"Al. I. Cuza " University, Faculty of Chemistry
Iaşi, Romania

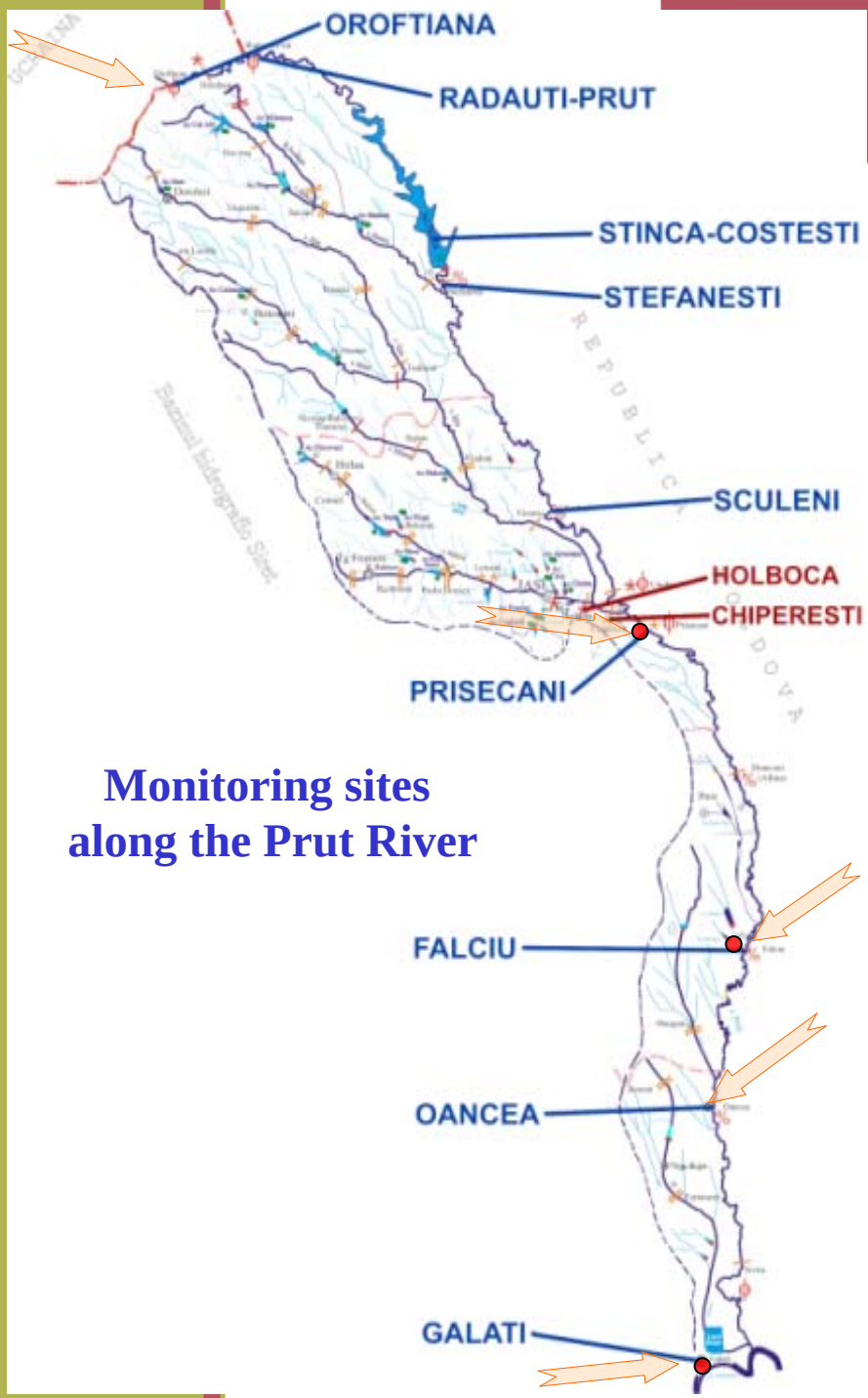
The last Eastern frontier of EU: Prut River Basin

Le dernier grand bassin de l'Est de l'UE:la riviere Prut,Roumanie

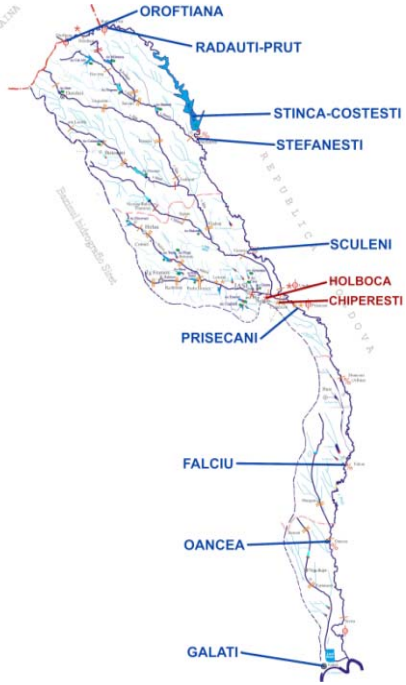
Simona Cucu-Man, Doina Dragan, Manuela Gheorghes, Cornel Pancu, Carmen Hura and Raluca Mocanu

e-mail: ralucamocanu2003@yahoo.com

COMPLETE STUDY OF POSSIBLE TRANSBOUNDARY POLLUTION

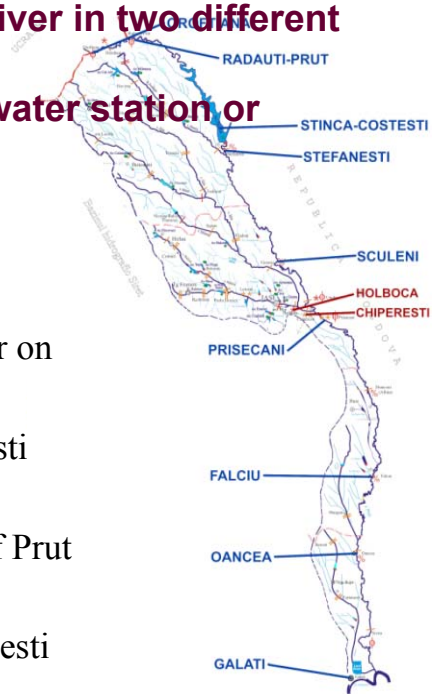


Monitoring sites along the Prut River



Criteria to select sampling sites:

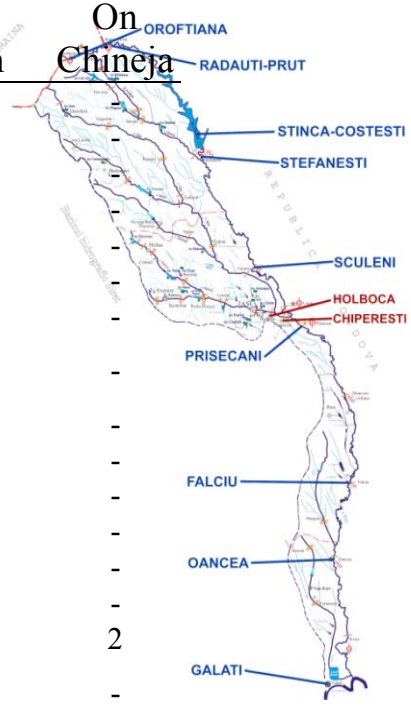
- existence of Stanca-Costesti reservoir, which divides Prut River in two different sectors-upstream and downstream reservoir;
- the monitoring points have to be placed upstream drinking water station or downstream important pollution sources;
- the accessibility of sampling sites in the field.



