POLITECNICO MILANO 1863

MICROINQUINANTI E CONTAMINANTI EMERGENTI

Stima degli apporti e modelli carichi/qualità: esempi/metodologie

Tools and methods for the source apportionment assessment

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Background

- Chemicals classified as Contaminants of Emerging Concern (CECs) have been found in most environmental compartments, including polar ice caps, groundwater, treated drinking water, soil, the atmosphere, precipitation, animal tissues, breast milk, and the blood and urine of infants.

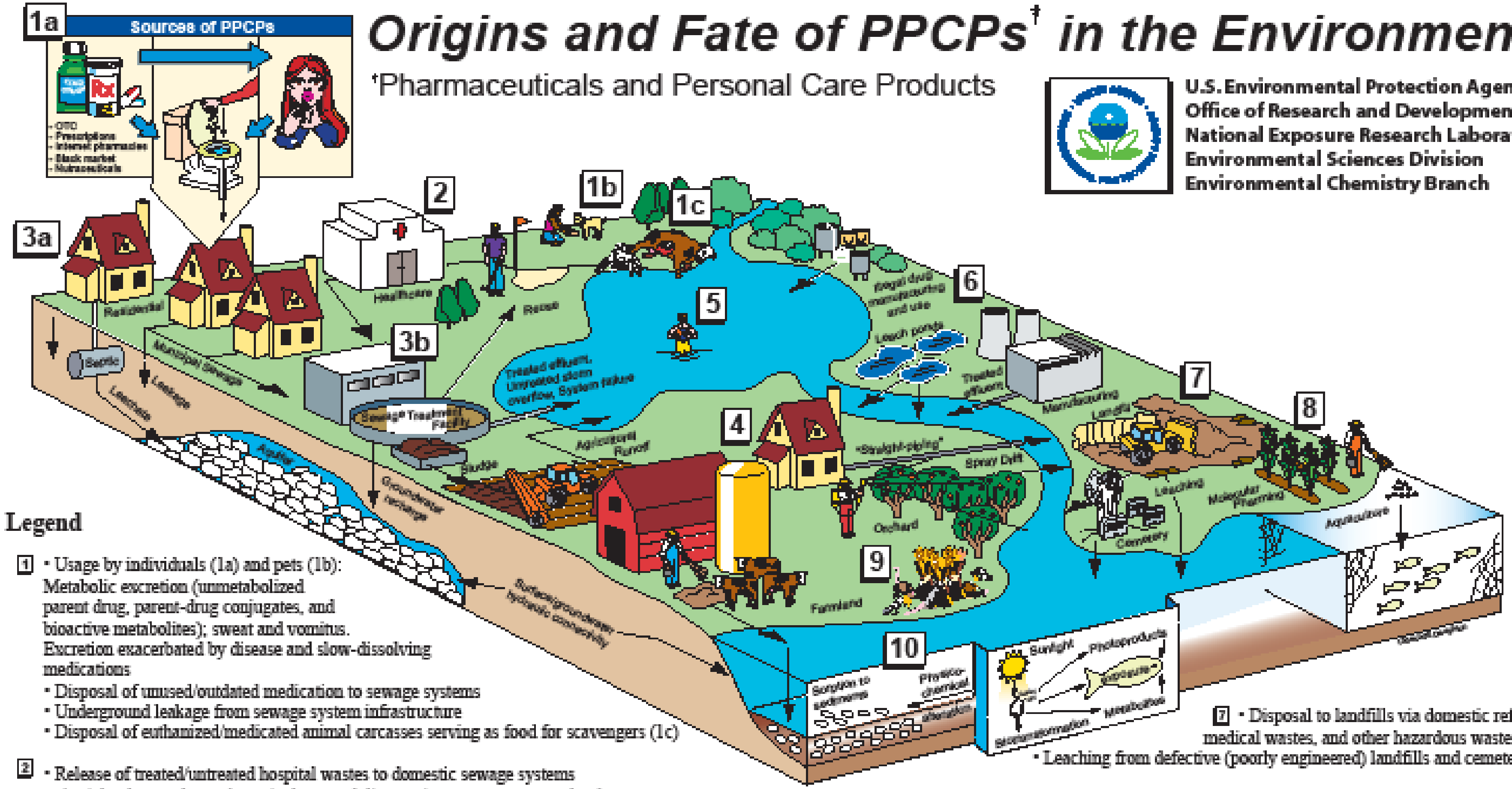
- Major CEC sources to surface waters include municipal wastewater treatment plants (WWTPs), industrial and commercial facilities, croplands, concentrated animal feeding operations (CAFOs), urban exterior landscapes, landfills, and septic systems.

- Transport to surface waters occurs via point and nonpoint mechanisms including pipe discharges, surface runoff, atmospheric deposition, and baseflow. Instream studies often indicate the potential for long-range transport.

Origins and Fate of PPCPs† in the Environment

†Pharmaceuticals and Personal Care Products

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch



Legend

1 • Usage by individuals (1a) and pets (1b): Metabolic excretion (unmetabolized parent drug, parent-drug conjugates, and bioactive metabolites); sweat and vomitus. Excretion exacerbated by disease and slow-dissolving medications
• Disposal of unused/outdated medication to sewage systems
• Underground leakage from sewage system infrastructure
• Disposal of euthanized/medicated animal carcasses serving as food for scavengers (1c)

2 • Release of treated/untreated hospital wastes to domestic sewage systems (weighted toward acutely toxic drugs and diagnostic agents, as opposed to long-term medications); also disposal by pharmacies, physicians, humanitarian drug surplus

3 • Release to private septic/leach fields (3a)
• Treated effluent from domestic sewage treatment plants discharged to surface waters, re-injected into aquifers (recharge), recycled/reused (irrigation or domestic uses) (3b)
• Overflow of untreated sewage from storm events and system failures directly to surface waters (3b)

4 • Transfer of sewage solids ("biosolids") to land (e.g., soil amendment/fertilization)
• "Straight-piping" from homes (untreated sewage discharged directly to surface waters)
• Release from agriculture: spray drift from tree crops (e.g., antibiotics)
• Dung from medicated domestic animals (e.g., feed) - CAFOs (confined animal feeding operations)

5 • Direct release to open waters via washing/bathing/swimming

6 • Discharge of regulated/controlled industrial manufacturing waste streams
• Disposal/release from clandestine drug labs and illicit drug usage

7 • Disposal to landfills via domestic refuse, medical wastes, and other hazardous wastes
• Leaching from defective (poorly engineered) landfills and cemeteries

8 • Release to open waters from aquaculture (medicated feed and resulting excreta)
• Future potential for release from molecular pharming (production of therapeutics in crops)

9 • Release of drugs that serve double duty as pest control agents: examples: 4-aminopyridine, experimental multiple sclerosis drug → used as avicide; warfarin, anticoagulant → rat poison; azacholesterol, antilipidemics → avian/rodent reproductive inhibitors; certain antibiotics → used for orchard pathogens; acetaminophen, analgesic → brown tree snake control; caffeine, stimulant → *coqui* frog control

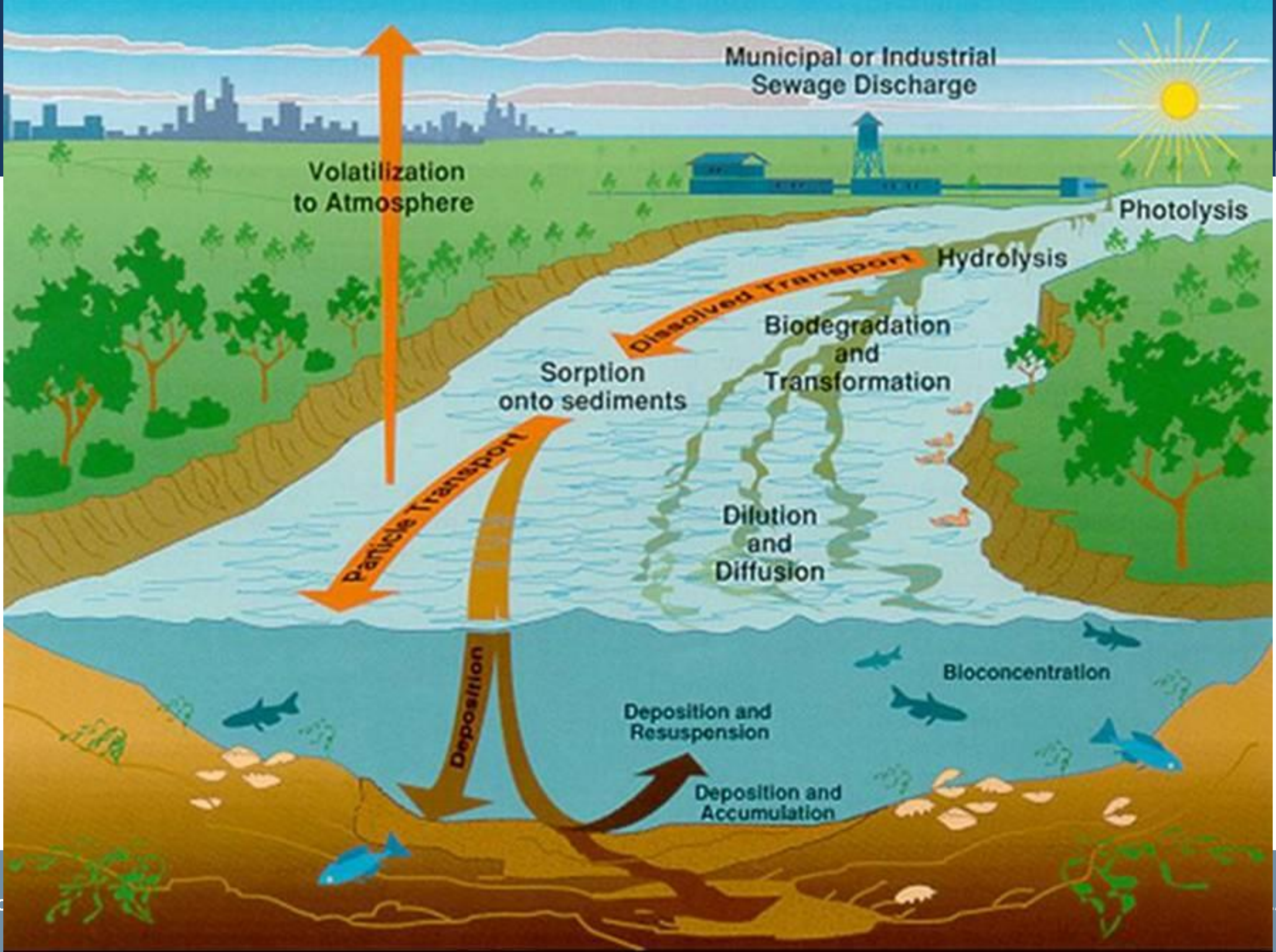
10 Ultimate environmental transport/fate:
• most PPCPs eventually transported from terrestrial domain to aqueous domain
• phototransformation (both direct and indirect reactions via UV light)
• physicochemical alteration, degradation, and ultimate mineralization
• volatilization (mainly certain anesthetics, fragrances)
• some uptake by plants
• respirable particulates containing sorbed drugs (e.g., medicated-feed dusts)

