-3
GPP-2
OP-10
P-3
VP-4
V-25
LP-1
OP-2
PTUJ
Legend
Sampling points
Direction of GW
Urban land use
Industrial land use
Agriculture land use
Forest
N
0 0,75 1,5 3 4,5 6
km


LAND USE AND URBAN COMPOUNDS RATIOS
MARIBOR
PCI-2
PBA-3
PAC-5
PAC-2
DP-3
OP-6
P-0
OP-5
P-1
GPP-1
GPP-3
HP-3
GPP-2
OP-10
P-3
VP-4
V-25
LP-1
OP-2
PTUJ
Legend
Sampling points
Direction of GW
Urban land use
Industrial land use
Agriculture land use
Forest
N
0 0,75 1,5 3 4,5 6
km


LAND USE AND INDUSTRIAL COMPOUNDS RATIOS
MARIBOR
PCI-2
PBA-3
PAC-5
PAC-2
DP-3
OP-6
P-0
OP-5
P-1
GPP-1
GPP-3
HP-3
GPP-2
OP-10
P-3
VP-4
V-25
LP-1
OP-2
PTUJ
Legend
Sampling points
Direction of GW
Urban land use
Industrial land use
Agriculture land use
Forest
N
0 0,75 1,5 3 4,5 6
km


PASSIVE VS. QUANTITATIVE SAMPLING
Legend
ATRAZINE (Passive sampling)
ATRAZINE (Quantitative)
N
PBA-3
PCI-2
PAC-5
PAC-2
DP-3
OP-6
P-0
OP-5
P-1
GPP-1
GPP-3
GPP-2
HP-3
OP-10
P-3
VP-4
V-25
LP-1
OP-2
MARIBOR
RAZVANJE
MIKLAVŽ NA DRAVSKEM POLJU
ZGORNJI DUPLEK
SPODNJI DUPLEK
ROGOZA
SPODNJE HOČE
HOTINJA VAS
RAČE
PTUJ
SPODNJA HAJDINA
KIDRIČEVO
PTUJSKO JEZERO
PRAGERSKO
LOVENSKA BISTRICA
DRAVA

CONCLUSIONS

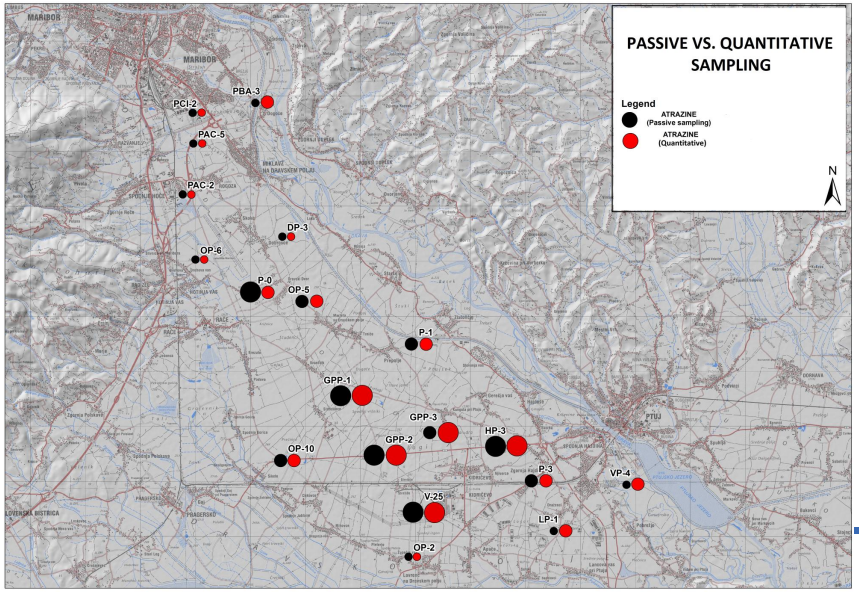
Passive sampling was proved as a proper tool to assess aquifer contamination with micro-organic compounds

- 382 micro-organic pollutants were identify in GW
- 47 typical indicators were classified into groups depending on the source of pollution
  - **Pesticides** are still one of the most problematic groups of pollutants (atrazine, metolachlor, terbuthylazine, etc.)
  - **Industrial pollutants** – tetrachloroetene, acetamide, trichloroetene
  - **Urban pollutants** – flavours, fragnances, cosmetics, reppelents, etc.

CONCLUSIONS

Comparison with distribution from the results of quantitative monitoring from spot sampling showed good correlation.

- Atrazine concentrations are highest in southern part of aquifer, which it was already evident in passive sampling picture.
- Some minor deviations on some points, can be result of **different time frame**.



CONCLUSIONS

Unknown compounds **- aware of the potential risk of presence in groundwater, even in small concentrations.**

Future challenges:

- improve analytical methods
- improve samplers
- set maximum levels of micro-organic pollutants in groundwater
- further examine the fate and transport of pollutants
- identify their sources

Thank you for your attention!

Contact information

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Slovenia