Sampling site	Characterisation
OROFTIANA	Entrance of the Prut River on Romanian territory
RADAUTI PRUT	Upstream Stanca-Costesti reservoir
STANCA COSTESTI RESERVOIR	The most important lake of Prut River
STEFANESTI	Downstream Stanca-Costesti reservoir
SCULENI	Upstream drinking water control point of Iasi
PRISECANI	Downstream Jijia River mouth
FALCIU	Downstream Vaslui county
OANCEA	Downstream Elan River mouth
GALATI	Upstream Danube River confluence

Major Manufacturing Discharges located on the Prut River main tributaries

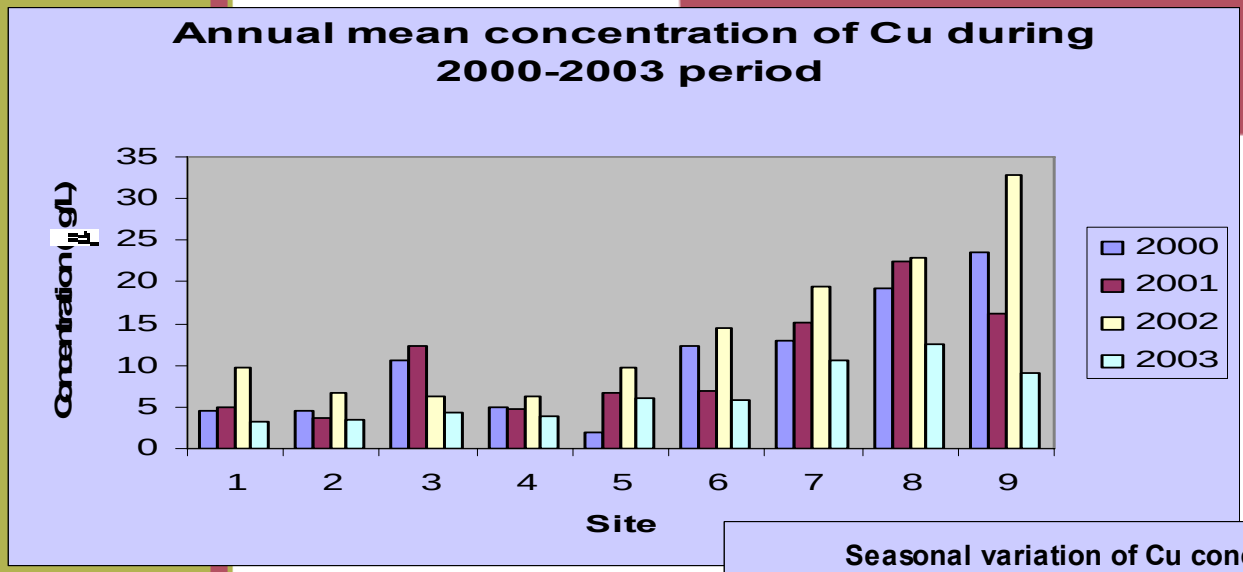
Main pollution sources	Total	On Başeu	On Jijia	On Bahlui	On Pruteț	On Elan	On Chineja
Textiles	-	-	-	-	-	-	-
Leather	-	-	-	-	-	-	-
Iron	1	-	-	1	-	-	-
Food	5	-	4	1	-	-	-
Wood processing	1	-	-	1	-	-	-
Furniture	2	-	2	-	-	-	-
Paper	-	-	-	-	-	-	-
Industrial chemicals and fertilizers	1	-	-	1	-	-	-
Other chemicals	-	-	-	-	-	-	-
Metallurgy	1	-	-	-	1	-	-
Non-ferrous	-	-	-	-	-	-	-
Agricultural activities	-	-	-	-	-	-	-
Zootechnic farms	6	-	6	-	-	-	-
Thermopower station	4	-	3	1	-	-	-
Other industrial	44	2	32	5	1	2	2
Inefficacious water purification stations	16	3	7	5	1	-	-
TOTAL	81	5	54	15	3	2	2

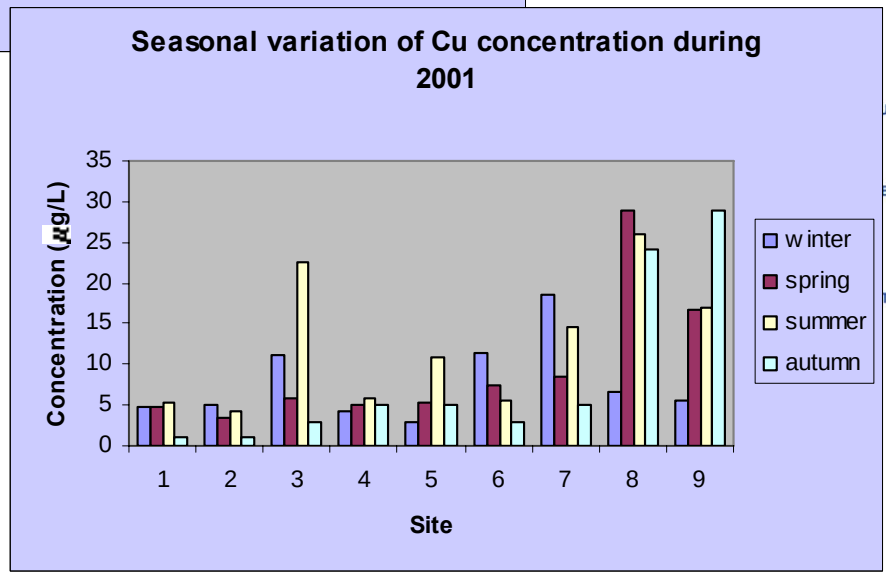


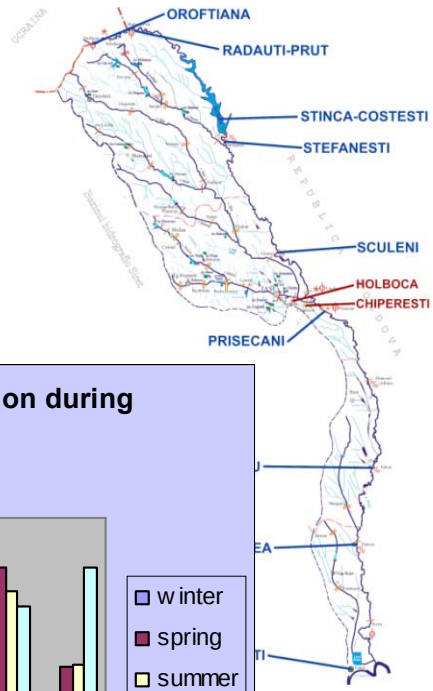
Main pollution sources located on the Prut River

Main pollution sources	No. of sources
Zootechnic farms	1- upstream Fălciu
Hospitals	1- upstream Fălciu
Residential	2 -1 - downstream Stânca - 1 - upstream Fălciu
Inefficacious water purification stations	1- upstream Fălciu
TOTAL	5

Heavy Metals (HM)