Christian G. Daughton, U.S. EPA-Las Vegas

March 2006
(original February 2001)

http://epa.gov/nerlesd1/chemistry/pharma/images/drawing.pdf
from: http://epa.gov/nerlesd1/chemistry/pharma/

http://www.epa.gov/ppcp/basic2.html



Municipal or Industrial Sewage Discharge
Volatilization to Atmosphere
Photolysis
Hydrolysis
Dissolved Transport
Biodegradation and Transformation
Sorption onto sediments
Particle Transport
Dilution and Diffusion
Deposition
Bioconcentration
Deposition and Resuspension
Deposition and Accumulation

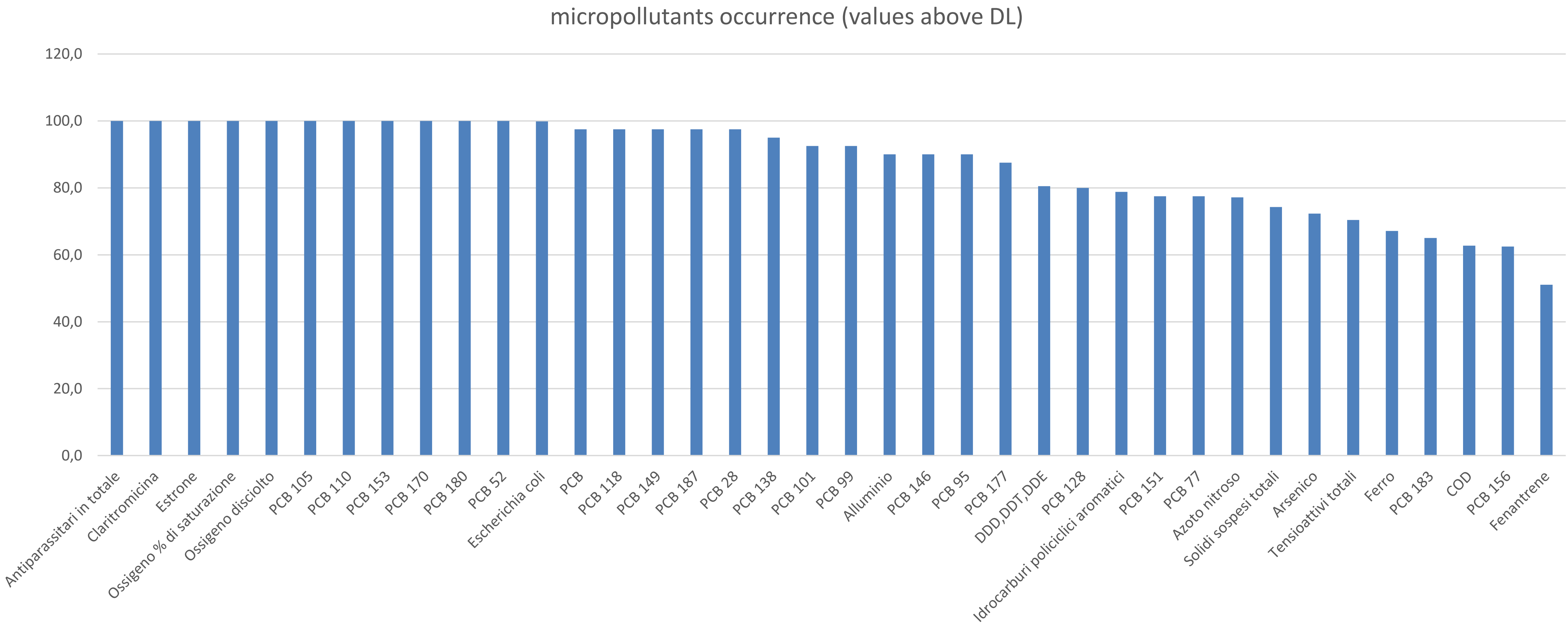
Fate and Transport

Despite numerous studies, significant gaps remain in our knowledge of CEC fate and transport, effects, and mitigation potential in complex environmental systems.

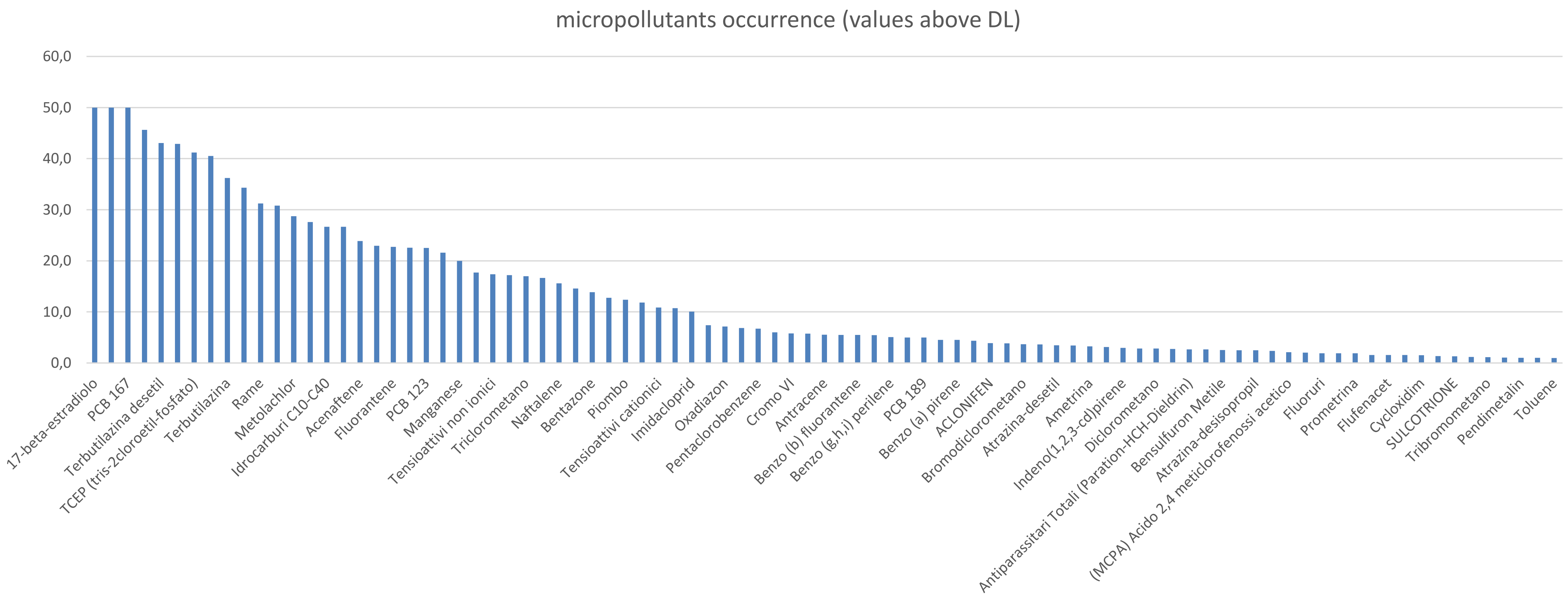
Source identification and apportionment studies rely on:

- Chemometric methods (PCA/FA –HCA/CA)
- Multiple Linear Regression

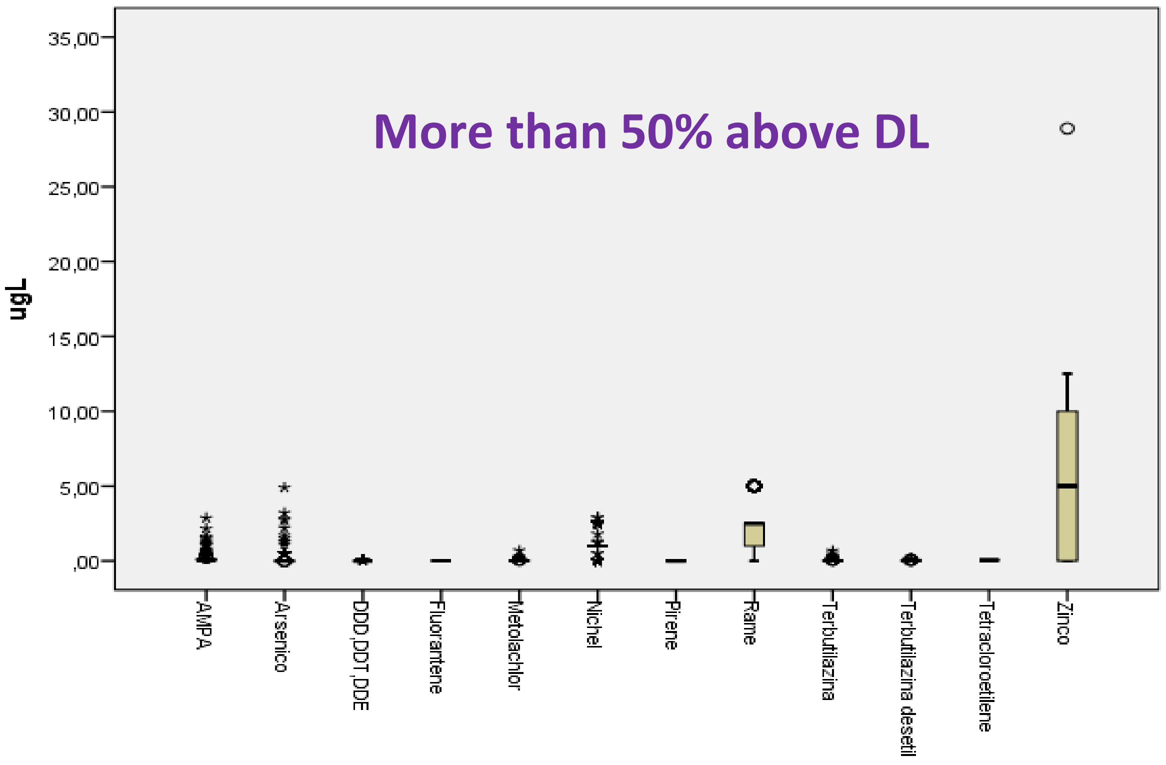
Micropollutants in Lombardy (1/2)

