



Monitoring and analysis of heavy metals in Rokytka and Botic creeks in Prague (Czech Republic)

Monitoraggio e analisi dei metalli pesanti nei fiumi Rokytka e Botic a Praga (Repubblica Ceca)

Relatore

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Candidati

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Monitoraggio delle acque

Sostanze inquinanti

- Nutrienti:

Azoto e Fosforo

- Metalli pesanti:

Hg, Zn, Cu, Pb, Cd, Cr, Ni



Organizzazione presentazione

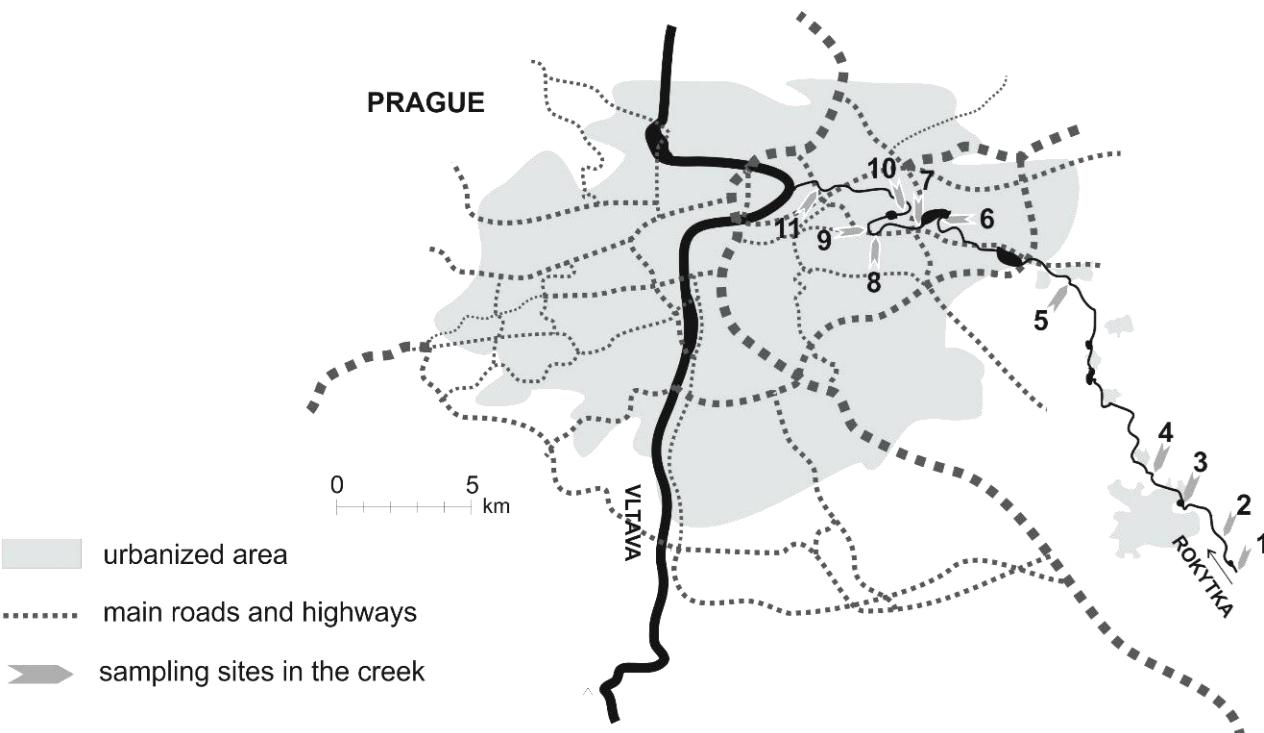
- Descrizione area di studio
- Campionamento
- Analisi di laboratorio (AAS)
- Quadro Normativo
- Parametri chimici
- Metalli Pesanti



- Analisi di laboratorio (Hg)
- Metalli Pesanti (Hg)
- Sostanza organica
- Confronto con dati storici
- Principali fonti di inquinamento
- Conclusioni

Area di studio

Rokytka



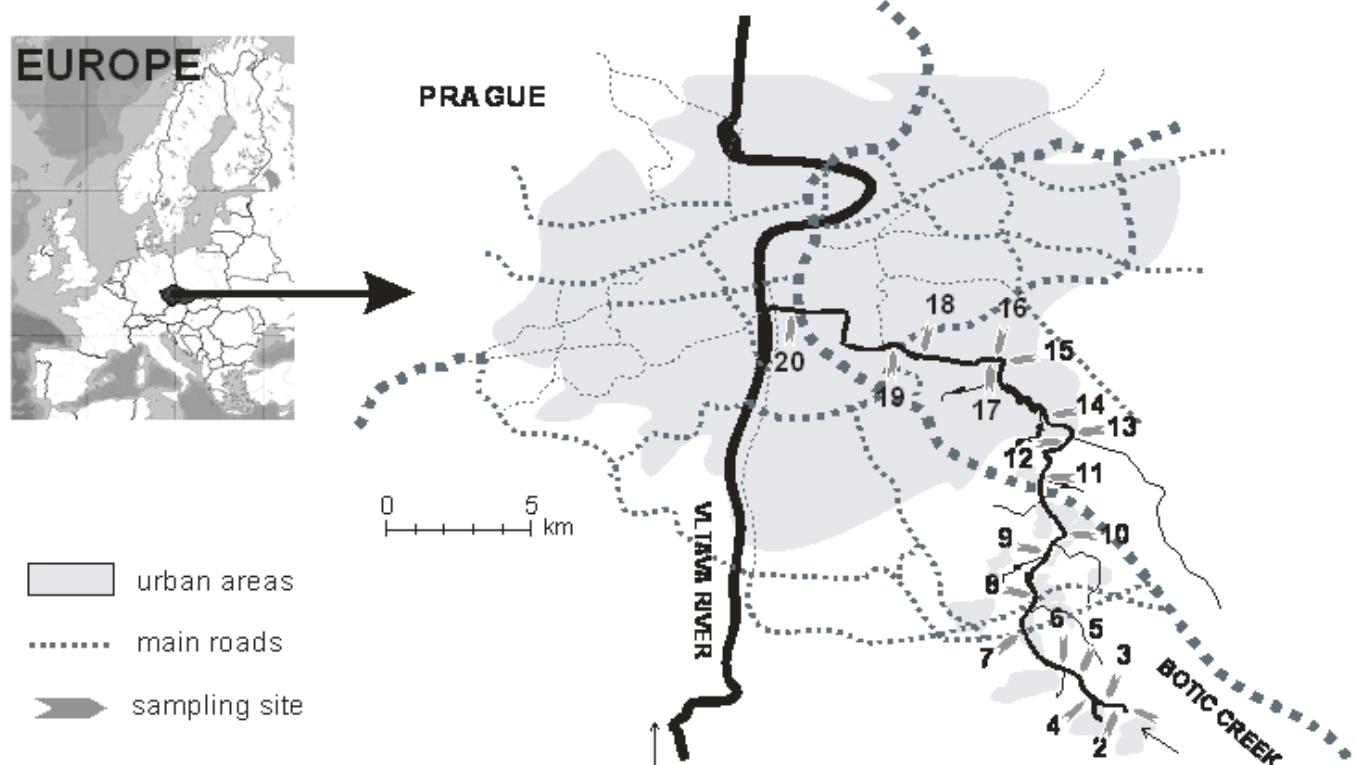
1° campionamento: 28 Marzo 2018

2° campionamento: 24 Maggio 2018

Sampling site	Locality description
RP1	spring close to village Tehovec
RP2	below the Tehovec village, surface runoff from road
RP3	below pond Jureček, Radošovice village
RP4	below Říčany village
RP5	below Běchovice village
RP6	above Kyjsky pond (Prague)
RP7	below Kyjsky pond
RP8	above a Combined sewer overflow (OK 33E Pod Taborem)
R9	below a Combined sewer overflow (OK 33E Pod Taborem)
R10	below revitalised section of Rokytka
R11	before entering Vltava

Area di studio

Botic



1° campionamento: 13 Aprile 2018

2° campionamento: 25 Maggio 2018

Sampling site	Locality description
BP 1	spring
BP 2	below 1st pond
BP 3	above village Cenetice, surrounded by farm fields
BP 4	below 1st tributary and village Cenetice
BP 5	above 2nd tributary
BP 6	below 2nd tributary
BP 7	close to Prague highway ring, cottage area in surrounding
BP 8	below 3rd tributary
BP 9	below 4th tributary
BP 10	above the Pruhonice garden
BP 11	below retention pond for highway runoff
BP 12	above 5th tributary
BP 13	below 5th tributary
BP 14	below retention pond of SWD - runoff from housing estate area
BP 15	below CSO 1, app. 1 km below the Hostivar reservoir
BP 16	below SWDs above CSO 2
BP 17	below CSO 2
BP 18	car repair shop
BP 19	below SWDs from heavy traffic area, below the Hamersky pond
BP 20	above pipeline

Campionamento

In situ:

- pH
- Conduttività
- Temperatura
- Ossigeno dissolto



In laboratorio:

- Durezza e alcalinità
- COD, Cl^- , $\text{NH}_4^+ - \text{N}$, $\text{NO}_3^- - \text{N}$, $\text{PO}_4^{3-} - \text{P}$
- Metalli pesanti
- Mercurio

Trattamento sedimenti

1. Congelamento a -20°C

3. Setacciamento



2. Liofilizzazione



4. Digestione



Spettroscopia ad assorbimento atomico

- Ni
- Pb
- Cu
- Zn
- Cd
- Cr



- Valore medio;
- Deviazione standard relativa (RSD).

$$RSD \% = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2 + \dots + (x_n - \bar{x})^2}{\frac{n-1}{\bar{x}}}} \cdot 100$$

Elaborazione dati

Coefficiente di distribuzione K_d

$$K_d = \frac{C_s}{C_w}$$

- C_s = Concentrazione metallo nei sedimenti [mg/Kg]
- C_w =Concentrazione metallo in acqua [mg/L]

- $\log K_d < 3$ – Forma disciolta
- $3 < \log K_d < 4$ – Forma sospesa
- $\log K_d > 4$ – Legato alla frazione solida

Coefficiente di Pearson ρ

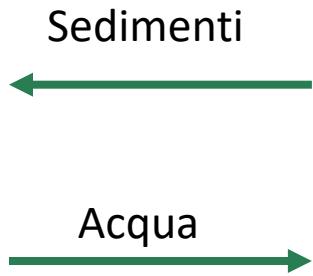
$$\rho_{XY} = \frac{\text{cov}(X, Y)}{\sigma_X \sigma_Y}$$

- $\text{Cov}(X, Y)$ = Covarianza tra X e Y
- σ_x e σ_y = Deviazioni standard

- Se $\rho_{XY} < 0.3$ debole
- Se $0.3 < \rho_{XY} < 0.7$ moderata
- Se $\rho_{XY} > 0.7$ forte