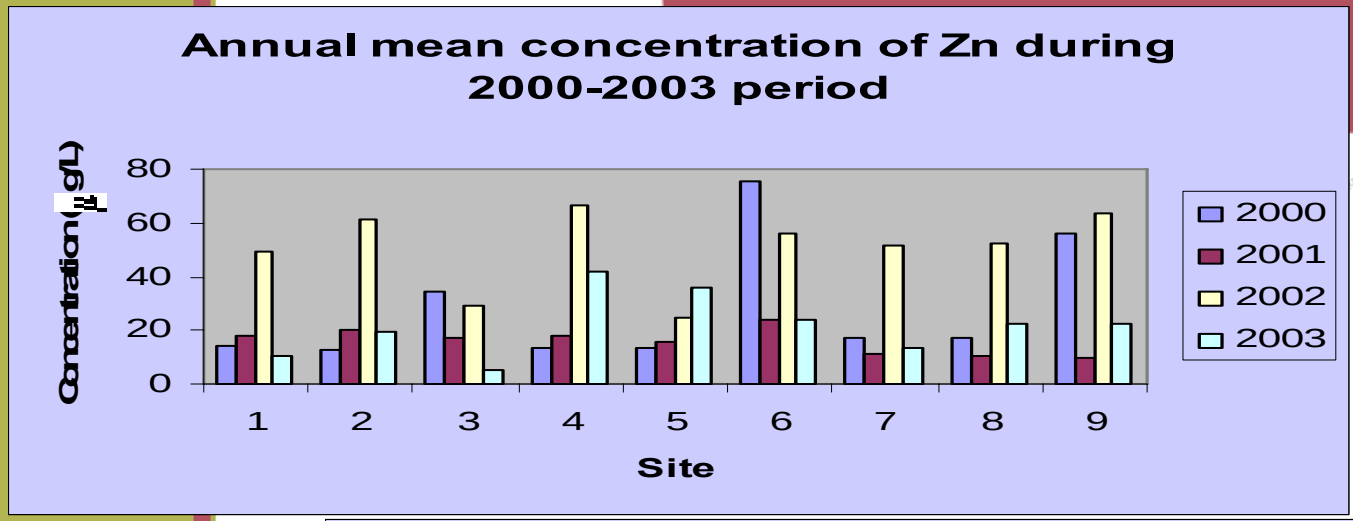


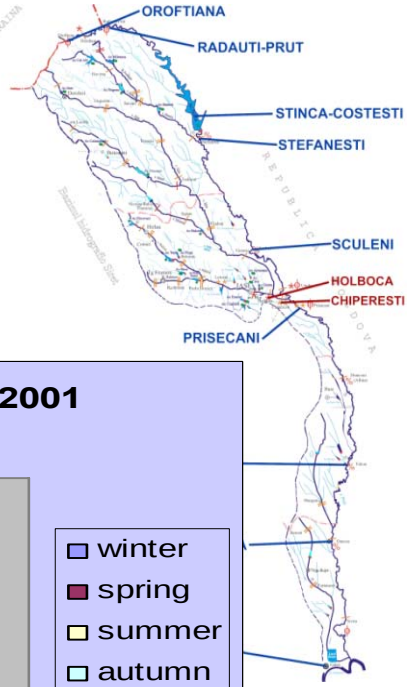


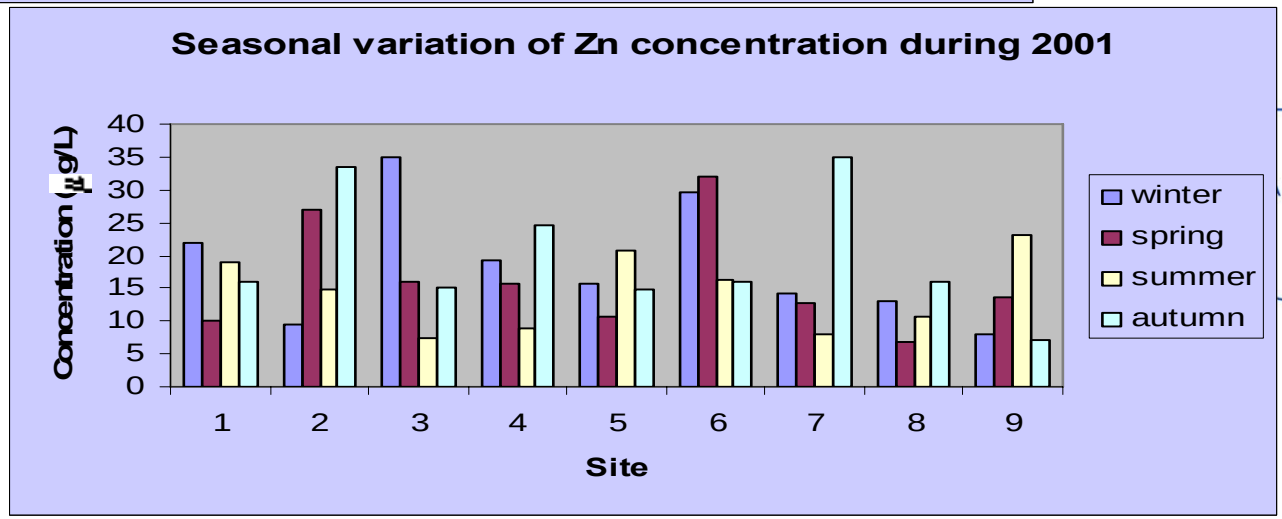
Possible Cu pollution sources:

→ **few small tributaries in the area of the river entrance which are passing through vineyards bringing about Cu pesticides;**

→ **industrial origin of Cu contamination starting from site 6.**





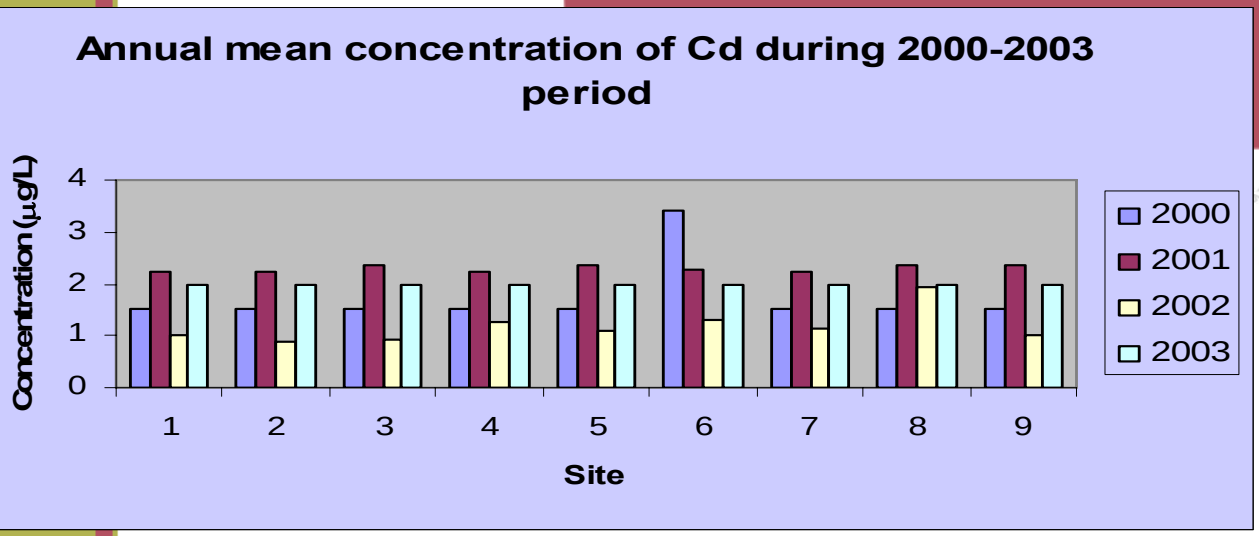


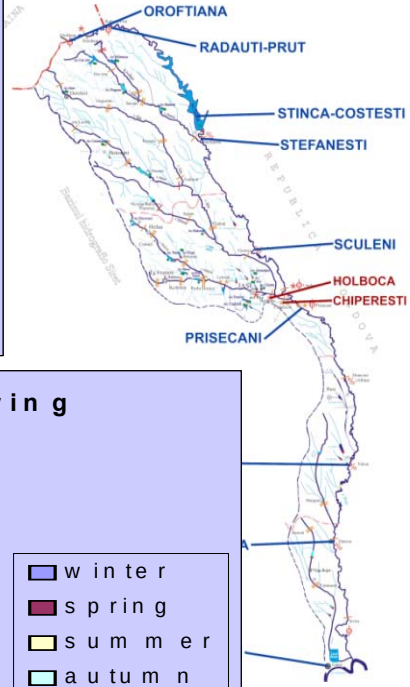
Possible Zn pollution sources:

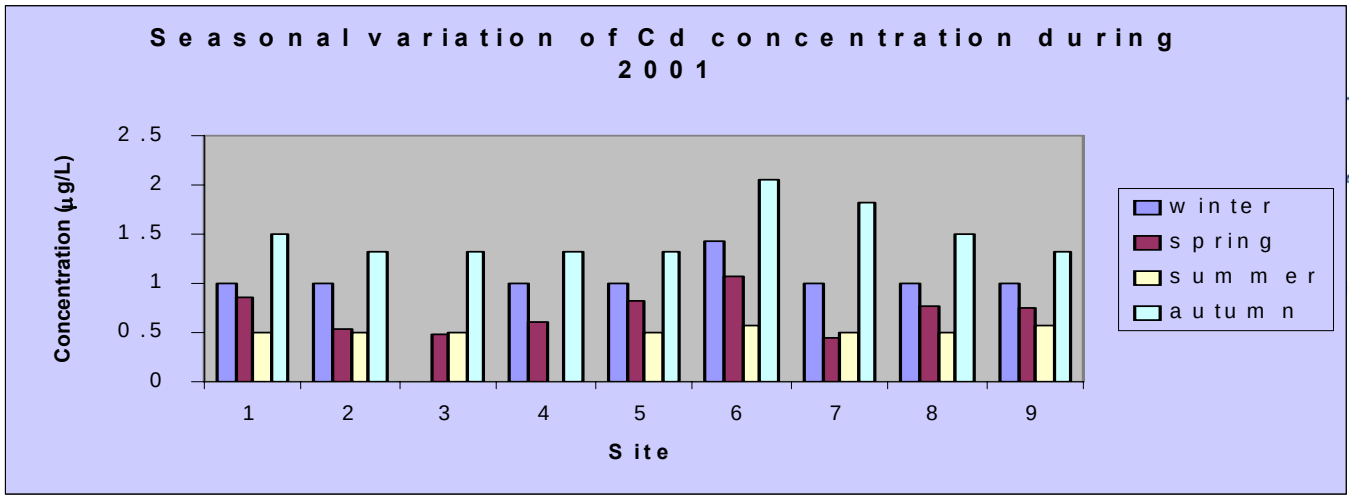
→ **few orchards to the north part of the Prut catchment;**

→ **existence of an important industrial source of pollution in the Iasi City (site 6).**

(HM)

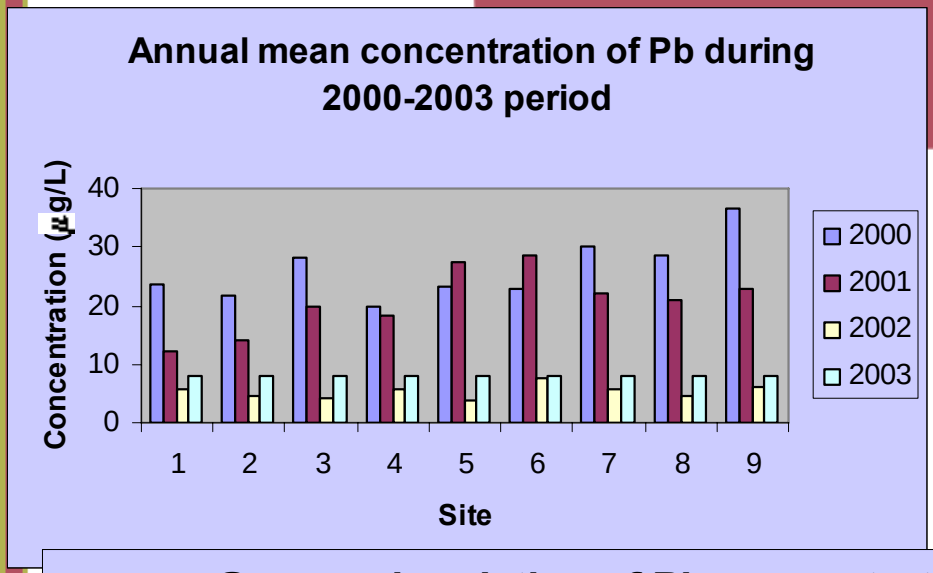


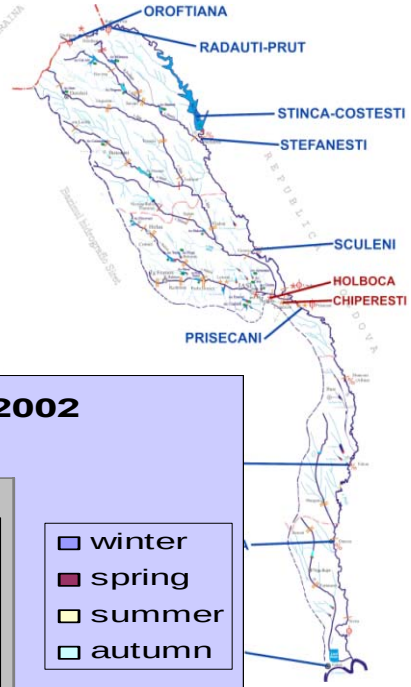


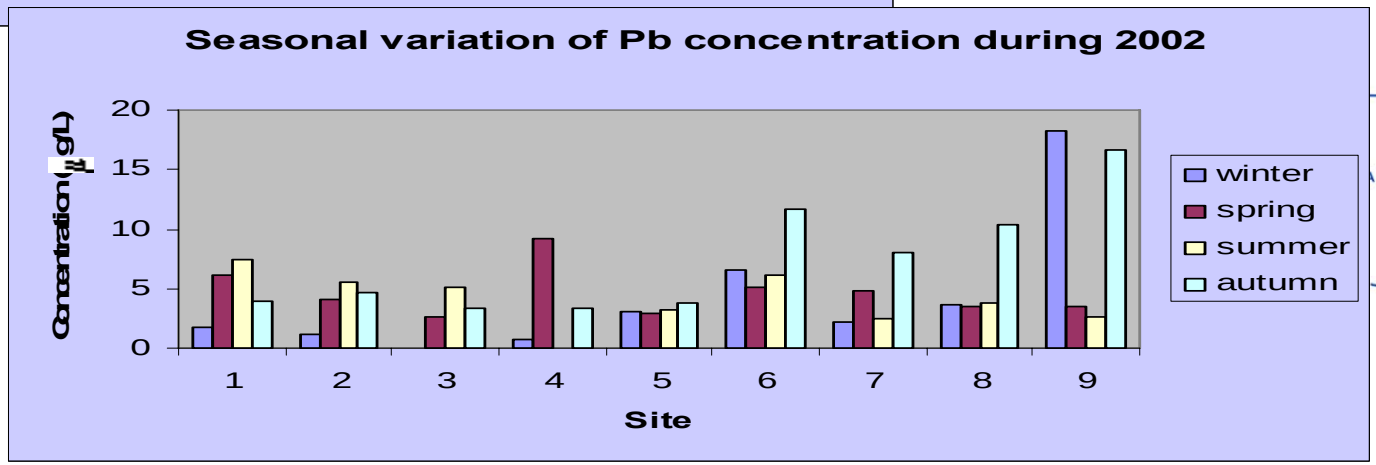


Possible Cd pollution sources:

- → **accidental waste spillway;**
- → **long-range atmospheric transport;**
- → **metal remobilisation from sediments.**







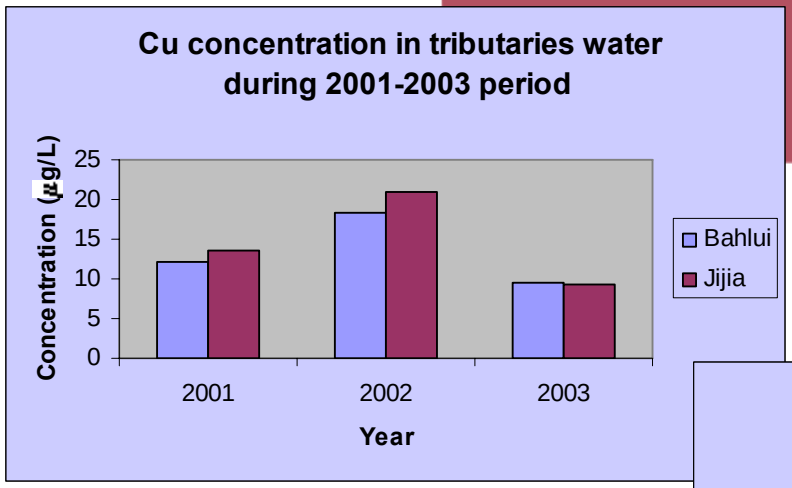
Possible Pb pollution sources:

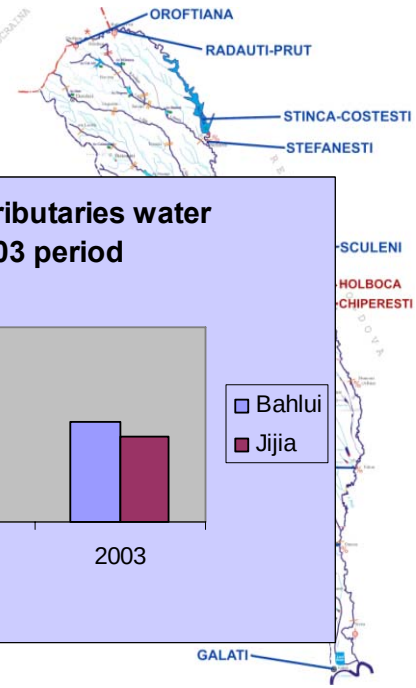
→ **until 2001 it was permitted in Romania possession and utilisation of old cars;**

→ **leaded gasoline;**

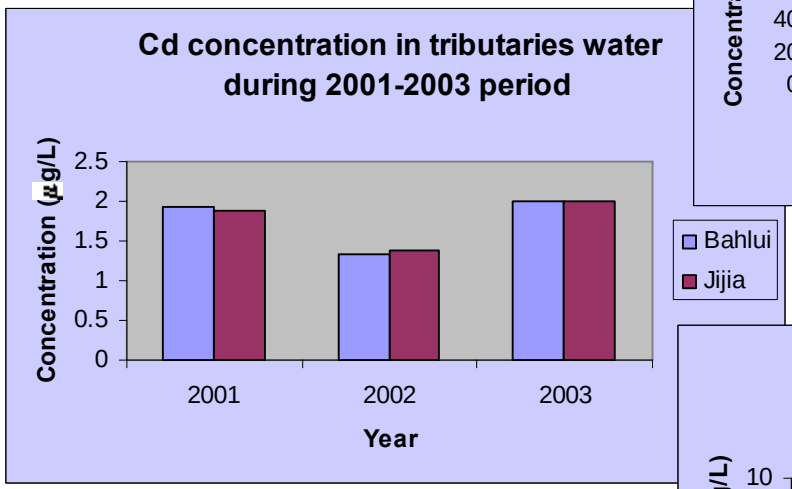
→ **air transboundary pollution.**

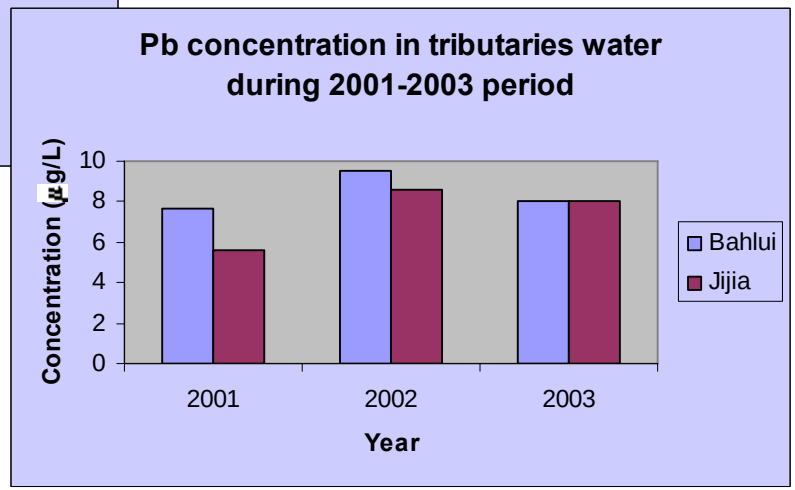
(HM)


Cu concentration in tributaries water during 2001-2003 period
Concentration (µg/L)
25
20
15
10
5
0
2001
2002
2003
Year
Bahlui
Jijia