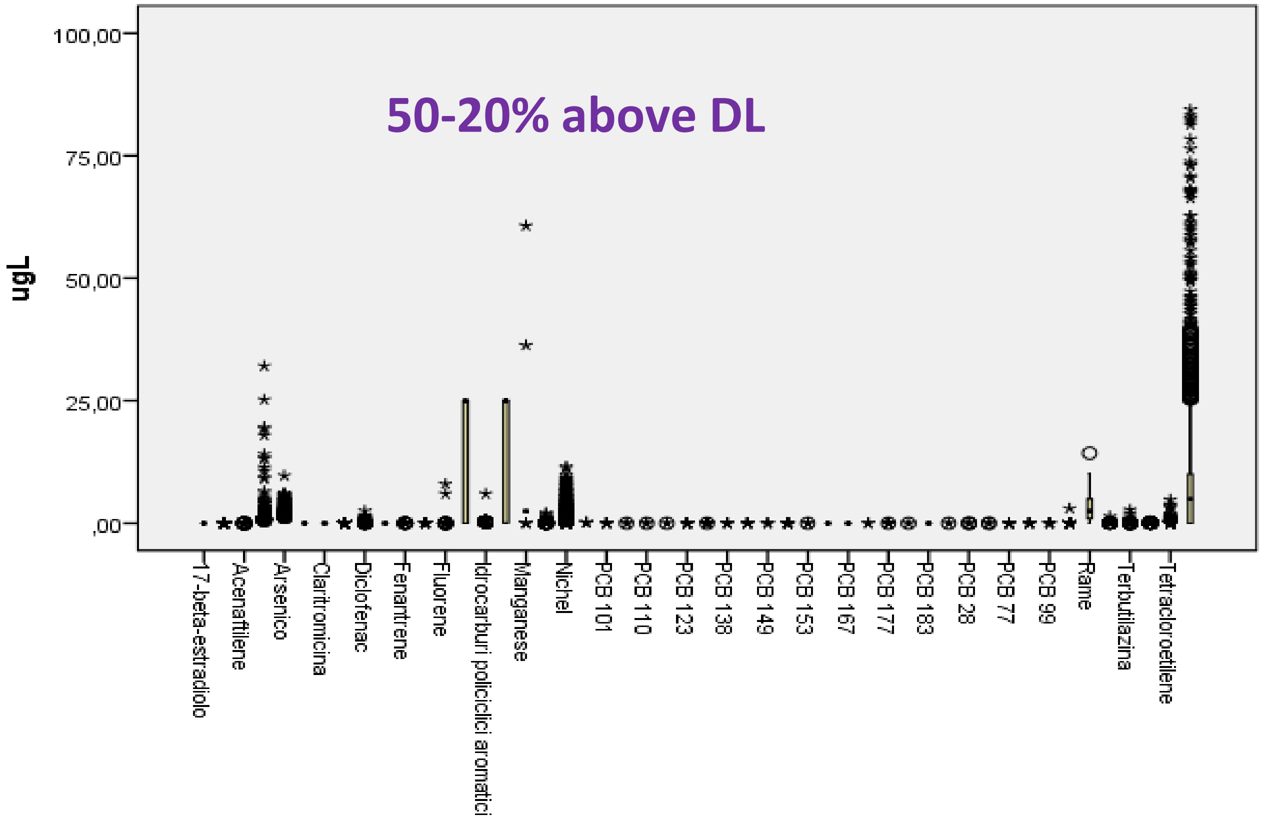


Micropollutants in Lombardy (2/3)



Micropollutants in Lombardy (3/3)

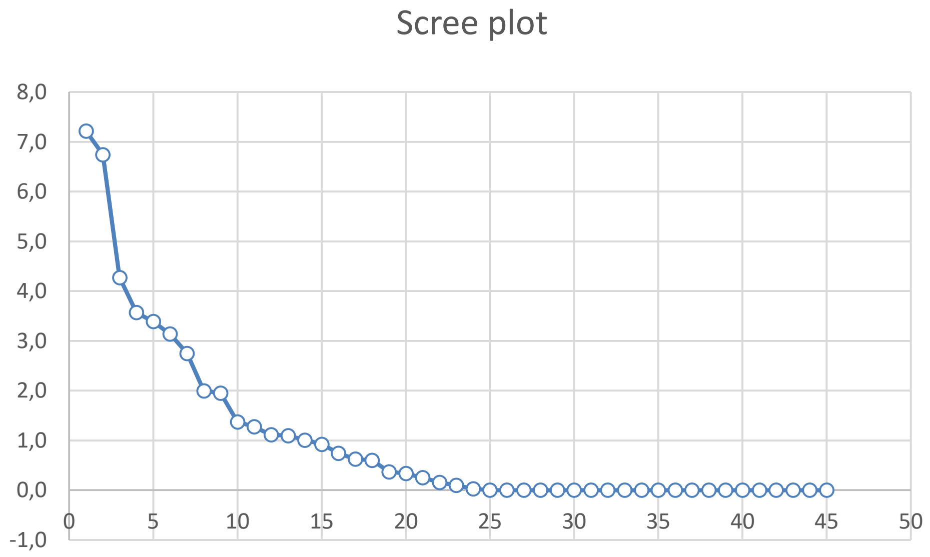




Correlation patterns of micropollutants

METHODS

Principal Component Analysis (PCA) rotated to a Factor Analysis (FA) allowing to reduce redundancy, and to highlight common patterns of variability



Total Variance Explained

Component	Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7,2	16,0	16,0	7,0	15,7	15,7
2	6,7	15,0	31,0	5,2	11,6	27,3
3	4,3	9,5	40,5	3,8	8,4	35,6
4	3,6	7,9	48,4	3,3	7,3	42,9
5	3,4	7,5	56,0	2,8	6,3	49,2
6	3,1	7,0	63,0	2,6	5,8	54,9
7	2,7	6,1	69,1	2,4	5,3	60,3
8	2,0	4,4	73,5	2,3	5,2	65,4
9	1,9	4,3	77,8	2,3	5,1	70,5
10	1,4	3,1	80,9	2,1	4,6	75,2
11	1,3	2,8	83,7	2,0	4,4	79,6
12	1,1	2,5	86,2	1,9	4,3	83,8
13	1,1	2,4	88,6	1,6	3,6	87,5
14	1,0	2,2	90,8	1,5	3,4	90,8
15						

Correlation patterns of micropollutants

F1 Pesticides;
F2 EC, COD, Alkalinity, DO, Freon10;
F3 MCPA, Cd Alkalinity, Ca, hardness;
F4 Atrazina, BOD, Ecoli;
F5 AMPA, Glyphosate, Cr-tot, Cu;
F6 Clorpirifos, Diuron;
F7 NNH3, NNH4, HCB, Hg;
F8 Ni, Pb, Cl;
F9 Prometryne, PCE;
F10 As, Quinclorac;
F11 Sulfates, Terbuthylazine;
F12 Alachlor, Metolachlor;
F13 Molinate, Diclofenac;
F14 Methiocarb;

Rotated Component Matrix[a]

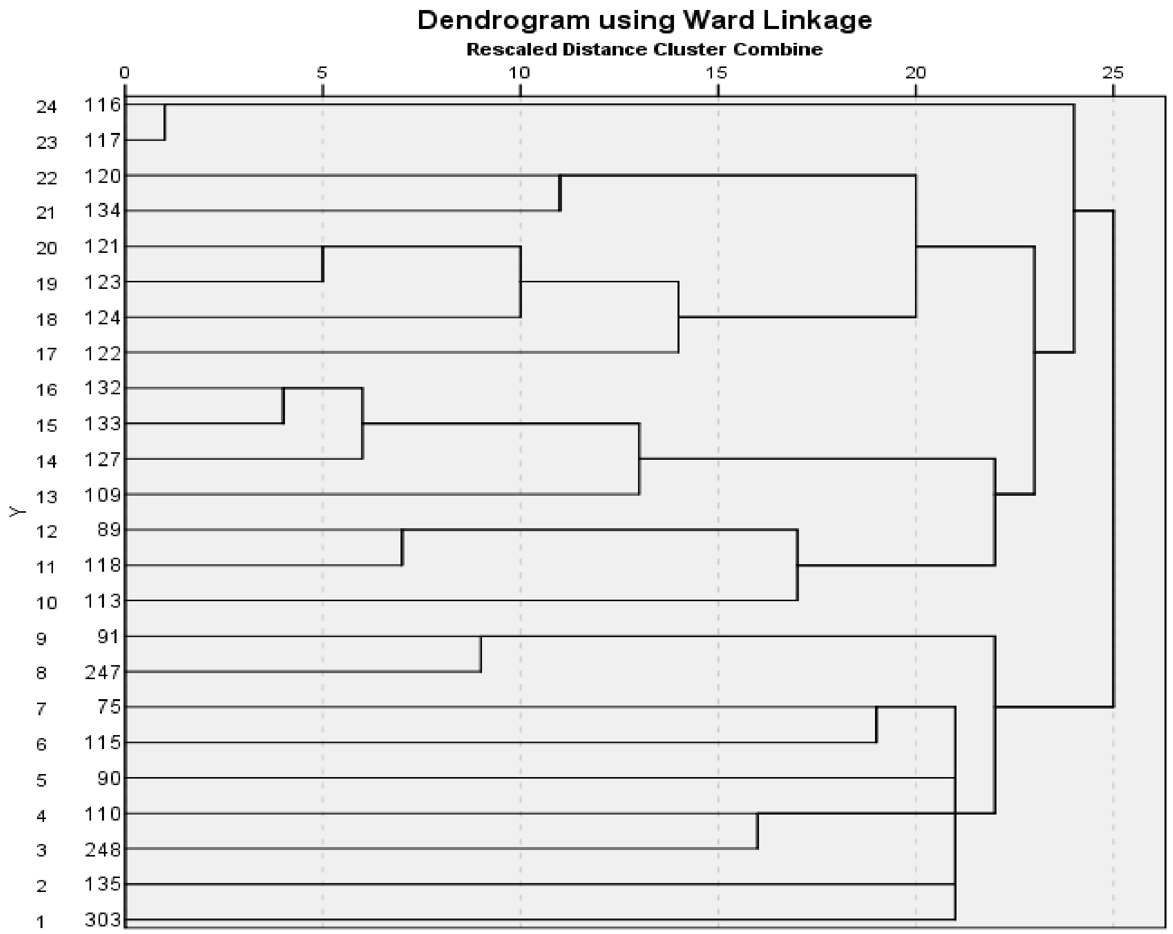
	Component													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
MCPA_mean			,757											
Alachlor_mean												,610		
Alcalinità_mean		,641	,671											
Aldrin_mean	,999													
NH3							,806							
NH4_NH4				-,454		,510	,458							
AMPA_mean					,933									
Arsenico_mean										,938				
Atrazina_mean				,628				,404						
Atrazina_desetil_mean				,950										
BOD_mean				,734										
Cadmio_mean			,765											
Calcio_mean			,838											
Clorpirifos_mean						,958								
Cloruri_mean								-,855						
COD_mean		-,939												
EC_mean		-,951												
Cr_tot_mean		-,433			,589									
DDT_mean	,999													
Diclofenac_mean													,655	
Dieldrin_mean	,999													
Diuron_mean						,957								
durezza_mean			,846											
endosulfan_alfa_beta_mean	,999													
Esaclorobenzene_mean							,529			-,403		-,536		
Ecoli_mean				,846										
Glifosate_mean					,878									
Malathion_mean	,999													
Mercurio_mean							,905							
Methiocarb_mean														,936
Metolachlor_mean											,415	,641		
Molinate_mean													,778	
Nichel_mean								,603						
OD_mean		,803												
pH_mean		,938												
Piombo_mean		,449						,604						
Prometrina_mean									,851					
Propazina_mean	,999													
Quinclorac_mean										,714				
Rame_mean				-,419	,524									
Simazina_mean	,999													
Solfati_mean											,851			
Terbutilazina_mean											,817			
Tetracloroetilene_mean									,854					
Tetraclorurocarbonio_mean		-,730												