Quadro normativo

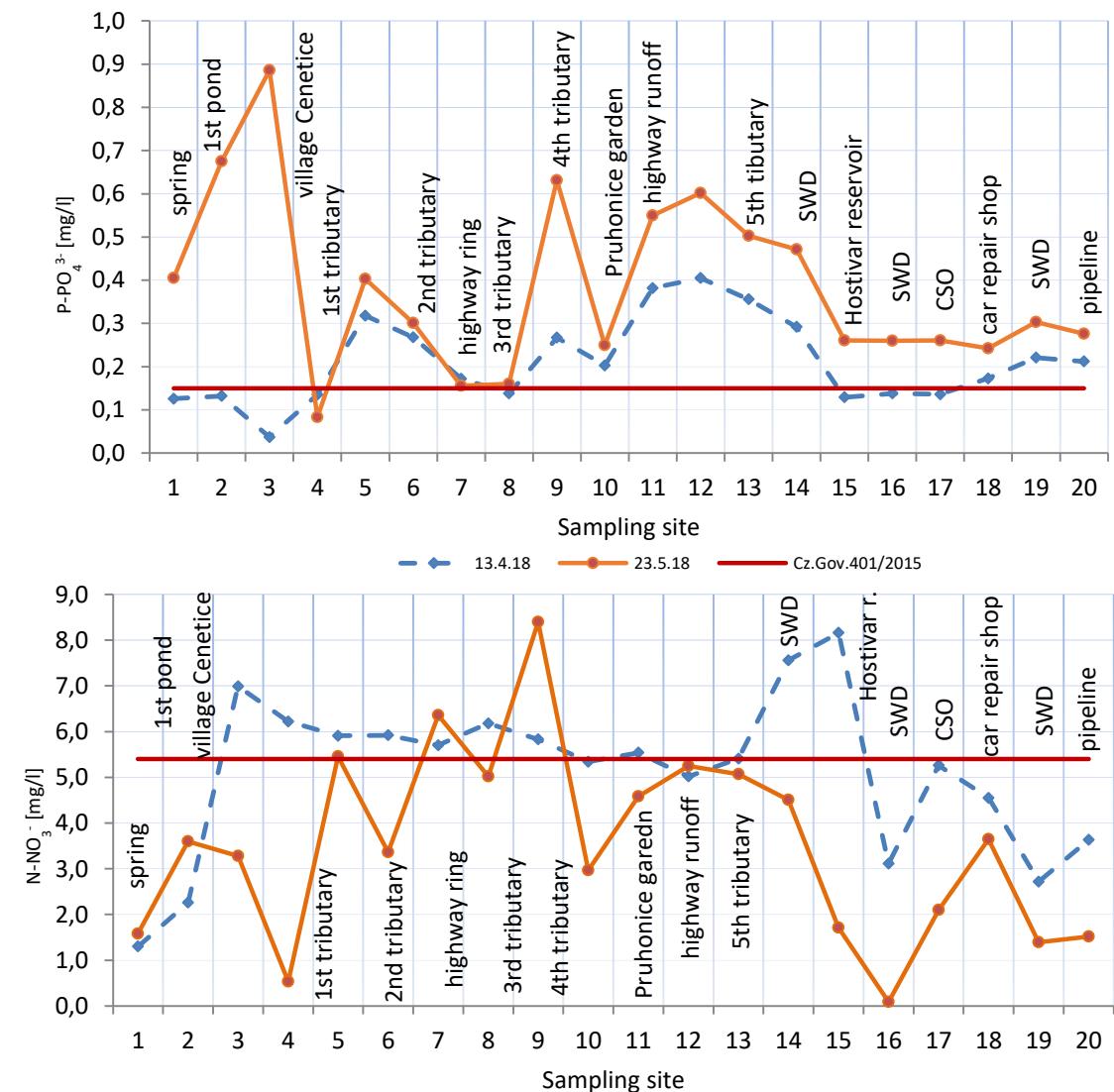
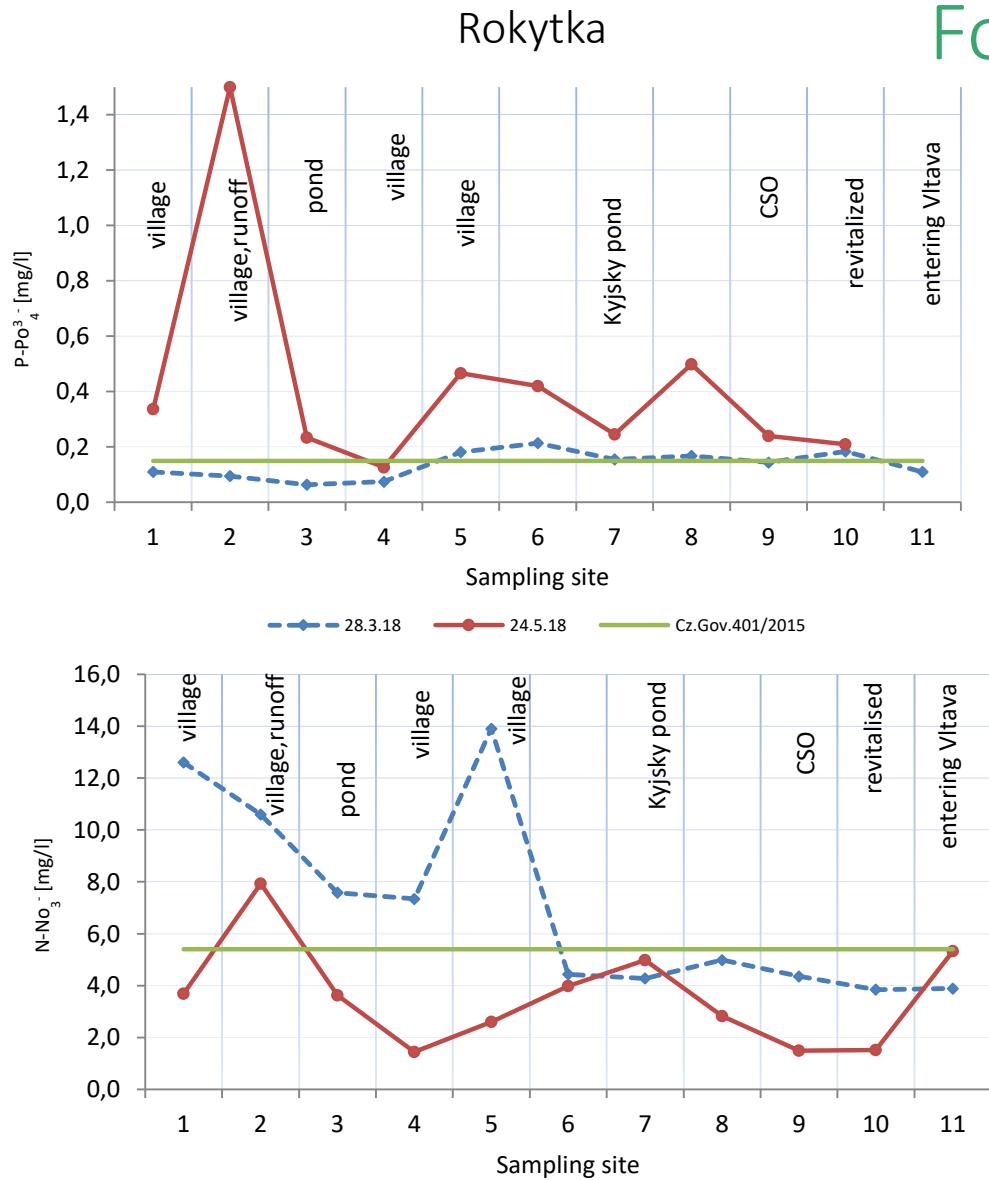
	Limite		EQS
Cd	0,592	mg/Kg	TEC
	11,7	mg/Kg	PEC
Cr	56	mg/Kg	TEC
	159	mg/Kg	PEC
Cu	28	mg/Kg	TEC
	77,7	mg/Kg	PEC
Ni	39,6	mg/Kg	TEC
	38,5	mg/Kg	PEC
Pb	34,2	mg/Kg	TEC
	396	mg/Kg	PEC
Hg	0,18	mg/Kg	TEC
	1,06	mg/Kg	PEC
Zn	159	mg/Kg	TEC
	1539	mg/Kg	PEC



	Limite	
Temperatura	< 29	°C
pH	5-9	-
Conduttività	110	mS/m
OD	> 9	mg/l
COD	26	mg/l
PO ₄ ³⁻ -P	0,15	mg/l
NO ³⁻ - N	5,4	mg/l
NH ⁴⁺ -N	0,23	mg/l
Cl ⁻	150	mg/l
Mg	120	mg/l
Ca	190	mg/l
Cd	0,45	µg/l
Cr	18	µg/l
Cu	14	µg/l
Ni	< 34	µg/l
Pb	< 14	µg/l
Hg	< 0,07	µg/l
Zn	92	µg/l

Parametri Chimici

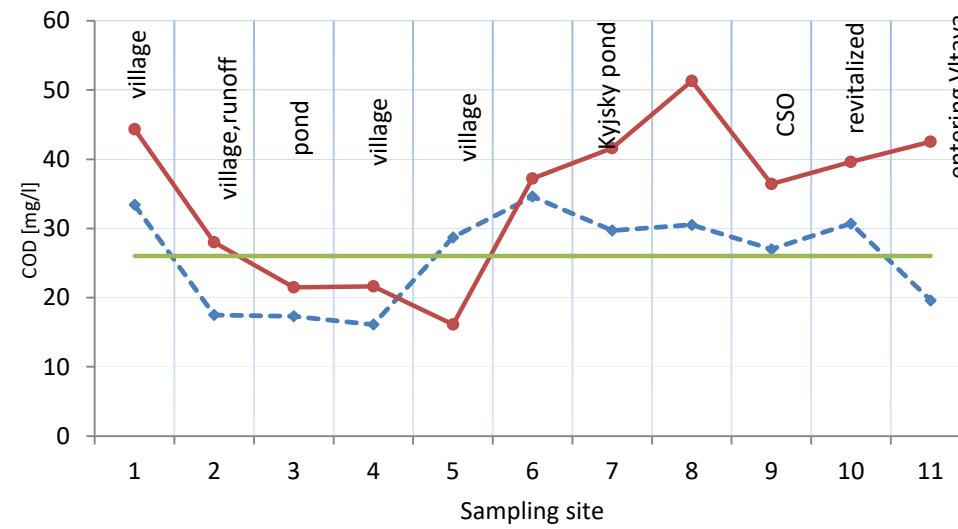
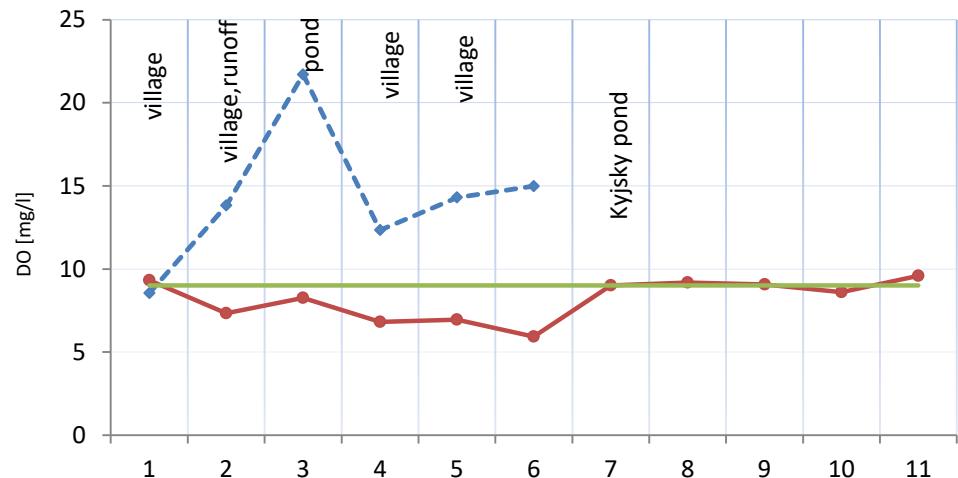
Fosfati e Nitrati