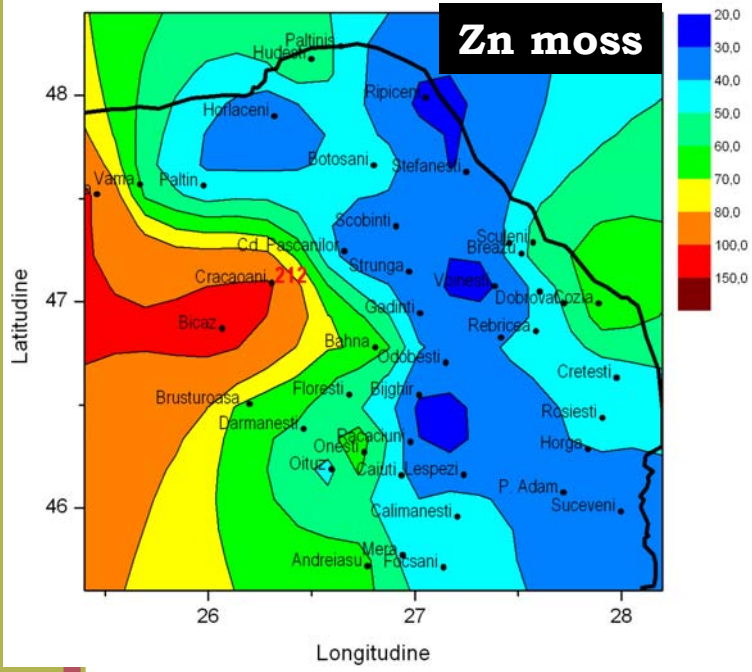

OROFTIANA
RADAUTI-PRUT
STINCA-COSTESTI
STEFANESTI
SCULENI
HOLBOCA
CHIPERESTI
GALATI

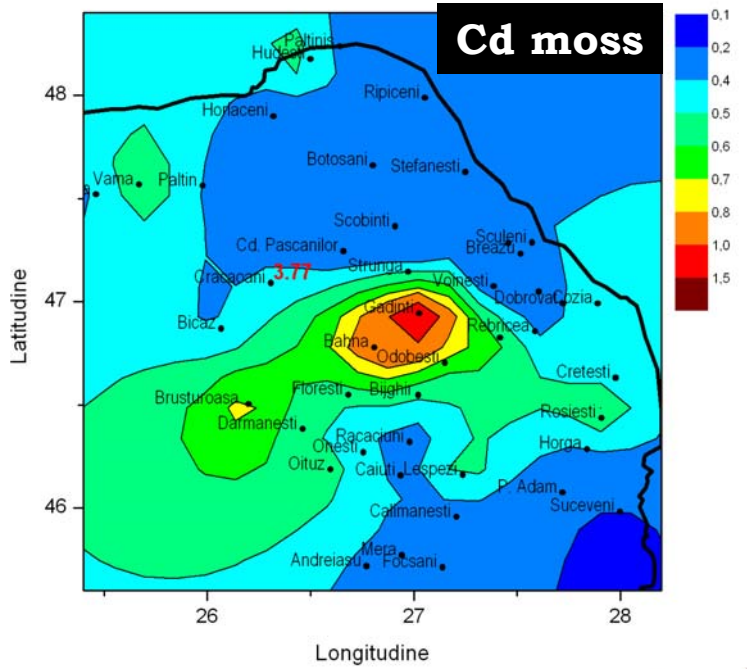
Zn concentration in tributaries water during 2001-2003 period
Concentration (µg/L)
120
100
80
60
40
20
0
2001
2002
2003
Year
Bahlui
Jijia


Cd concentration in tributaries water during 2001-2003 period
Concentration (µg/L)
2.5
2
1.5
1
0.5
0
2001
2002
2003
Year
Bahlui
Jijia

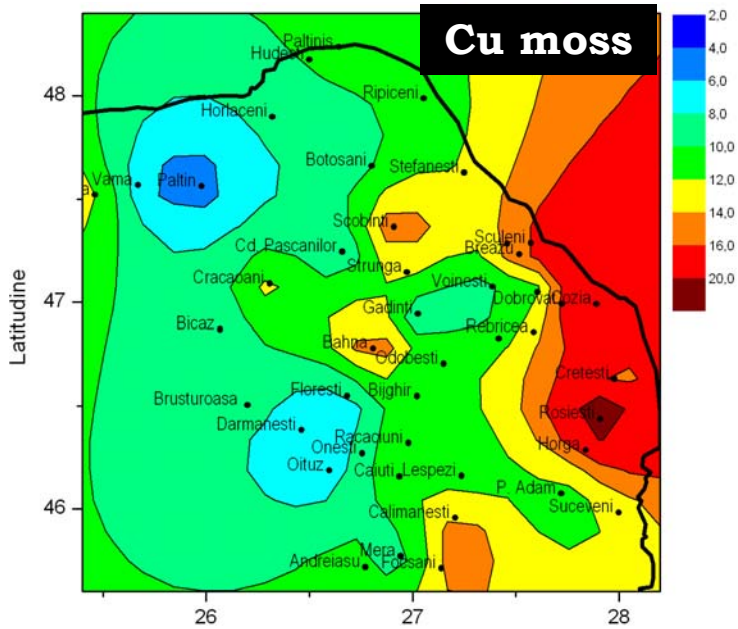

Pb concentration in tributaries water during 2001-2003 period
Concentration (µg/L)
10
8
6
4
2
0
2001
2002
2003
Year
Bahlui
Jijia

(HM)

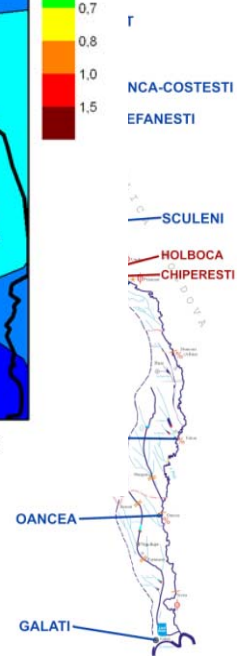




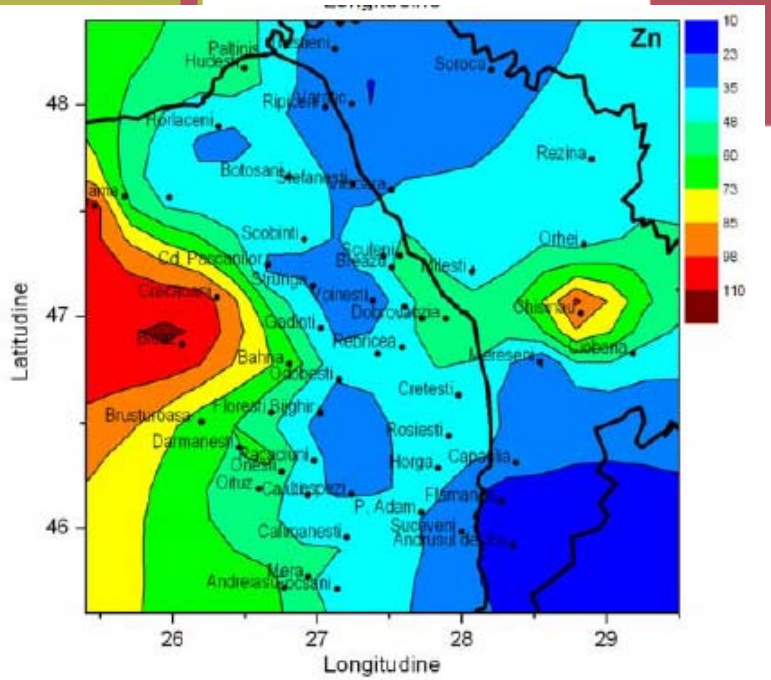
Zn and Cd concentration (mg·kg^{-1}) in moss