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 16 iterations.

Correlation patterns of micropollutants

Finally, a Cluster Analysis (CA) was used to analyse the similarities among the water quality profiles using the Euclidean Distance as distance metric



Correlation patterns of micropollutants

Cluster Analysis (CA) identified four clusters

F1 Pesticides;
F2 EC, COD, Alkalinity, DO, Freon10;
F3 MCPA, Cd Alkalinity, Ca, hardness;
F4 Atrazina, BOD, Ecoli;
F5 AMPA, Glyphosate, Cr-tot, Cu;
F6 Clorpirifos, Diuron;
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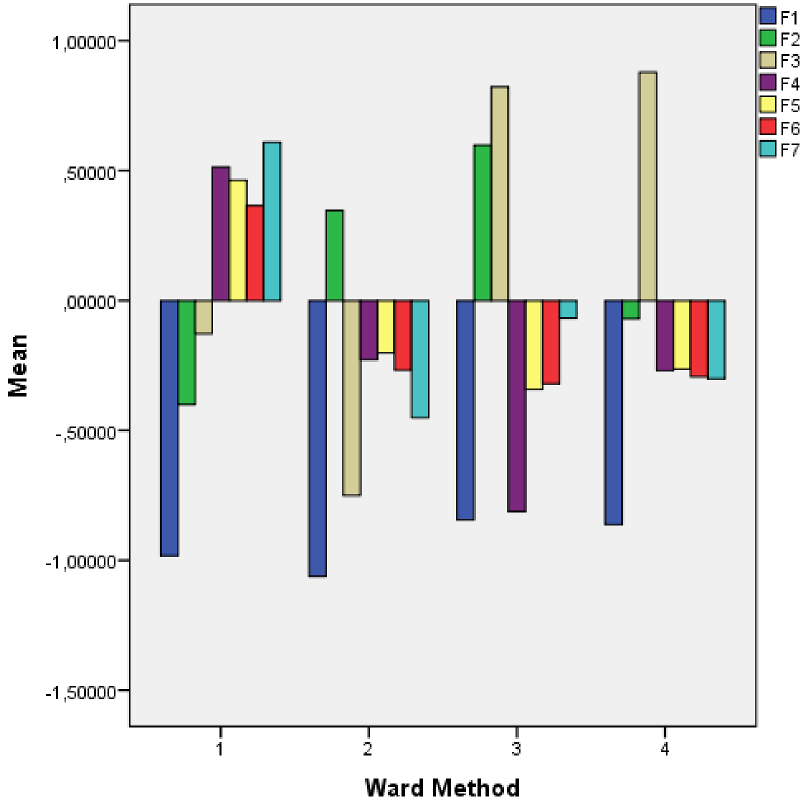

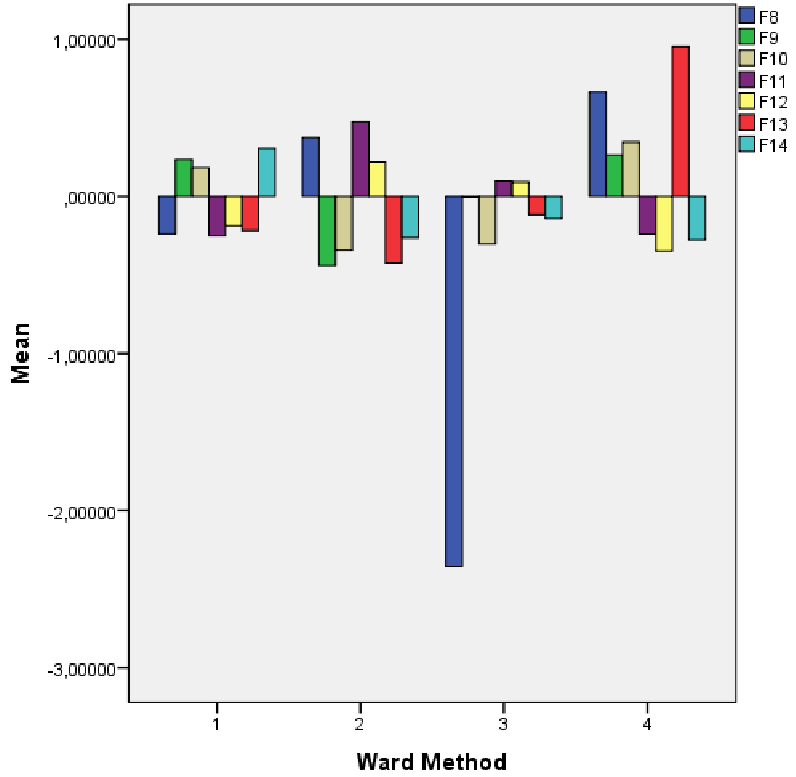

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F14 Methiocarb;

	Cluster1	Cluster2	Cluster3	Cluster4
F1	--	--	--	--
F2	-	+	++	mean
F3	mean	--	++	++
F4	++	-	--	-
F5	++	-	-	-
F6	+	-	-	-
F7	+	-	mean	mean
F8	-	+	--	+
F9	+	-	mean	mean
F10	mean	-	-	mean
F11	mean	+	mean	mean
F12	mean	mean	mean	mean
F13	mean	-	mean	+
F14	+	mean	mean	mean

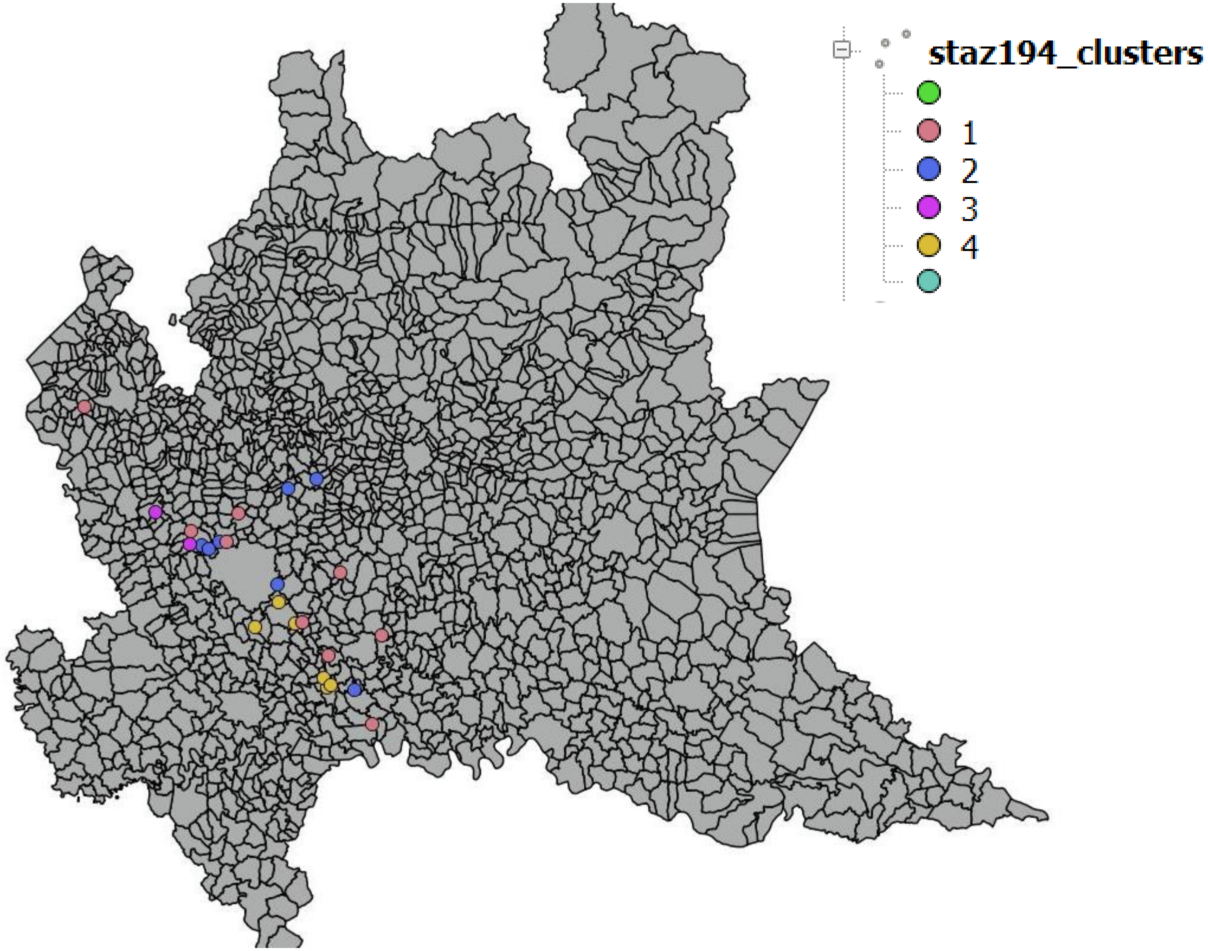
Cluster 1: high Atrazine, BOD, Ecoli, AMPA, Glyphosate, Cr-tot, Cu, Clorpirifos, Diuron, HCB, Hg, Prometryne, PCE;