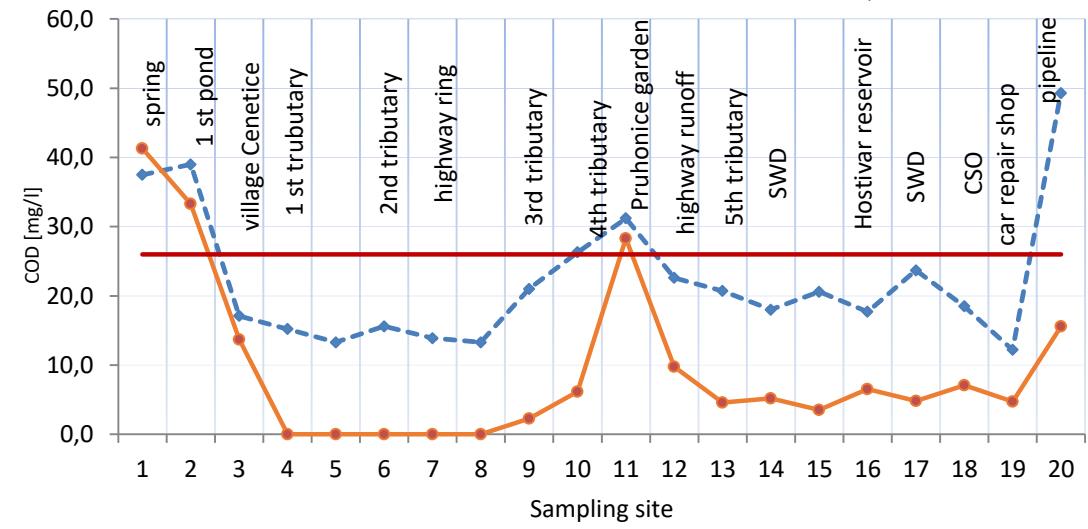
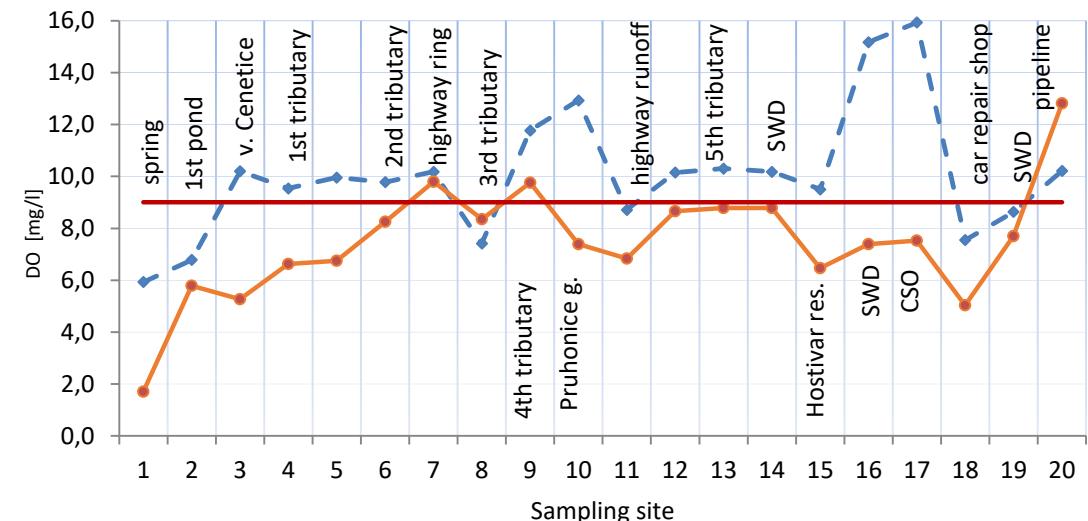
Parametri Chimici

Ossigeno disciolto e COD

Rokytka



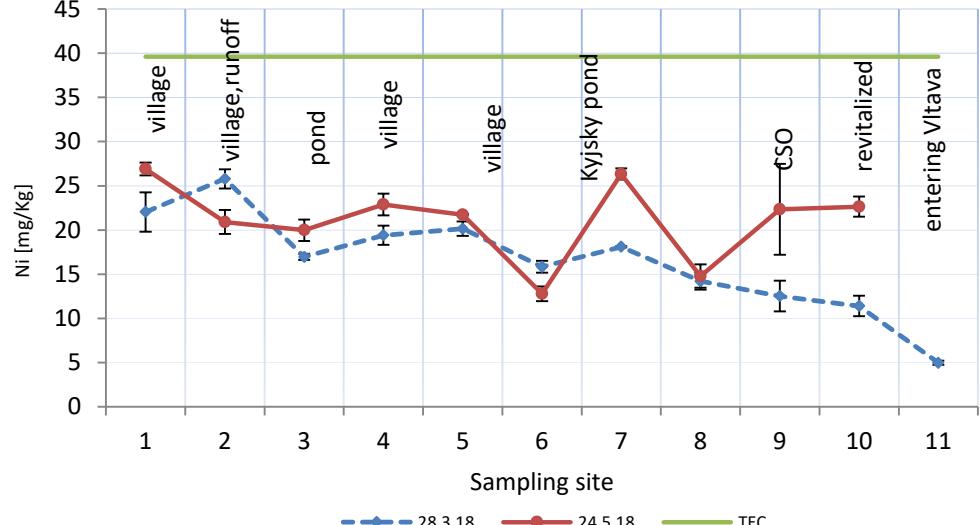
Botic



Metalli pesanti nei sedimenti

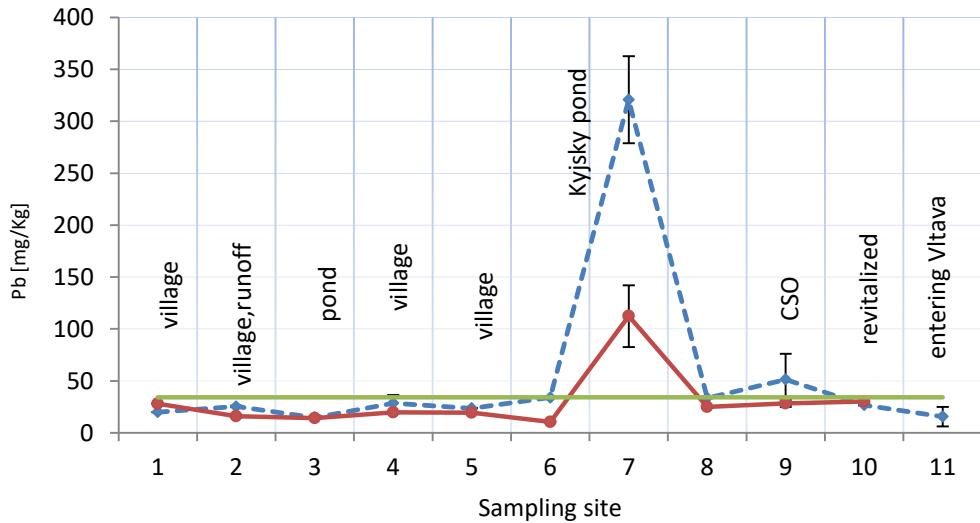
Nichel e Piombo

Rokytka



$$K_d = 3,5$$

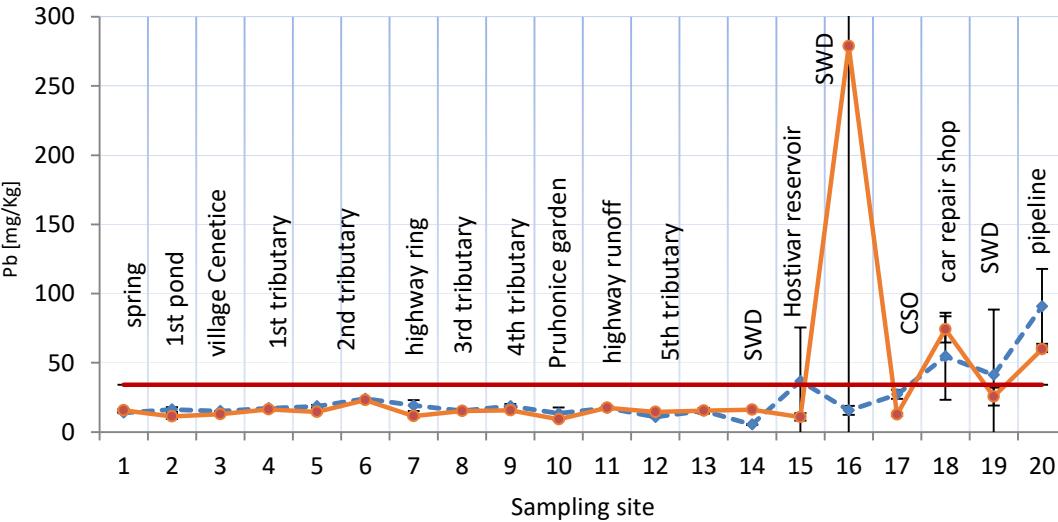
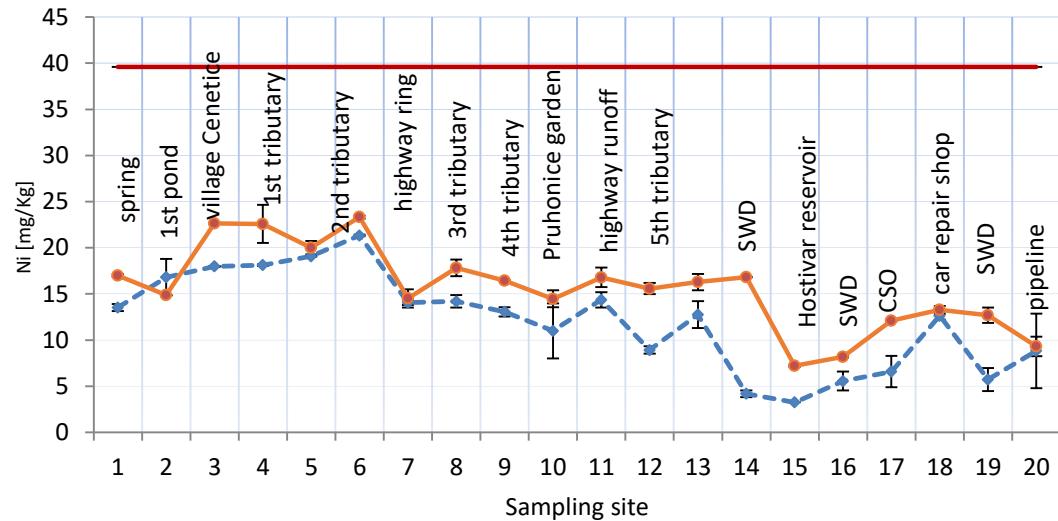
$$K_d = 3,6$$