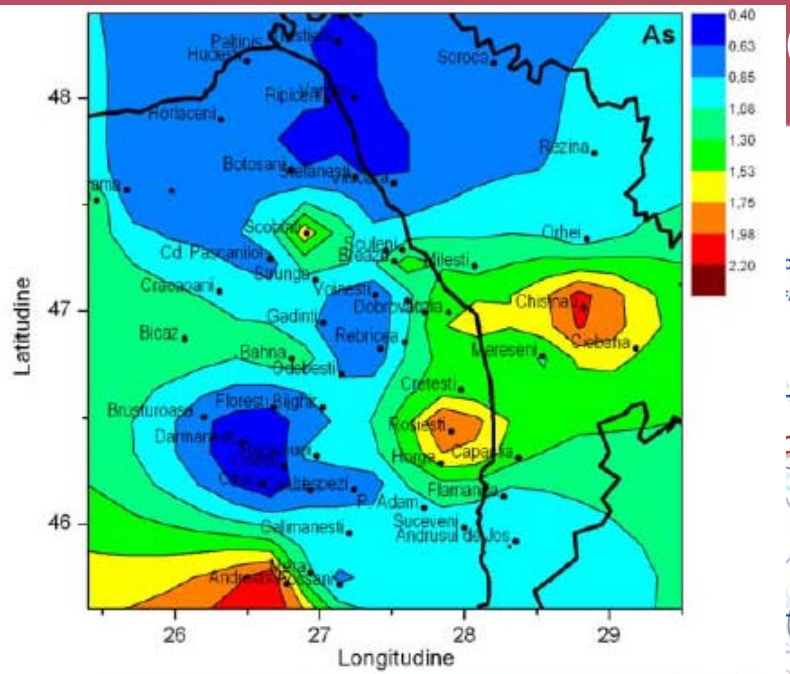


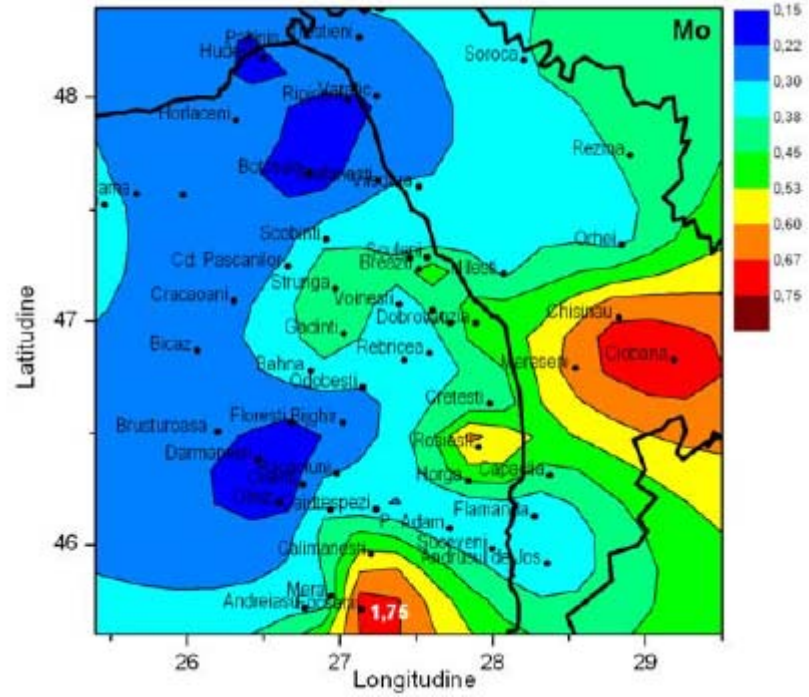
Cu concentration (mg·kg^{-1}) in moss

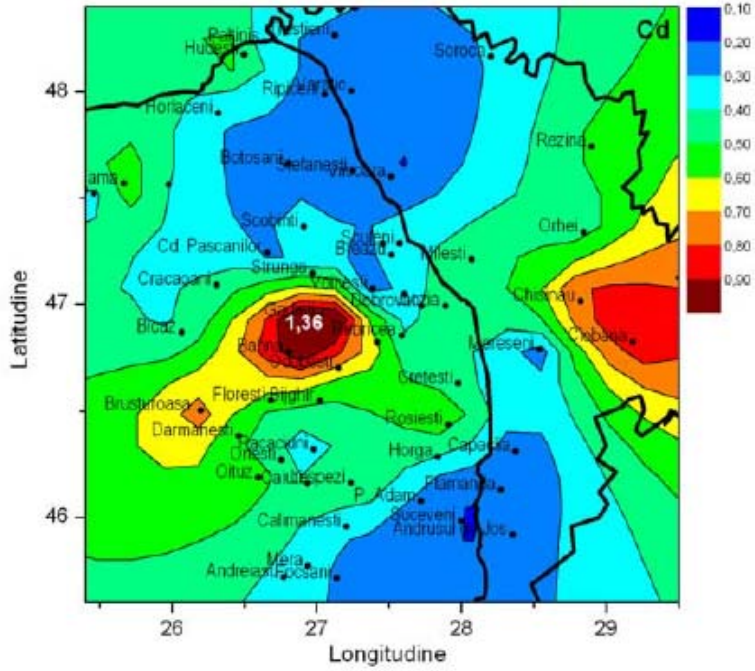


(HM)


Zn
10
23
35
48
60
73
85
98
110
Latitudine
Longitudine
48
47
46
26
27
28
29

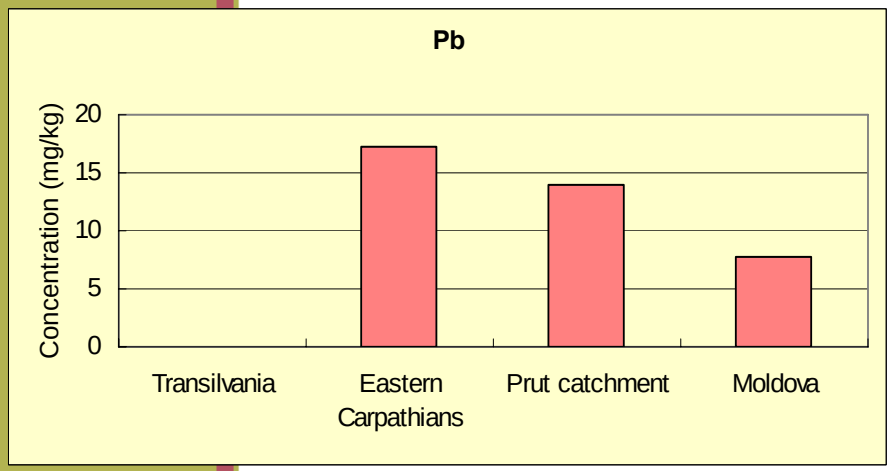

As
0.40
0.63
0.85
1.08
1.30
1.53
1.75
1.98
2.20
Latitudine
Longitudine
48
47
46
26
27
28
29

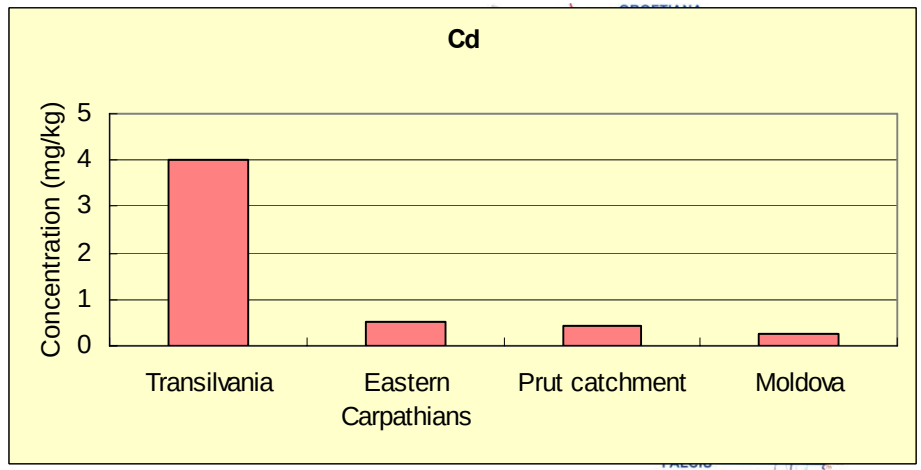

Mo
0,15
0,22
0,30
0,38
0,45
0,53
0,60
0,67
0,75
1,75
Latitudine
Longitudine
48
47
46
26
27
28
29