Cluster 2: high Freon, Ni, Pb, Terbuthylazine;

Cluster 3: high MCPA, Cd, Ca, hardness, Atrazine; BOD, Ecoli

Cluster 4: high Atrazine, Ni, Pb, Cl, Molinate, Diclofenac;

Spatial patterns of micropollutants



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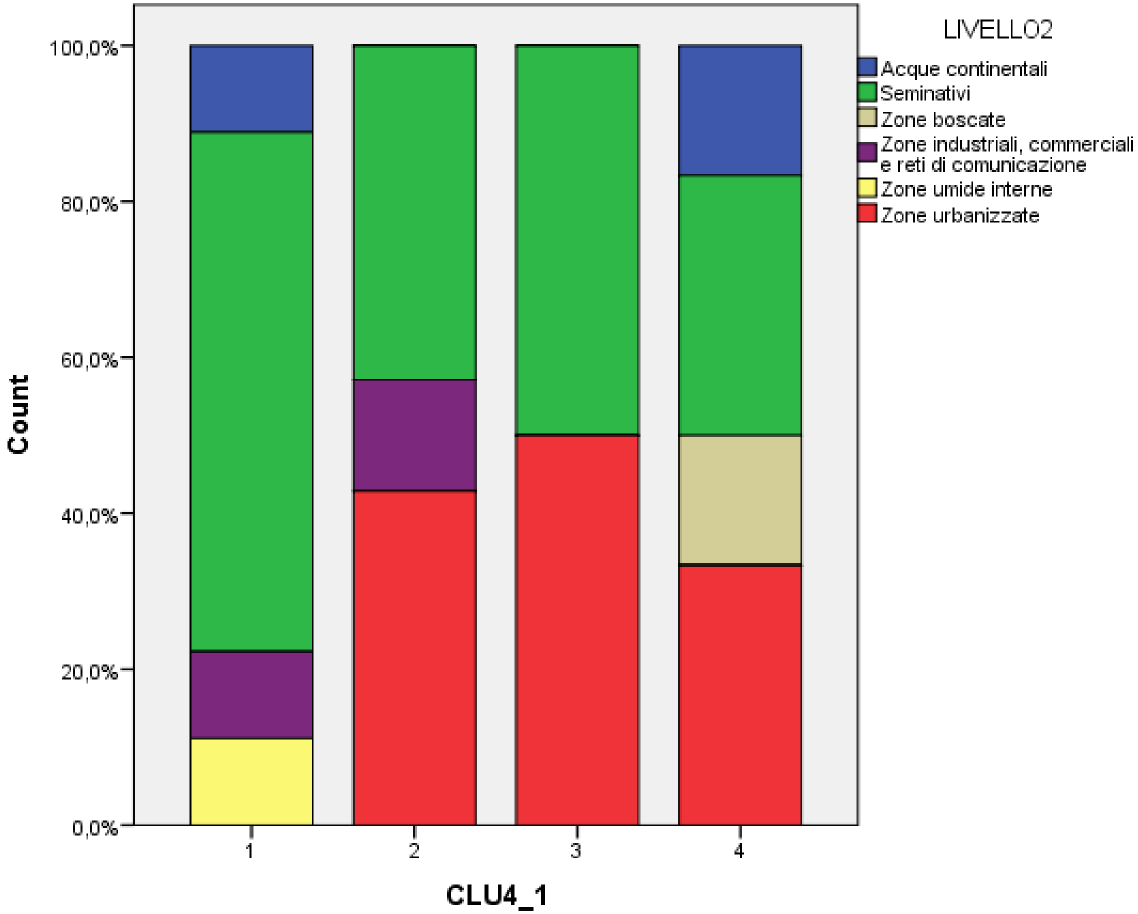

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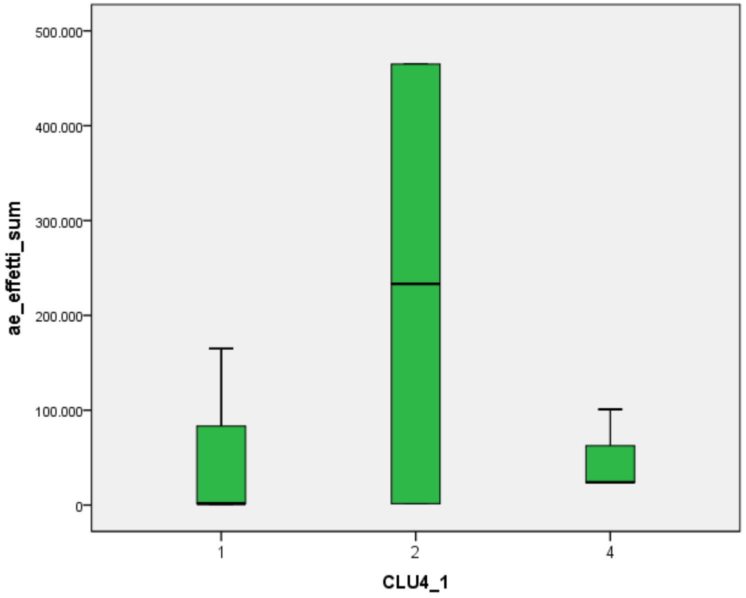
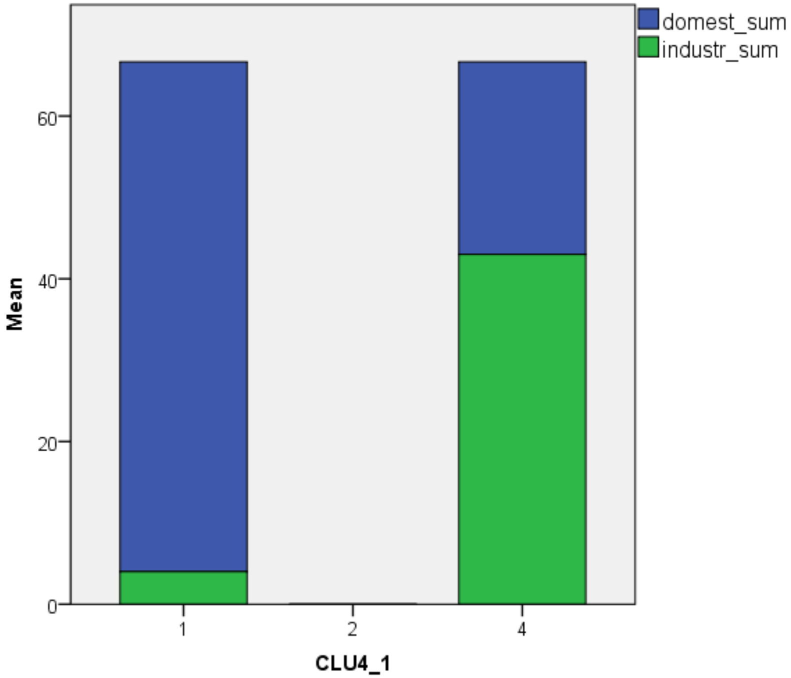
Predictors for the patterns of micropollutants





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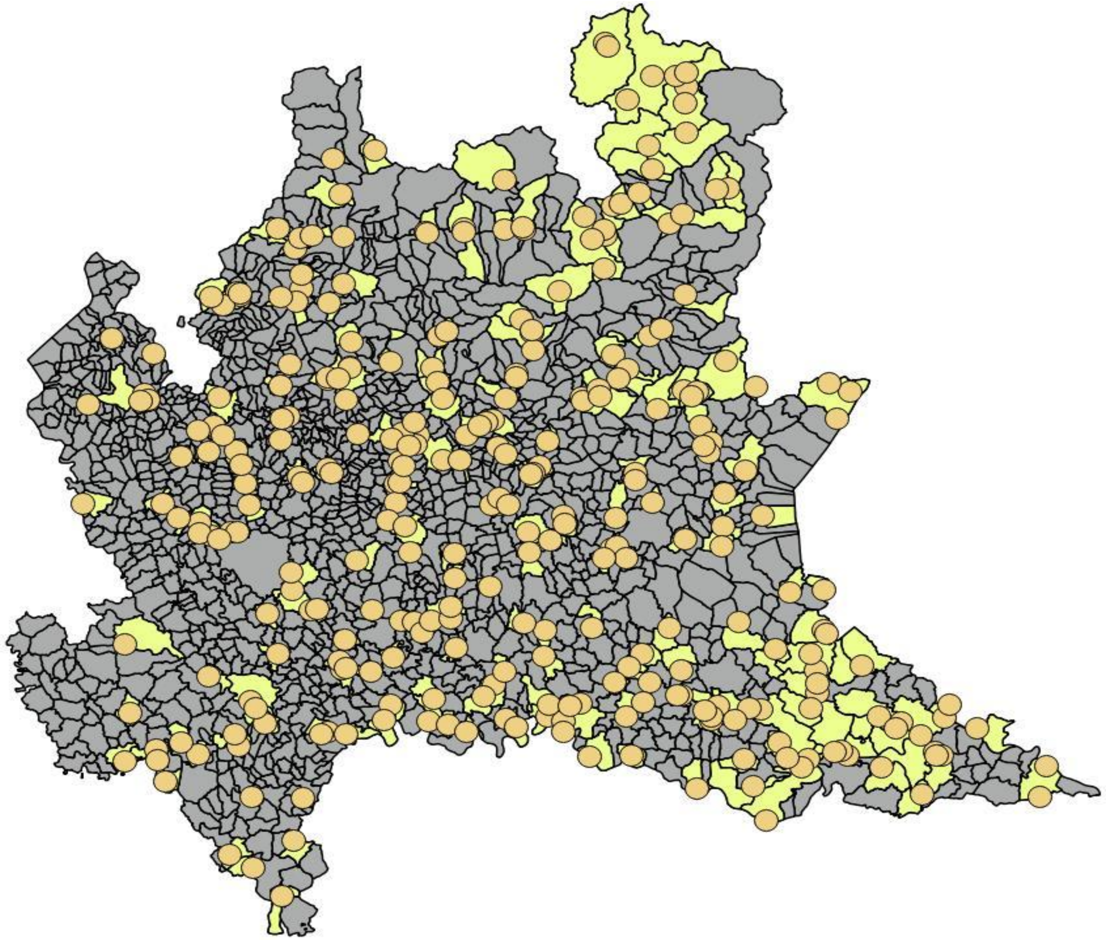
Predictors for the patterns of micropollutants: EPTR emissions catalogue