$$K_d = 4,3$$

$$K_d = 4,5$$

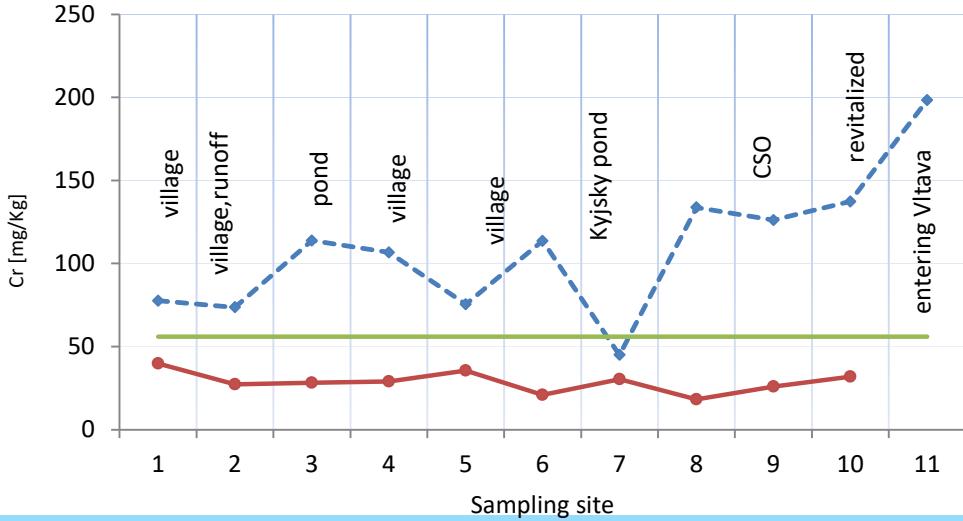
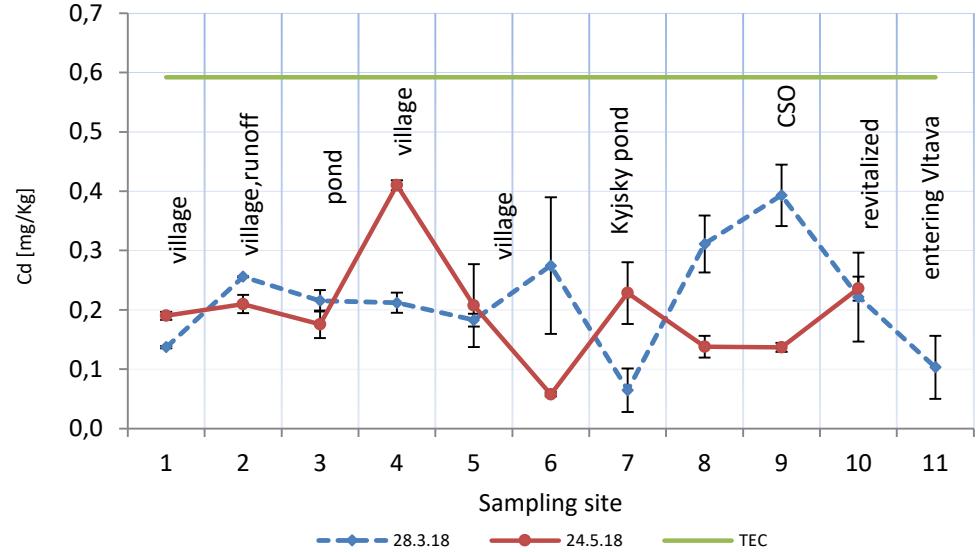
Botic



Metalli pesanti nei sedimenti

Cadmio e Cromo

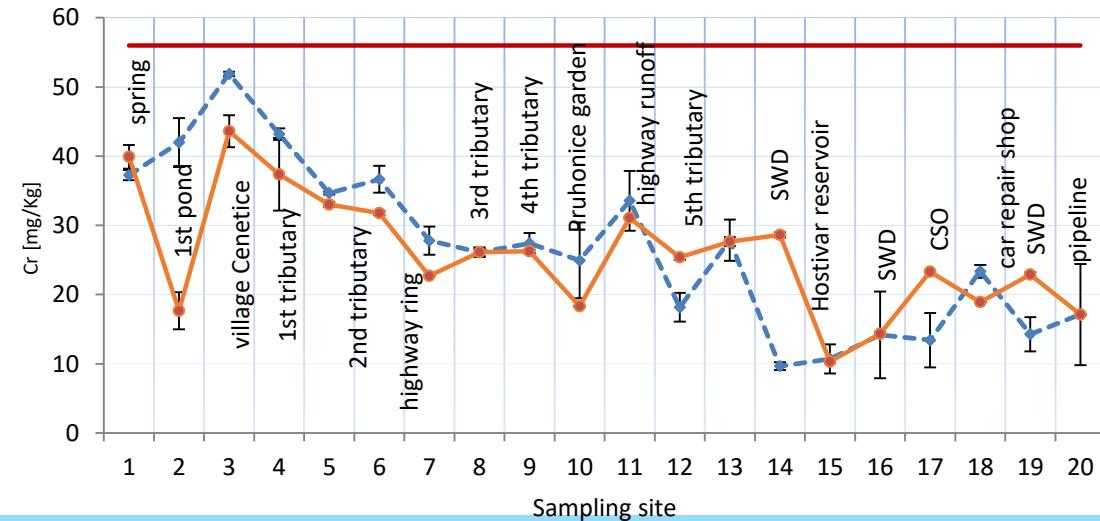
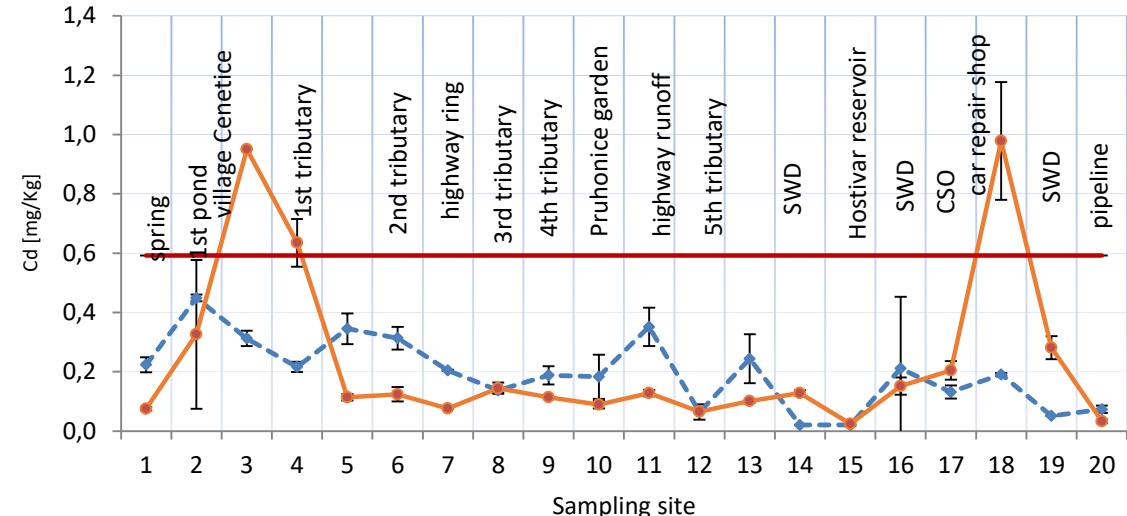
Rokytka



$K_d = 4-4,5$

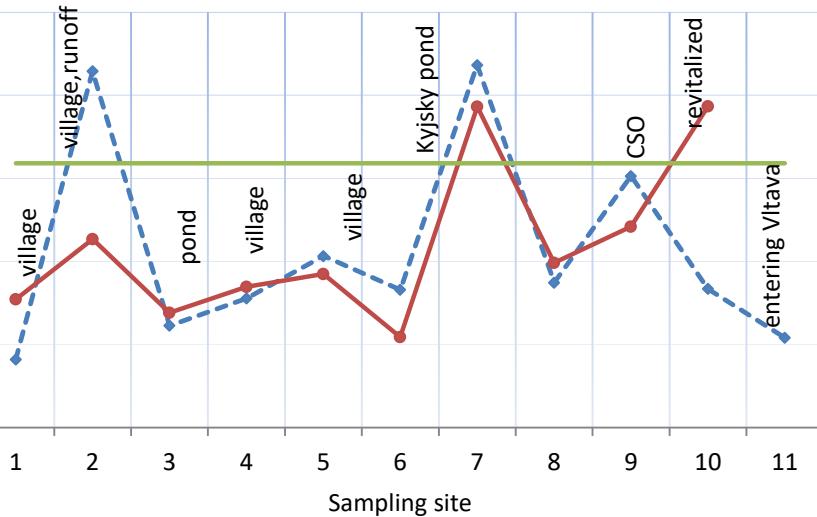
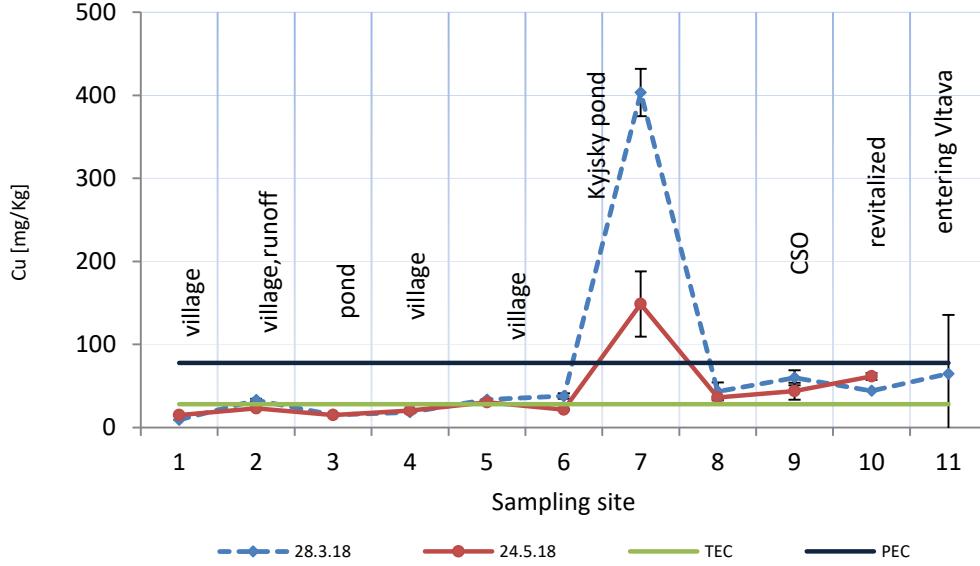
$K_d = 3,4$