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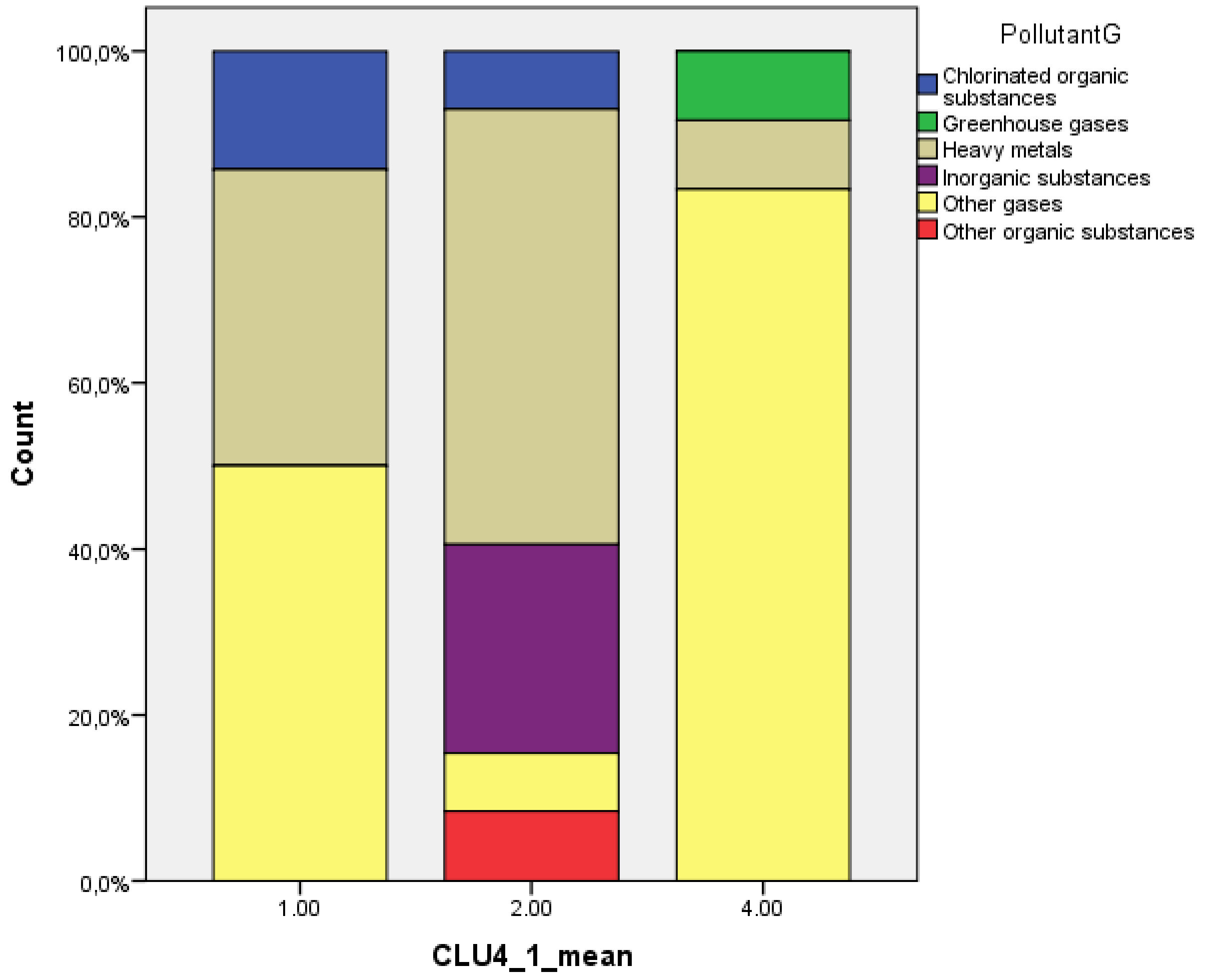

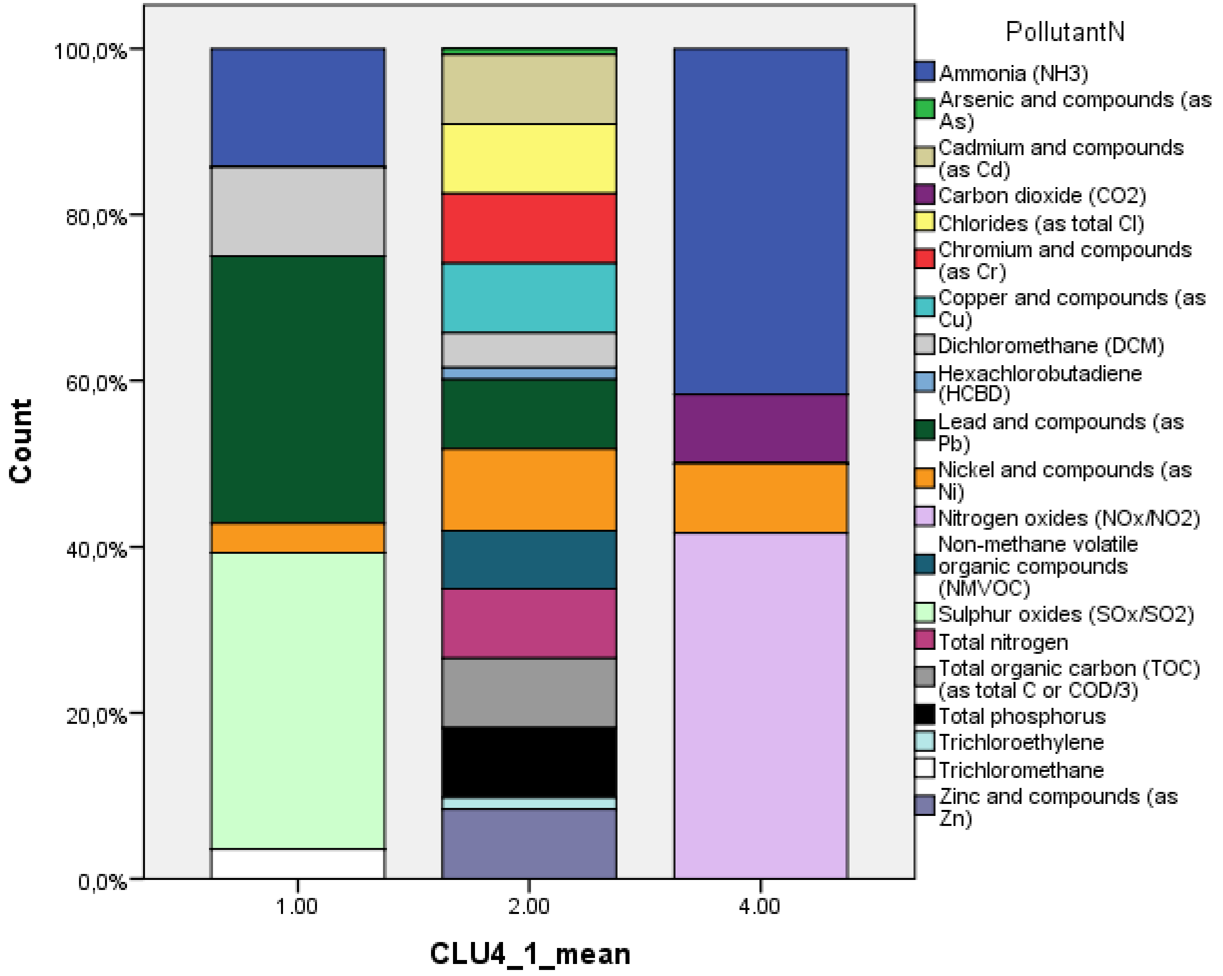

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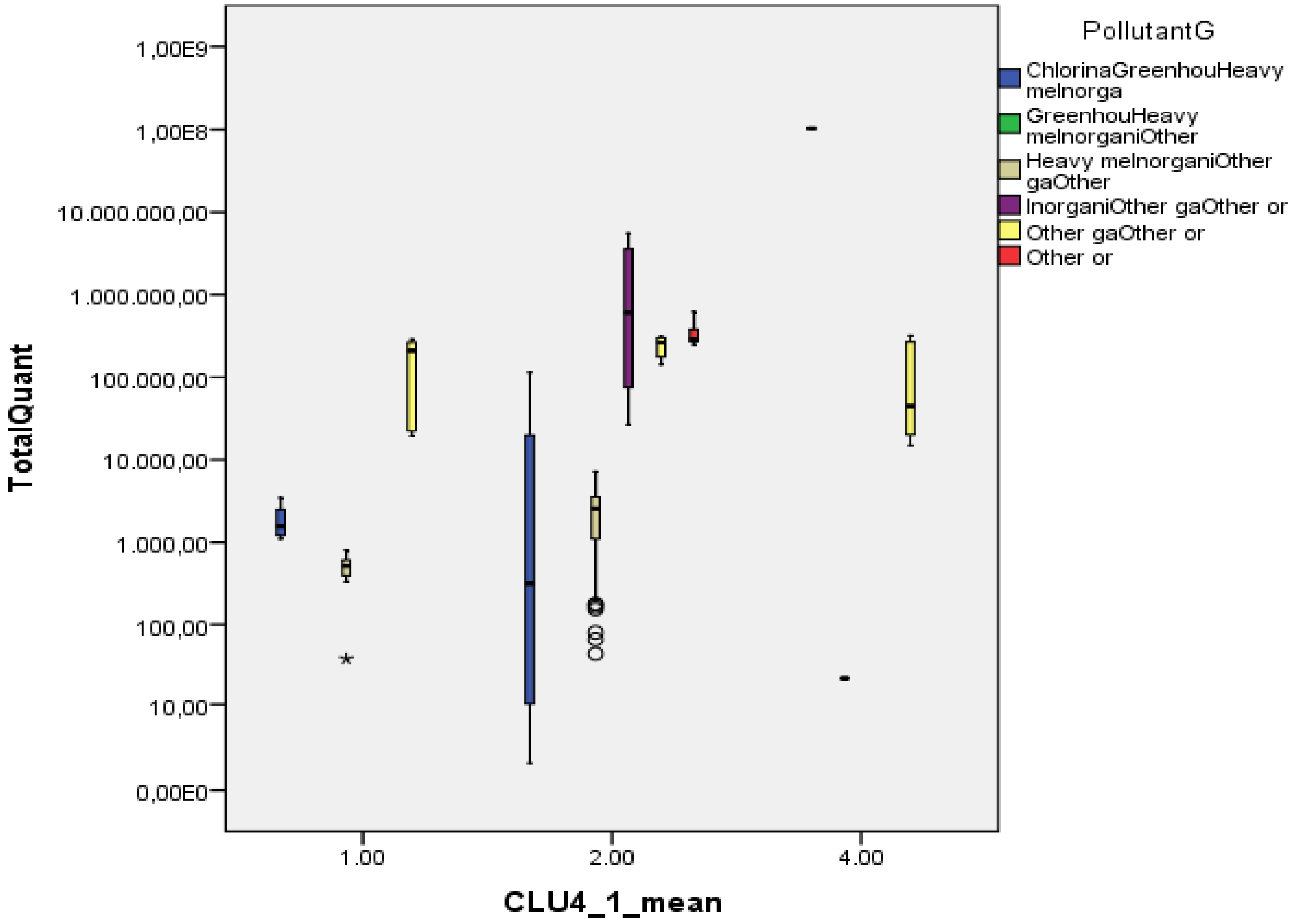

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Suface and ground water quality profiles

- 1,377 samples from groundwater and surface water during 2015 from ARPA Lombardia

54 parameters of surface water — 74 parameters of ground water

Summary statistic of the water quality measurements

SW.Elements	N	Min	Max	Mean	GW.Elements	N	Min	Max	Mean
AMPA	484	0.10	24.80	0.81	AMPA_gw	29	0.05	0.05	0.05
As	780	1.00	37.00	2.79	As_gw	272	0.50	291.00	5.64
NNH4	777	0.02	14.78	0.97	Bentazone_gw	262	0.02	0.40	0.03
NNO3	780	0.14	20.20	2.79	Boron_gw	272	5.00	1170.00	57.99
NNO2	779	0.00	9.90	1.80	Chlorides_gw	270	0.50	80.00	16.96
Bentazone	360	0.03	7.00	0.09	Conductivity_gw	266	66.00	1176.20	524.73
Boron	8	0.10	0.10	0.10	Gliphosate_gw	29	0.05	0.05	0.05
Chlorides	780	0.50	293.00	26.17	NNH4_gw	224	10.00	4980.00	281.58
Conductivity	1077	18.20	2324.00	457.87	Metolachlor_gw	272	0.01	0.15	0.02
Glyphosate	483	0.10	11.20	0.20	Ni_gw	272	0.50	86.00	2.90
Metolachlor	756	0.02	7.00	0.15	NNO3_gw	268	0.50	118.00	18.38
Ni	1174	1.00	823.00	7.34	NNO2_gw	225	2.50	365.00	23.06
Sulfates	780	2.00	271.00	36.97	Sulfates_gw	272	1.00	132.00	31.28
Terbuthylazine	739	0.02	7.00	0.20	Terbuthylazine_gw	272	0.01	0.10	0.02
Terbuthylazine desetil	738	0.02	7.00	0.26	Terbuthylazine desetil_gw	272	0.01	0.22	0.03
Tetrachloroethylene	542	0.05	12.00	0.32	Tetracloroetilene_gw	271	0.03	29.40	1.25
Trichloroethane	546	0.03	7.00	0.28	Triclorometano_gw	270	0.02	3.40	0.18
Vanadium	8	0.01	0.01	0.01	Vanadio_gw	272	0.50	10.00	2.48

Factor Analysis

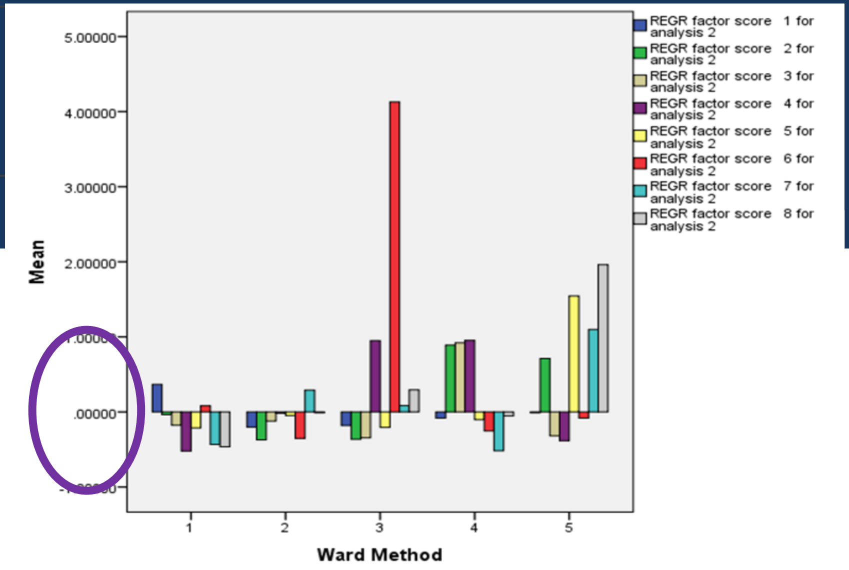
- ✓ Surface and groundwater contaminants lie on different factors;
- ✓ Apart from As for which surface and groundwater concentration load the same varifactor, and groundwater Nickel which load the same varifactor of surface water metolachlor and terbuthylazine desethyl;
- ✓ all nitrogen components and pesticide mother component and metabolites (e.g. glyphosate and AMPA, and terbuthylazine and terbuthylazine desethyl) load different varifactors,
- ✓ groundwater terbuthylazine and terbuthylazine desethyl concentrations are apparently more correlated.

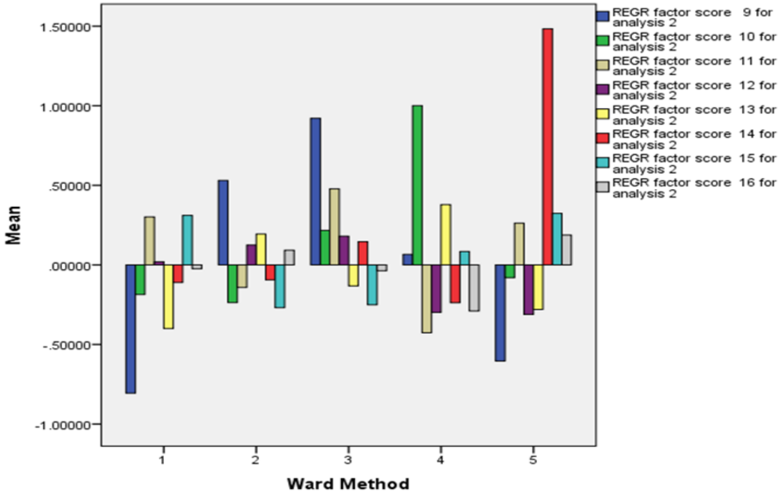
Rotated Component Matrix[a]

	Component															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
AMPA	**0.663**	0.251	0.024	-0.173	0.039	0.068	-0.227	-0.192	-0.075	-0.361	0.074	-0.131	-0.296	0.049	-0.056	0.102
As	0.021	-0.045	**0.901**	0.045	-0.016	-0.062	0.077	0.003	-0.028	0.004	-0.077	-0.003	0.114	-0.075	0.001	-0.153
NNH4	0.048	0.067	-0.026	0.048	-0.086	-0.111	0.016	0.040	-0.116	-0.003	-0.022	-0.028	-0.059	0.103	**0.894**	0.167
NNO3	0.436	-0.010	-0.009	0.065	0.142	0.090	-0.023	-0.025	-0.077	-0.240	-0.156	0.108	0.075	-0.048	0.025	**0.761**
NNO2	-0.157	-0.023	0.220	0.070	-0.036	-0.189	-0.003	-0.006	0.199	-0.050	-0.098	0.115	**0.843**	0.040	-0.086	0.036
Chlorides	**0.901**	0.125	-0.065	-0.086	0.043	0.119	-0.042	-0.007	-0.128	0.118	0.040	-0.016	-0.143	0.054	0.055	-0.001
Conductivity	**0.881**	-0.001	0.037	0.033	0.008	0.001	0.113	0.082	0.023	0.066	-0.120	0.256	0.135	0.058	0.055	0.143
Glyphosate	0.191	0.196	-0.100	-0.194	0.153	0.107	0.376	-0.219	-0.249	-0.006	-0.021	-0.107	-0.126	-0.058	0.264	0.268
Metolachlor	0.031	0.083	-0.070	0.053	**0.838**	0.014	-0.043	-0.015	0.110	-0.006	-0.095	0.013	0.094	-0.062	0.028	-0.013
Ni	0.038	0.011	-0.075	-0.039	-0.037	0.048	-0.075	-0.014	-0.009	-0.077	-0.077	-0.047	-0.017	**0.954**	0.001	-0.012
Sulfates	**0.919**	-0.018	-0.026	-0.050	-0.019	-0.081	0.041	0.016	-0.042	0.148	0.036	-0.105	-0.012	-0.036	0.018	0.058
Terbuthylazine	0.011	0.060	-0.009	-0.005	-0.015	-0.010	-0.011	0.012	0.085	0.015	-0.120	**0.827**	0.090	-0.104	-0.105	0.059
Terbuthylazine_desetil	0.016	0.058	0.016	0.281	**0.632**	-0.095	-0.042	0.243	-0.126	-0.156	-0.066	-0.054	0.107	-0.001	-0.233	0.195
As_gw	-0.081	-0.190	**0.830**	-0.032	-0.025	-0.082	0.202	0.000	0.183	-0.053	-0.068	0.068	0.119	-0.033	-0.010	0.159
Bentazone_gw	0.007	0.080	-0.001	-0.110	0.000	-0.075	-0.035	**0.923**	-0.054	-0.039	0.084	-0.036	-0.014	-0.007	0.038	-0.003
Boron_gw	0.118	0.077	-0.111	0.170	0.208	**0.841**	0.210	-0.028	-0.029	0.003	0.104	0.098	-0.182	0.034	-0.006	-0.055
Chlorides_gw	0.200	**0.826**	-0.063	-0.021	0.061	0.189	0.157	-0.076	-0.087	-0.168	0.100	0.043	-0.071	-0.011	0.017	-0.167
Conductivity_gw	0.022	**0.899**	-0.019	0.103	0.006	-0.130	0.090	0.107	0.028	0.101	0.033	0.132	0.037	0.027	0.069	0.031
NNH4_gw	-0.010	0.067	0.352	-0.082	-0.059	-0.083	**0.848**	-0.052	0.046	-0.109	-0.077	-0.054	0.049	-0.079	-0.062	0.009
Metolachlor_gw	-0.123	-0.030	0.095	0.014	-0.027	-0.071	-0.044	-0.105	**0.869**	0.206	-0.057	0.044	0.090	0.026	-0.128	-0.040
Ni_gw	0.370	0.134	-0.024	0.103	**0.600**	0.048	-0.006	-0.170	-0.053	0.284	0.049	-0.023	-0.225	-0.010	0.042	0.037
NNO3_gw	0.079	**0.664**	-0.176	0.124	0.150	0.156	-0.444	-0.182	-0.013	0.182	-0.108	-0.140	0.094	-0.041	0.058	0.039
NNO2_gw	0.173	0.179	-0.053	-0.003	-0.002	-0.036	-0.162	-0.052	0.139	**0.827**	-0.126	0.045	-0.082	-0.083	-0.071	-0.167
Sulfates_gw	-0.042	**0.687**	-0.208	-0.020	-0.003	-0.053	-0.034	0.350	-0.183	0.259	0.118	-0.189	-0.076	-0.001	0.083	0.285
Terbuthylazine_gw	-0.027	-0.075	0.011	**0.906**	0.128	0.177	-0.010	-0.080	0.196	0.015	0.117	-0.013	-0.069	0.034	-0.114	0.043
Terbuthylazine desetil_gw	-0.115	0.279	0.006	**0.859**	0.008	-0.139	-0.115	-0.068	-0.162	0.004	-0.128	-0.006	0.159	-0.060	0.056	-0.004
Tetrachlorethylene_gw	0.135	0.307	-0.091	-0.307	0.186	0.127	-0.033	-0.372	-0.378	-0.087	0.270	-0.258	-0.080	0.279	0.043	0.246
trichloromethane_gw	0.006	-0.024	-0.092	-0.010	-0.069	**0.919**	-0.126	-0.071	-0.058	-0.028	0.047	-0.056	-0.073	0.041	-0.056	0.070
Vanadiom_gw	-0.030	0.073	-0.125	0.013	-0.081	0.104	-0.051	0.084	-0.087	-0.090	**0.918**	-0.013	-0.064	-0.054	0.025	-0.072