Botic



Metalli pesanti nei sedimenti

Rokytka



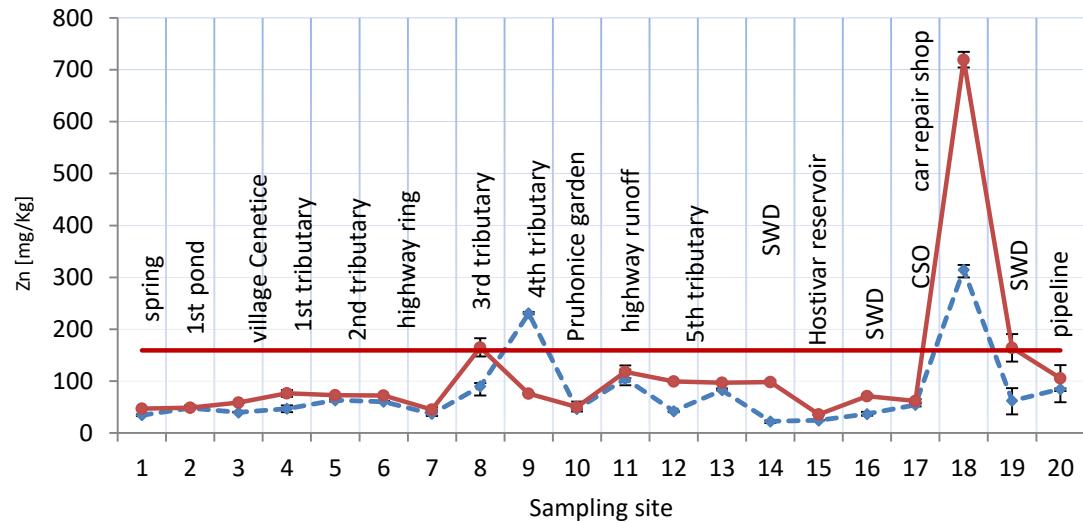
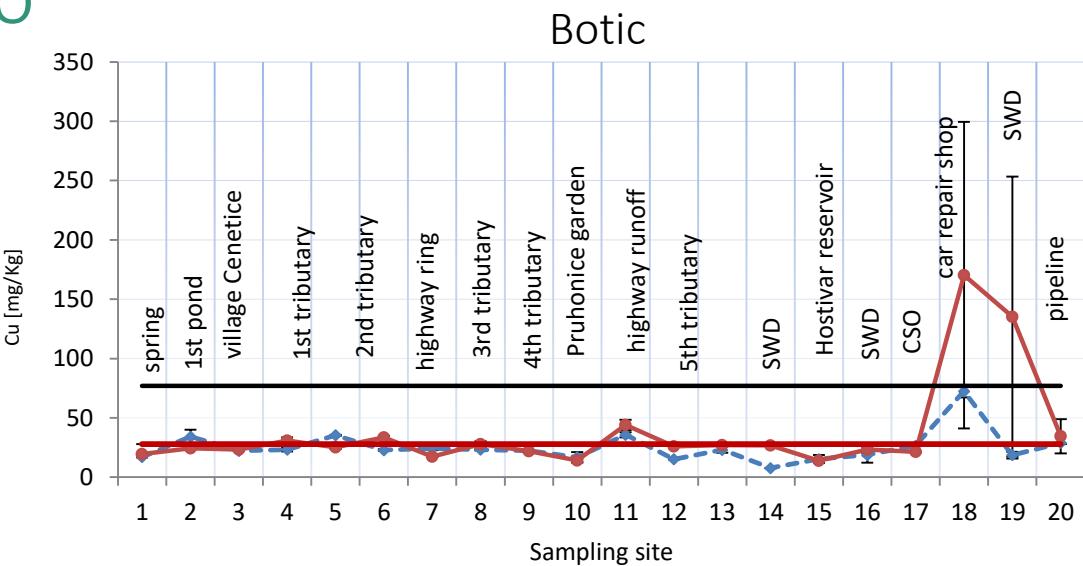
Rame e Zinco

$$K_d = 3,5$$

$$K_d = 4,0$$

$$K_d = 4,5$$

$$K_d = 4,6$$



Organizzazione presentazione

- Analisi di laboratorio (Hg)
- Metalli Pesanti (Hg)
- Sostanza organica
- Confronto con dati storici
- Principali fonti di inquinamento
- Conclusioni

Advanced mercury analyzer

AMA 254

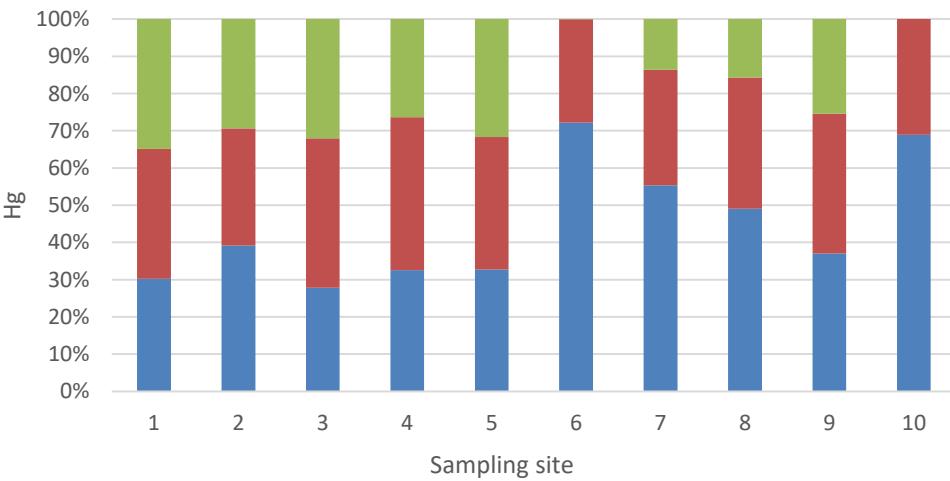
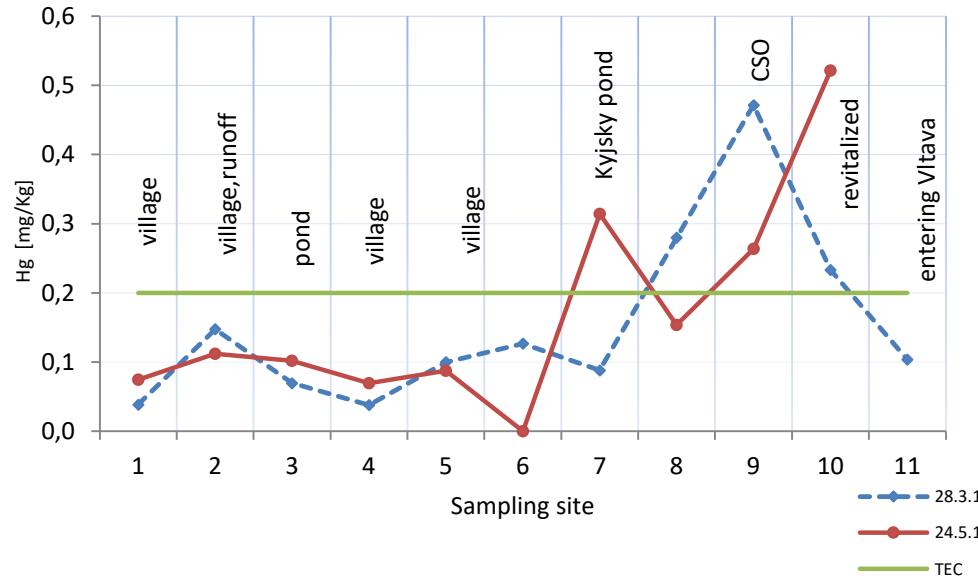


- Campioni di sedimenti:
100 mg-200 mg
- Campioni di acqua: 100 µl

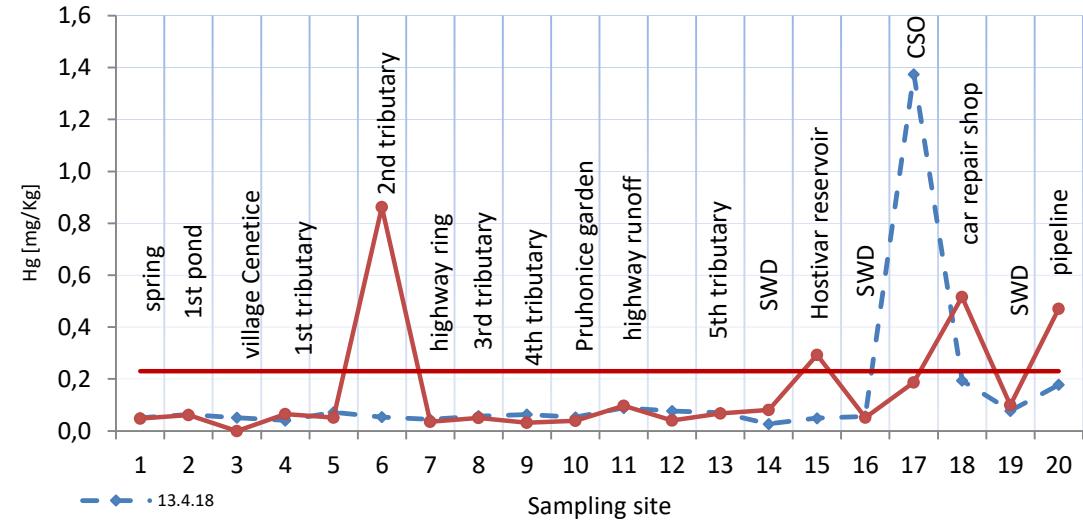


Metalli pesanti

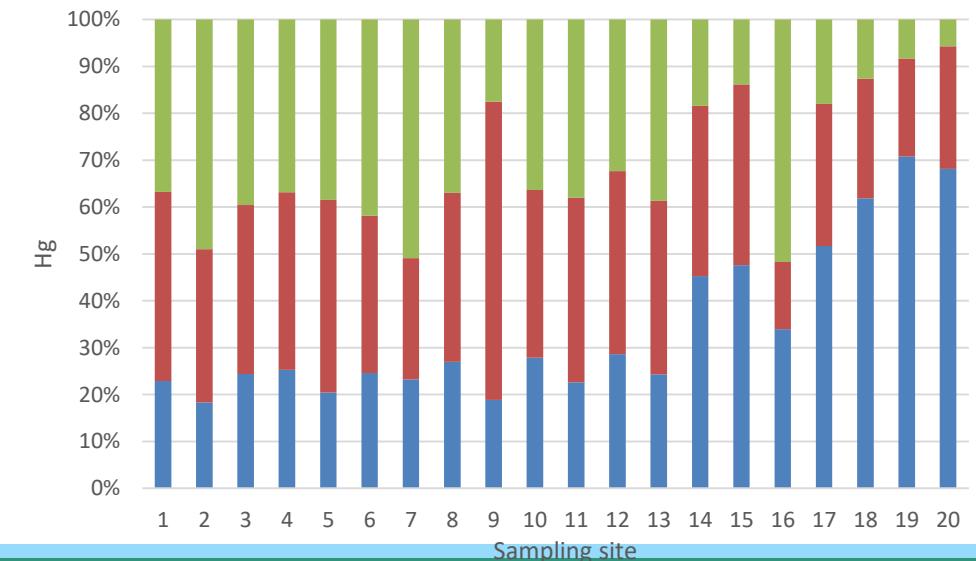
Rokytka



Mercurio



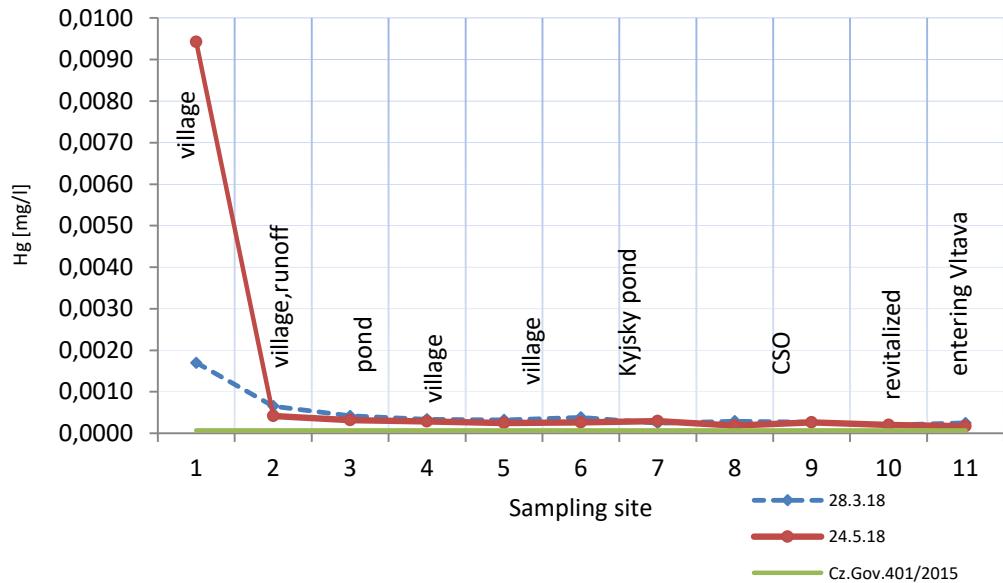
Botic



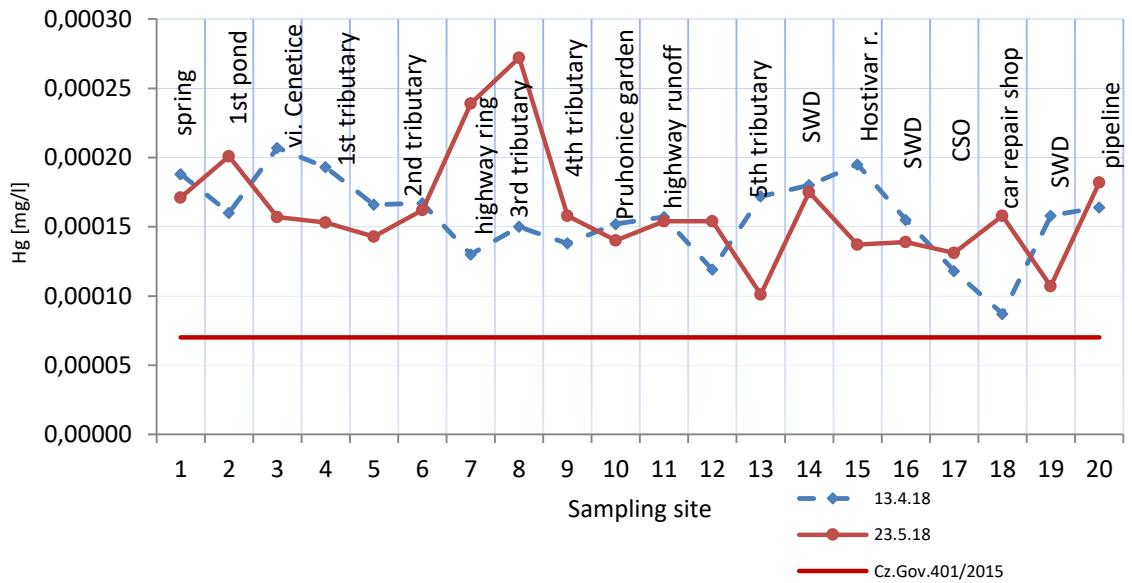
Metalli pesanti

Mercurio

Rokytká



Botic



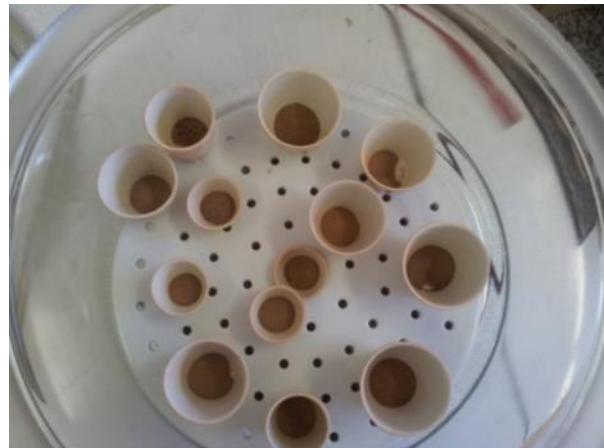
overall	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11
1°	1,4	2,4	2,2	2,1	2,5	2,5	-0,02	2,6	3,0	2,9	3,3
2°	0,9	2,4	2,5	2,4	2,6			3,0	2,9	3,0	3,4

overall	BP1	BP2	BP3	BP4	BP5	BP6	BP7	BP8	BP9	BP10
1°	2,4	2,6	2,4	2,3	2,6	2,5	2,5	2,6	2,6	2,5
2°	2,4	2,5	0,03	2,6	2,6	3,7	2,2	2,3	2,3	2,4

overall	BP11	BP12	BP13	BP14	BP15	BP16	BP17	BP18	BP19	BP20
1°	2,8	2,8	2,6	2,2	2,4	2,6	4,1	3,3	2,7	3,0
2°	2,8	2,4	2,8	2,7	3,3	2,6	3,2	3,5	3,0	3,4

Sostanza organica LOI

1. Preparazione campioni;
2. Riscaldamento a 550°C per 4 ore;
3. Raffreddamento in essiccatore;
4. Calcolo LOI.

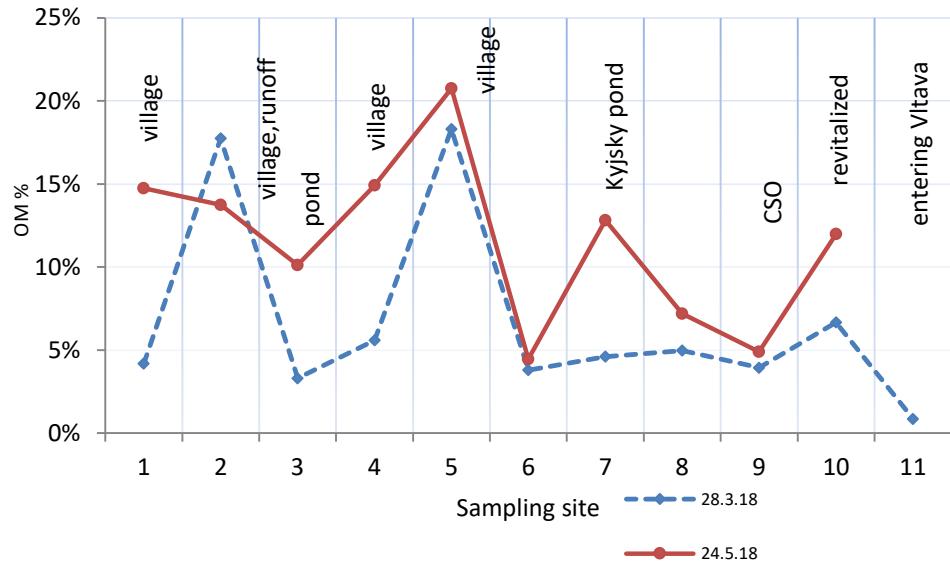


$$\text{LOI (\%)} = \frac{\Delta m}{m_s} * 100$$

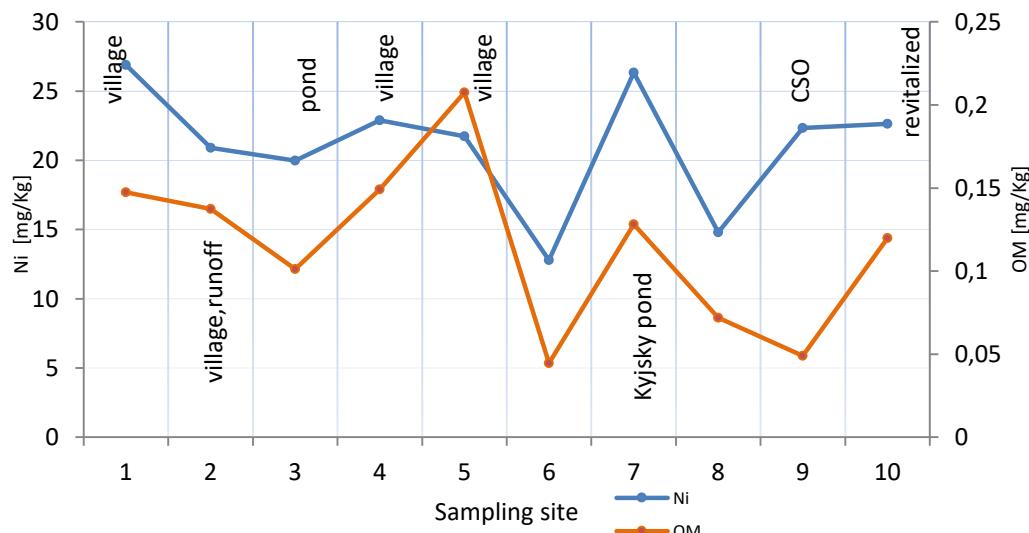
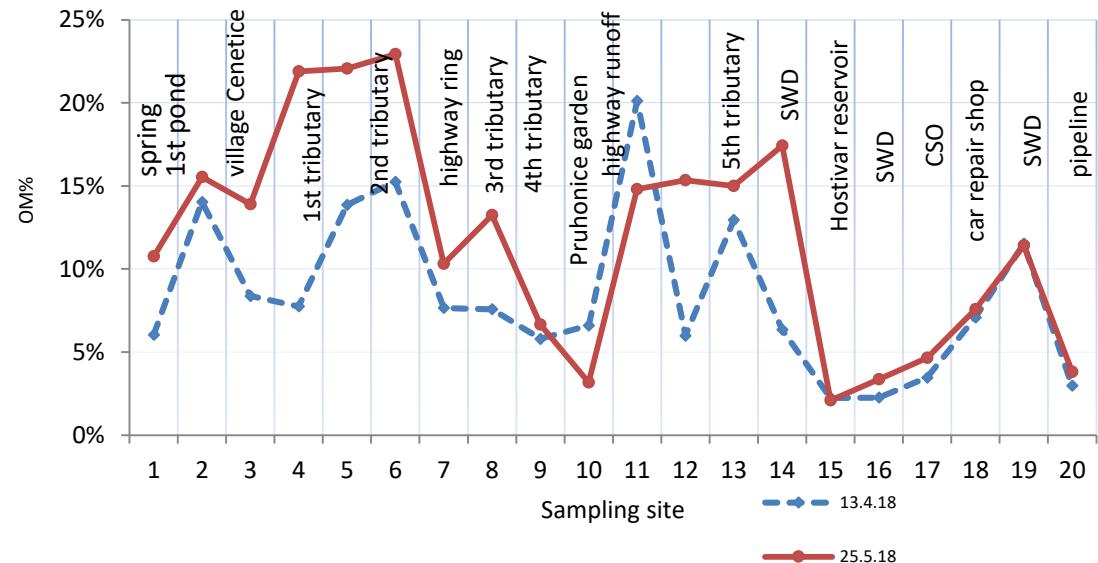
- $m_s = m_2 - m_0$
- Δm : peso perso dopo riscaldamento a 550°C (g)
- m_0 : peso vaso di terracotta (g)
- m_1 : peso campione + peso vaso (g)
- m_2 : peso campione + peso vado dopo riscaldamento a 550°C (g)
- m_s : peso di campione asciutto (g)