Hierarchical Cluster Analysis

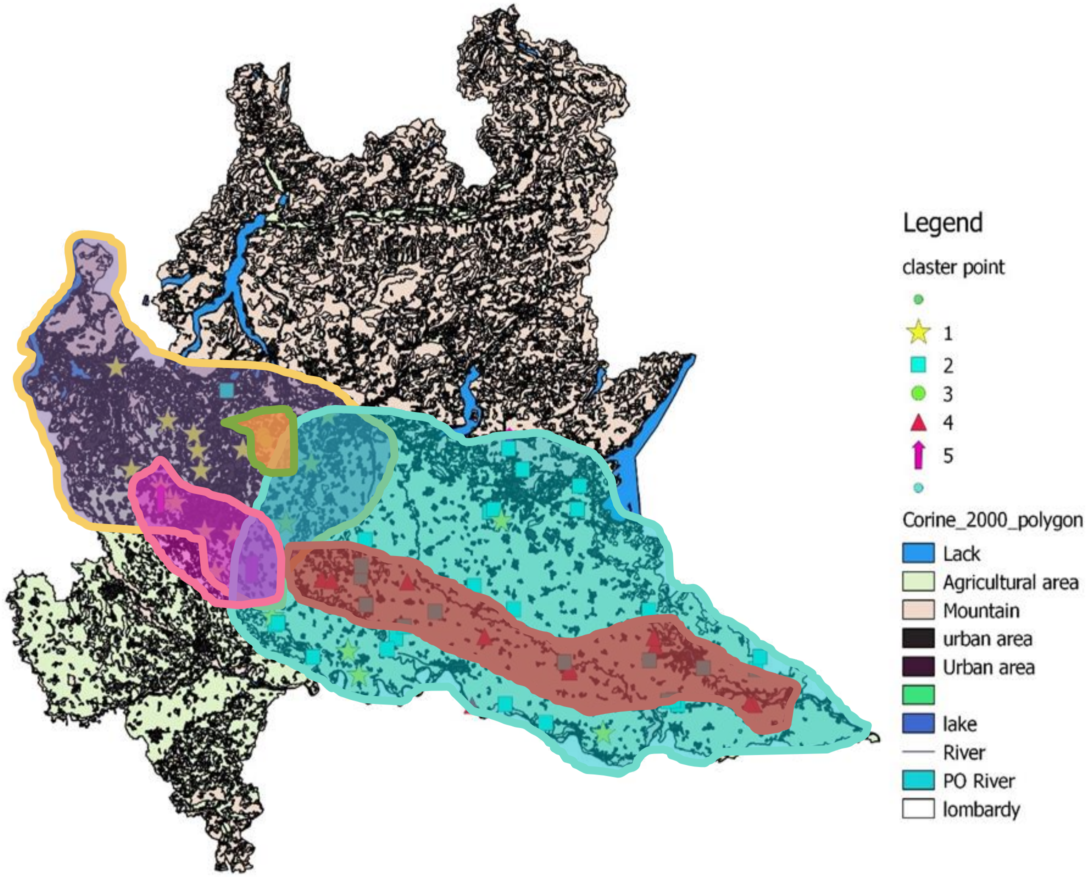
- **Cluster 1:** concentrations higher than the average concerning <u>AMPA</u>, <u>chlorides</u>, <u>EC</u>, <u>sulfates</u> (varifactor 1), and ammonium (varifactor 15) in surface waters and <u>vanadium</u> concentrations in groundwater.
- **Cluster 2:** groundwater metolachlor concentrations which are higher than the average.
- **Cluster 3:** are made of outliers and it is characterized by high boron and trichloromethane concentrations in groundwater.
- **Cluster 4:** shows a high concentration in terms of terbuthylazine, chlorides, EC, nitrates, and sulfates, and arsenic both in groundwater and in surface water.
- **Cluster 5:** are made of outliers and shows the high concentration of chlorides, nitrates and sulfates , bentazone and ammonium.





Hierarchical Cluster Analysis

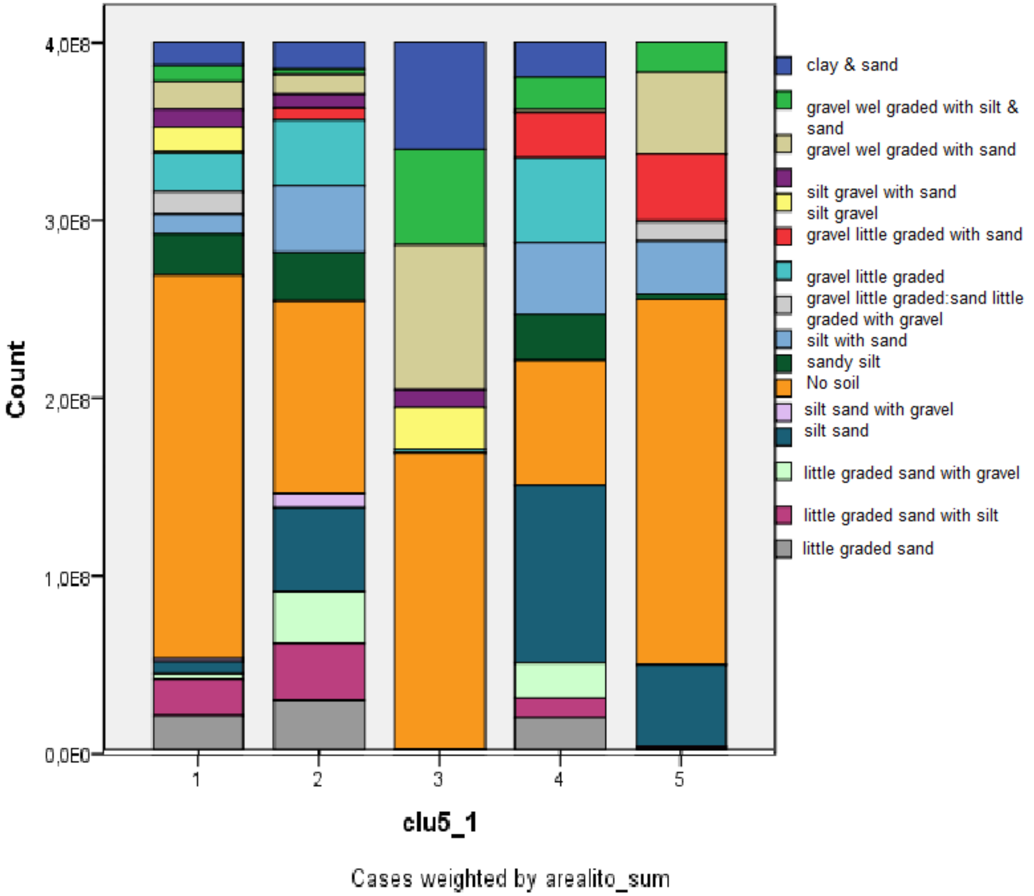
- **Cluster 1:** Urban Area. Strong relationship between **NO3-gw** and **NO3** Cl and EC and **Cl-gw** and **Cl**, NH4 , EC and glyphosate
- **Cluster 2:** Agricultural area. the **As-gw** has a negative correlation with the surface water **Cl** and glyphosate
- **Cluster 3:** Industrial activity and use of solvents might be responsible for the observed high concentrations of boron and tricholoromethan
- **Cluster 4:** mostly in agricultural area. **As-gw** is correlated with **As** (local geogenic process)
- **Cluster 5:** The area is typically rural, but it is crossed by some of the most important regional rail and infrastructures



Cluster lithological characteristics

- **Cluster 1 and 5** are located in urban area which the "no soil" class is the most significant class.

- **Cluster 2 and 4** are referred to the agricultural area. The presence of As in cluster 4 might be due to the sandy class of the area. So, this cluster is more permeable than cluster 2.



Conclusions

More CEC monitoring studies are needed to improve our understanding of CECs spatial patterns, sources, fate and transport processes

CECs should be monitored during high-flow events and seasons because the increased concentrations that occur at these times will also represent the greatest loadings.

Also, monitoring in upstream areas is advisible for risk assessments of agriculturally associated CECs

WWTP-dominated CECs should be measured in low-flow periods if instream exposures are of concern; relatively consistent loading can be expected year-round.

Monitoring at watershed collection points below WWTPs is suitable for screening of WWTP-dominated and mixed-transport CECs.