Sostanza organica

Rokytka

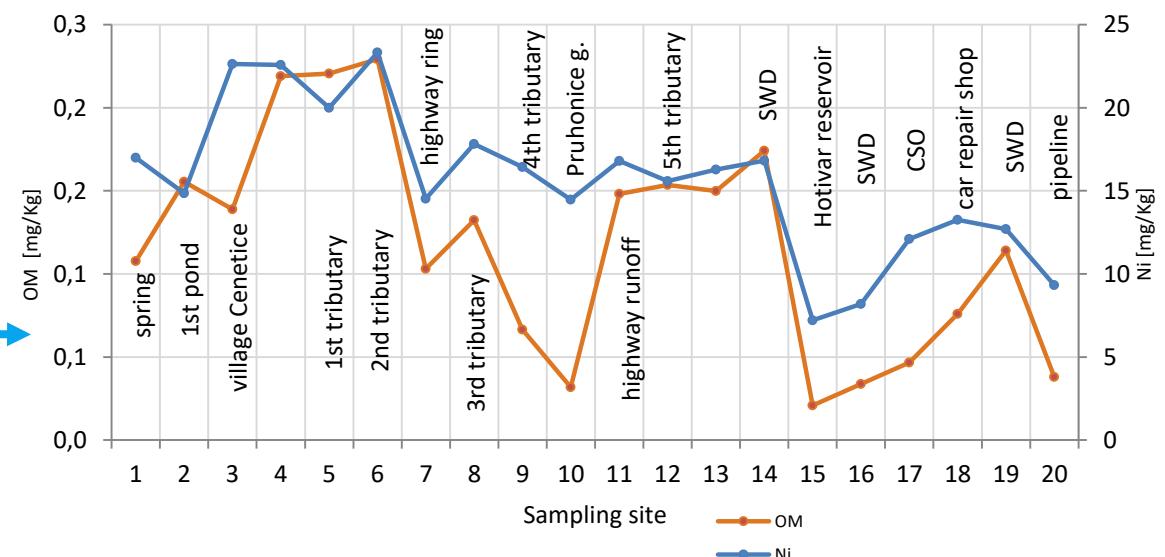


Botic



$$P^1 = 0,6$$

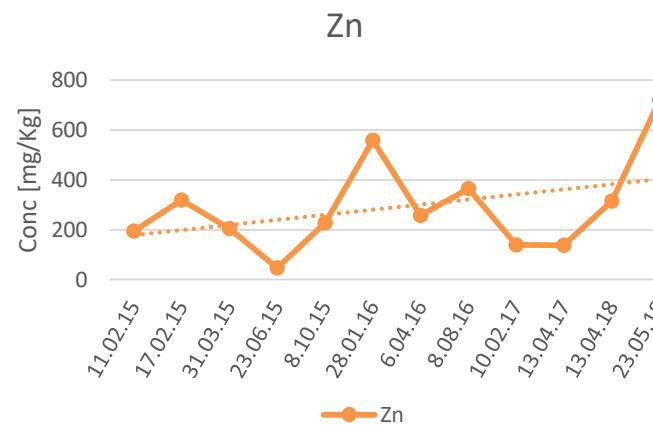
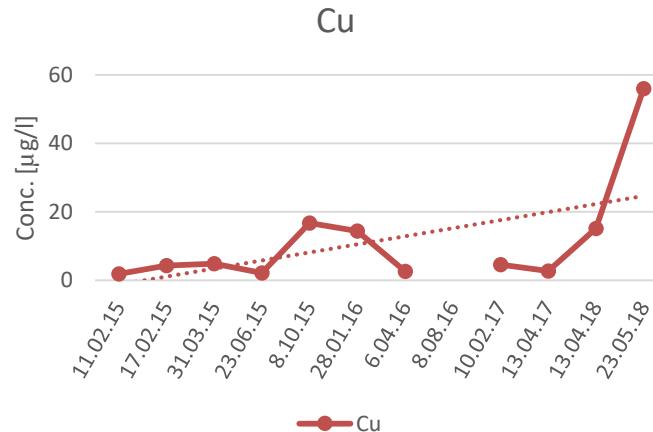
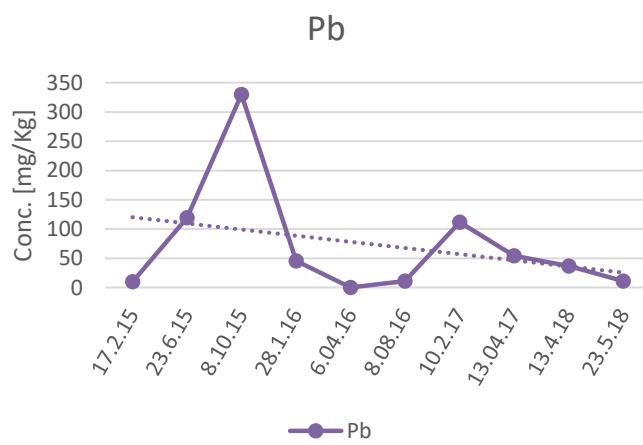
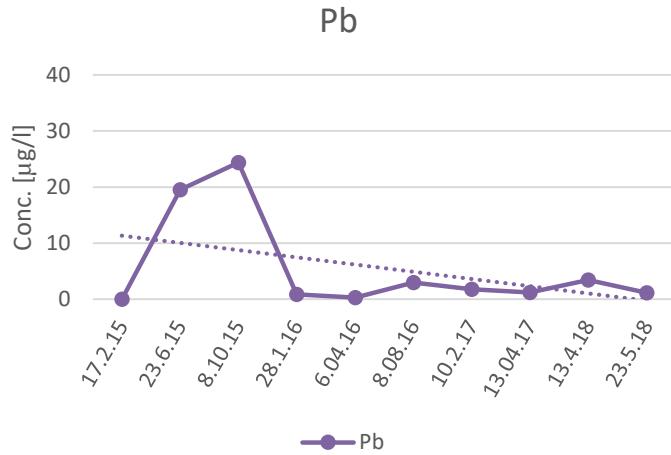
$$P^2 = 0,8$$



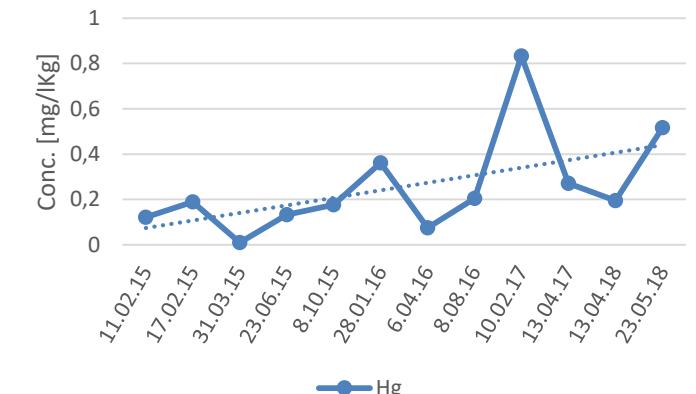
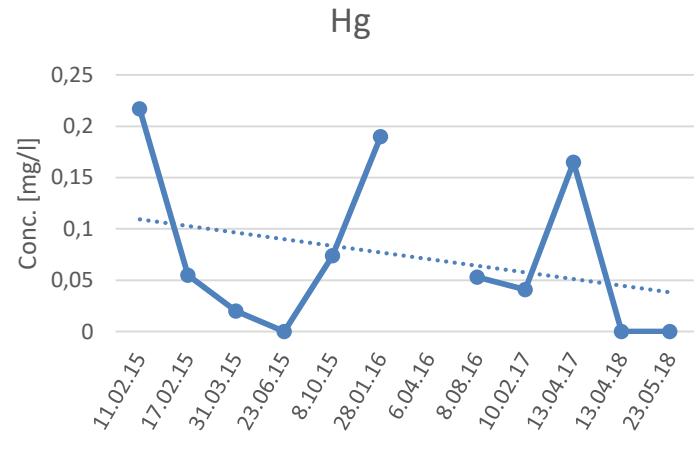
Confronto con dati storici

Botic

Riserva Hostivar



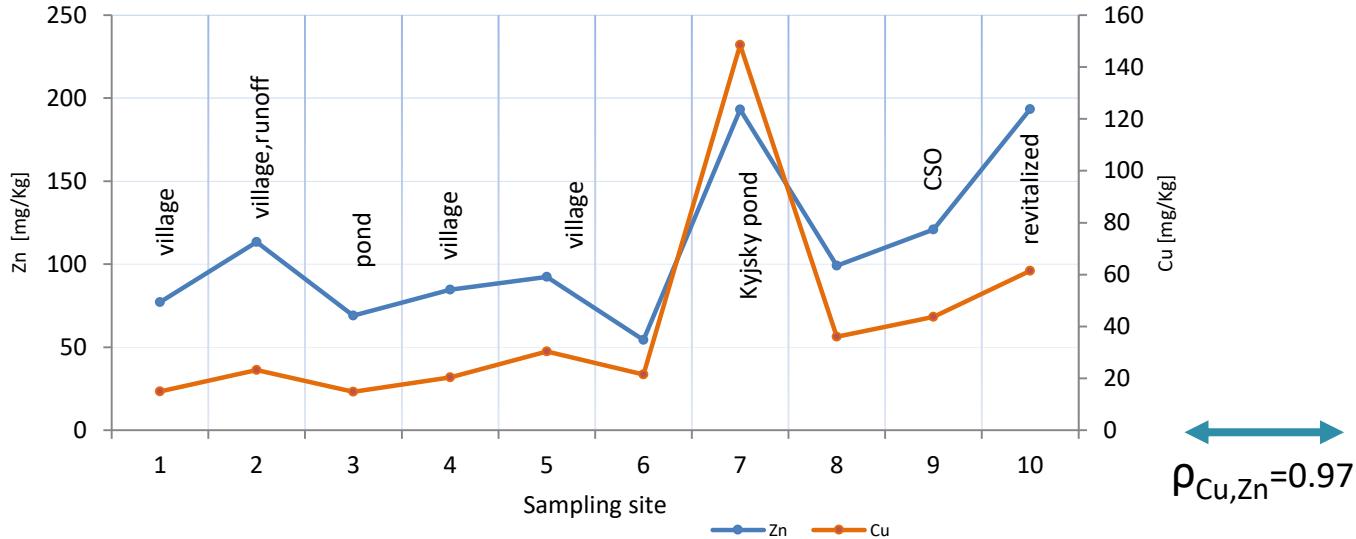
Sito 18



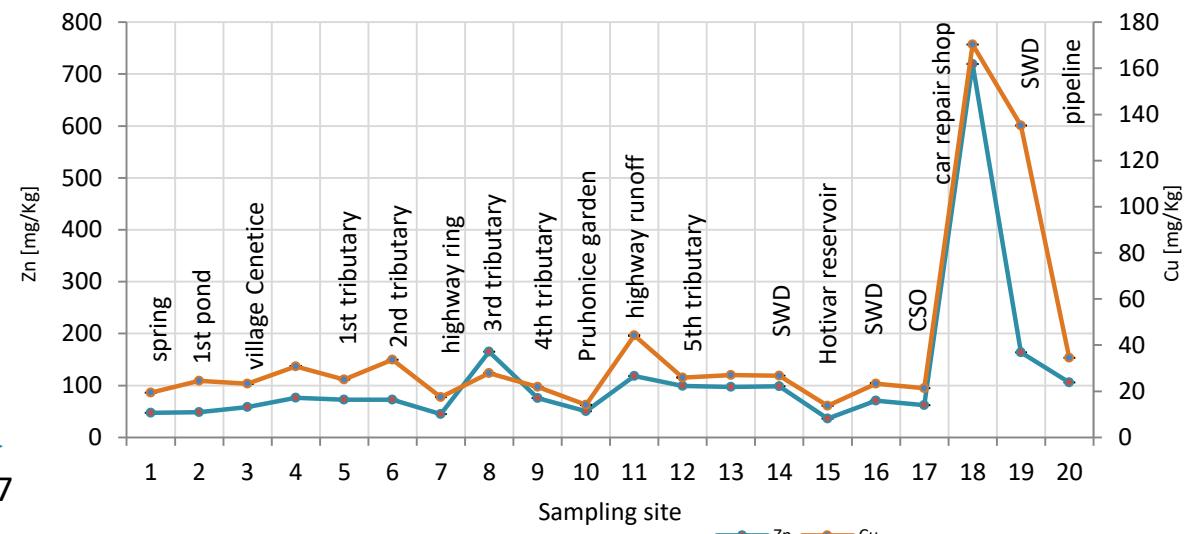
Principali fonti di inquinamento

Rokytka e Botic

Rokytka



Botic



	Cd	Cu	Ni	Pb	Hg	Cr	Zn
Cd	1,00	0,91	0,22	0,13	0,21	0,25	0,89
Cu	0,91	1,00	0,21	0,13	0,24	0,15	0,97
Ni	0,22	0,21	1,00	-0,16	-0,14	0,42	0,28
Pb	0,13	0,13	-0,16	1,00	-0,07	-0,06	0,13
Hg	0,21	0,24	-0,14	-0,07	1,00	0,06	0,17
Cr	0,25	0,15	0,42	-0,06	0,06	1,00	0,11
Zn	0,89	0,97	0,28	0,13	0,17	0,11	1,00

Principali fonti di inquinamento

Siti

- Aree agricole
- Sito BP18
- Stagni



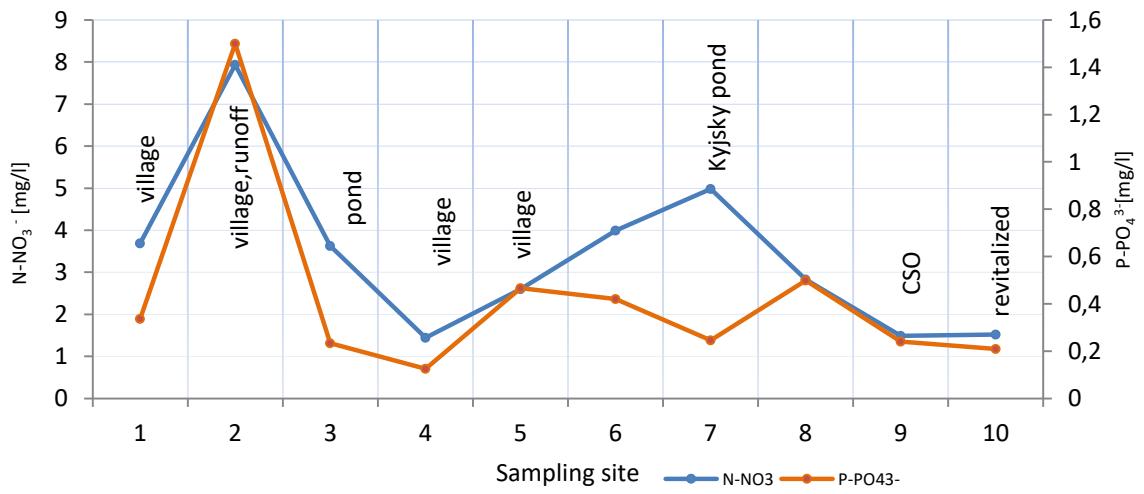
Sedimenti	Cd [mg/Kg]	Ni [mg/Kg]	Cu [mg/Kg]	Pb [mg/Kg]	Cr [mg/Kg]	Zn [mg/Kg]	Hg [mg/Kg]
1 st sampling	0,19	12,63	<u>72,43</u>	<u>54,62</u>	23,35	<u>314,72</u>	<u>0,19</u>
2 nd sampling	<u>0,98</u>	13,26	<u>170,31</u>	<u>74,10</u>	18,89	<u>719,22</u>	<u>0,52</u>
TEC	0,59	39,60	28,00	34,20	56,00	159,00	0,20

Acqua	Cd [µg/l]	Ni [µg/l]	Cu [µg/l]	Pb [µg/l]	Cr [µg/l]	Zn [µg/l]	Hg [µg/l]
1 st sampling	0,03	1,93	<u>15,12</u>	1,55	2,84	7,16	<u>0,09</u>
2 nd sampling	0,00	5,61	<u>55,98</u>	0,42	3,05	51,42	<u>0,16</u>
EQS	0,30	20,00	14,00	7,20	18,00	92,00	0,07

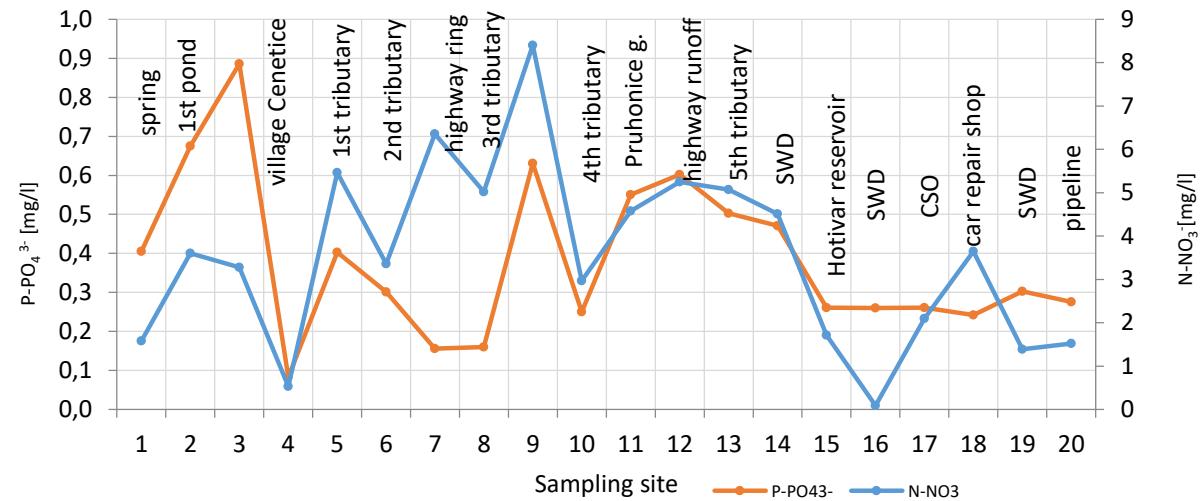
Principali fonti di inquinamento

Siti

- Aree agricole

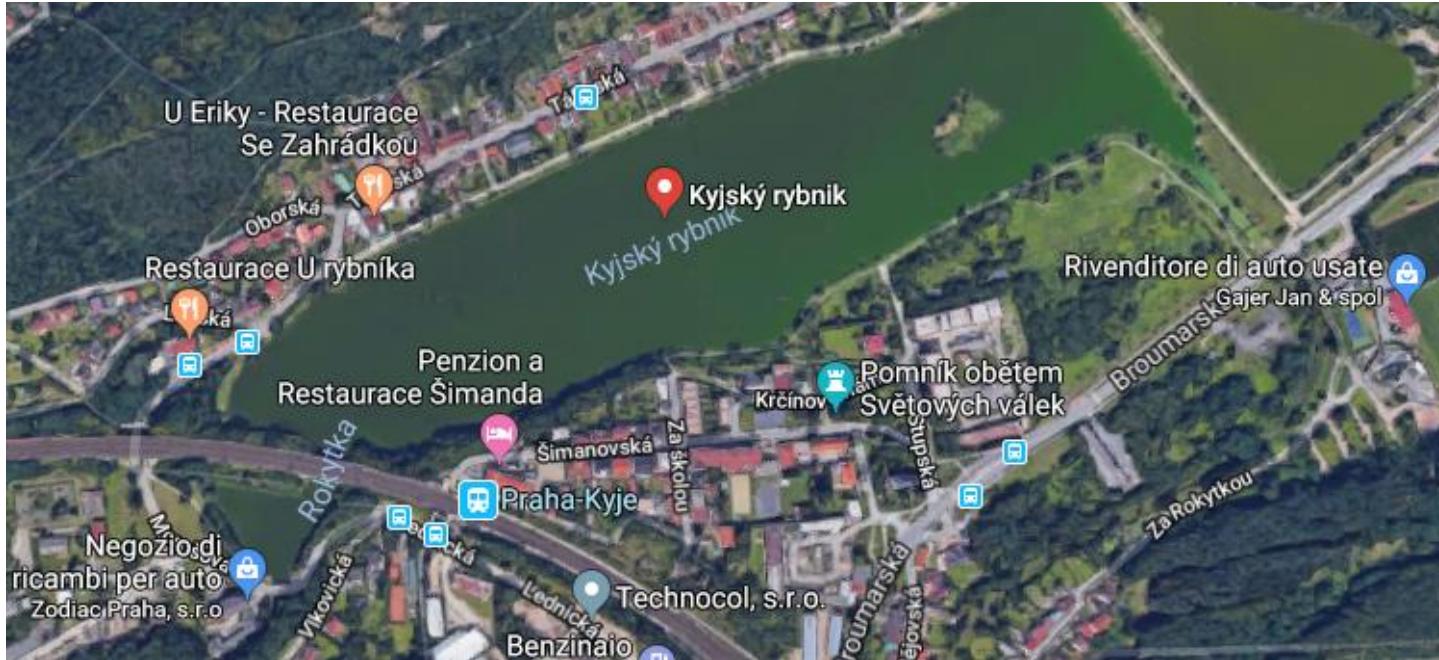


- Stagni



Principali fonti di inquinamento

Stagno Kyjsky



Sediment	Pb [mg/Kg]	Cu [mg/Kg]	Zn [mg/Kg]	Cr [mg/Kg]	Cd [mg/Kg]	Ni [mg/Kg]	Hg [mg/Kg]
1 st sampling	320,73	403,18	218,28	44,96	0,06	18,10	0,09
2 nd sampling	112,37	148,54	193,16	30,36	0,23	26,34	0,31
TEC	34,2	28	159	56	0,59	39,6	0,2
Kd	5,6	5,0	5,3	4,5	-	3,8	3

Conclusioni

- Il ruscellamento urbano è la principale fonte di inquinamento, soprattutto per Cu, Zn, Hg e Pb;
- I siti più contaminati sono lo stagno Kyjsky, in Rokytka, e il sito 18, in Botic;
- Limitata biodisponibilità dei metalli pesanti con eccezione del Rame e del Mercurio;
- I risultati non riflettono l'usuale correlazione tra la concentrazione di metalli pesanti e sostanza organica, eccetto per il Nichel;
- Elevata concentrazione di Fosfati e Nitrati nell'area agricola e negli stagni;
- Dal confronto dei parametri chimici e delle concentrazioni di metalli pesanti in acqua e sedimenti, il fiume Rokytka risulta essere più fortemente contaminato del fiume Botic.

Grazie per l'attenzione

Diky za pozornost