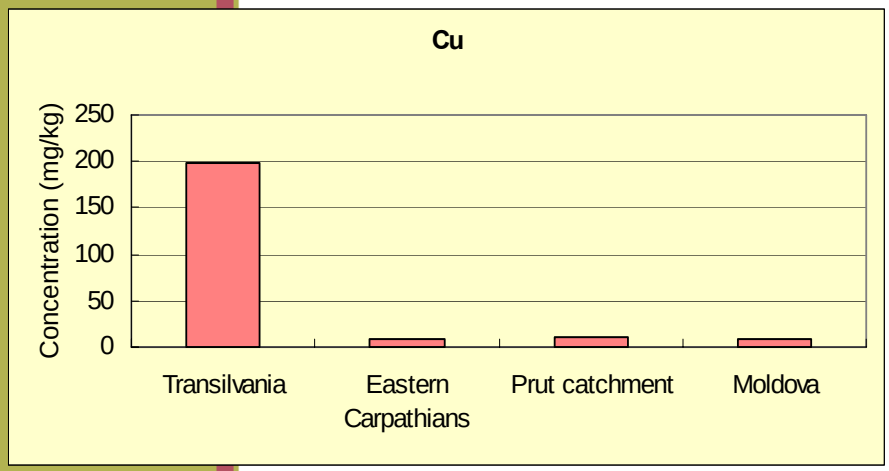

Cd
0,10
0,20
0,30
0,40
0,50
0,60
0,70
0,80
0,90
1,36
Latitudine
Longitudine
48
47
46
26
27
28
29

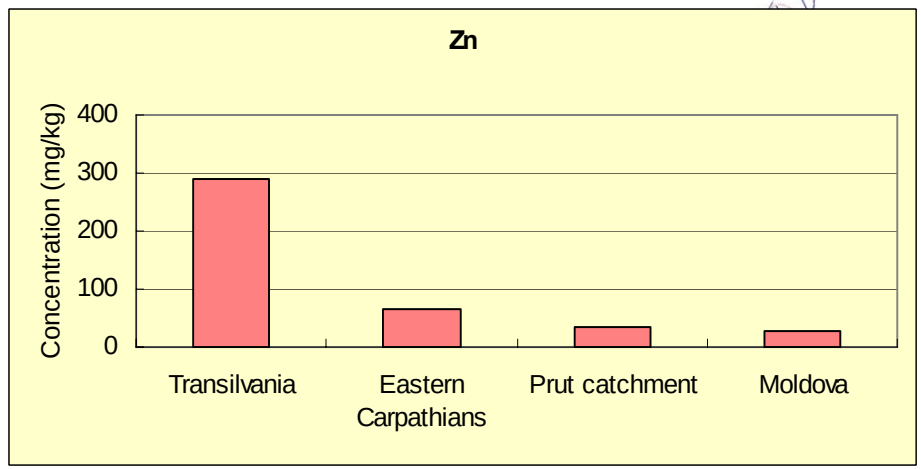

SCULENI
HOLBOCA
CHIPERESTI

Transboundary pollution







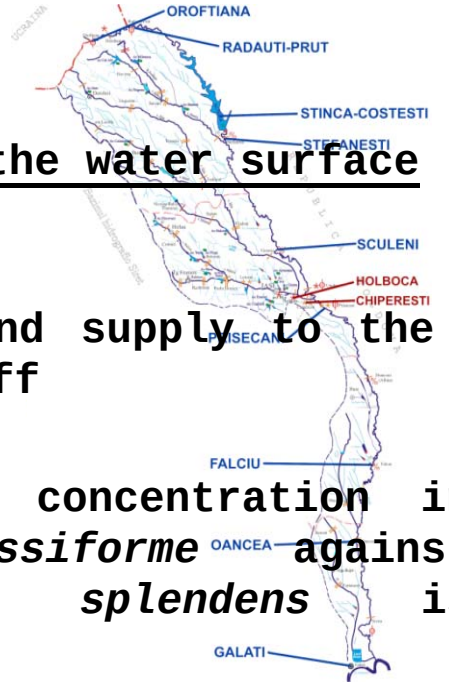


The obtained values for atmospheric deposition in Prut River catchment are lower than those obtained in Transilvania, similar to those obtained in the Eastern Carpathians and higher compared to Republic Moldova. This supports the conclusion that no transboundary pollution of the investigated elements from Romania to Republic of Moldova could be considered.

Contribution of atmospheric deposition to the pollution of Prut River

Ways of supply

- **Direct deposition on the water surface**
- **Deposition on land and supply to the river by surface runoff**



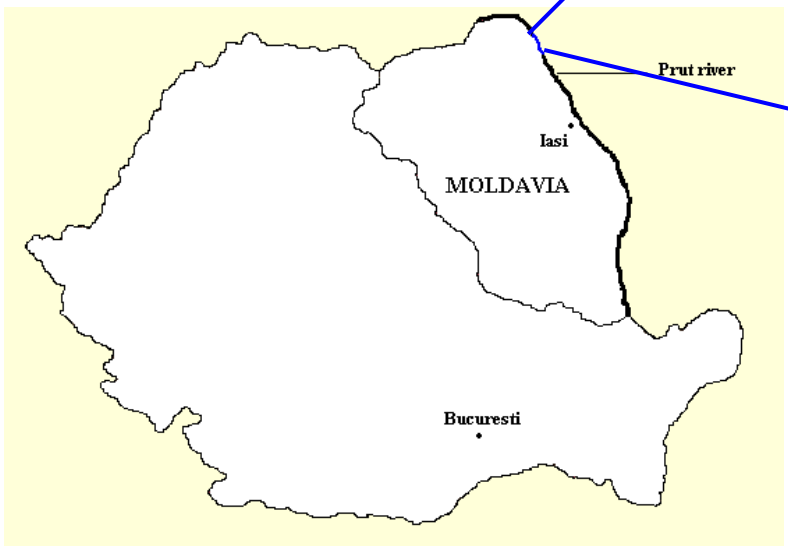
Assumption

- **The calibration of metal concentration in epiphytic *Hypnum cupressiforme* against transplanted *Hylocomium splendens* is considered.**
- **The uptake of metals is the same whether the moss *Hylocomium splendens* is used as active or passive biomonitor.**
- **The calibration of metal concentration in *Hylocomium splendens* against bulk deposition from Norway (Berg et al., 1995) are valid for the region concerned in the present work.**

Contribution of atmospheric deposition to the pollution of Prut River

Stanca Costesti Lake

- Volume – 7.5×10^8 m^3
- Mean depth – 12.5 m
- Surface – 59 km^2

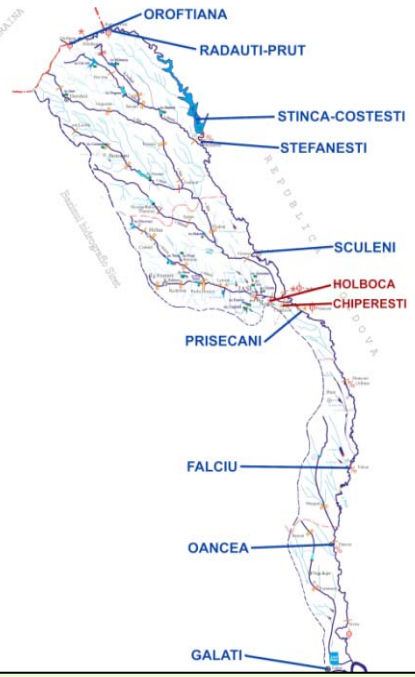


Stefanesti → The site most close to the Stanca Costesti reservoir

Contribution of atmospheric deposition to the pollution of Prut River

Concentration in *Hypnum cupressiforme* ($mg \cdot kg^{-1}$) →

Cu – 11.8
Zn – 28.9
Cd – 0.42
Pb – 14.4



Yearly deposition values ($mg \cdot m^{-2} \cdot y^{-1}$) →

Cu – 3.0
Zn – 9.0
Cd – 0.17
Pb – 4.5

Annual atmospheric addition of metals to the reservoir (kg) →

Cu – 200
Zn – 500
Cd – 10
Pb – 300

Atmospheric contribution to the concentrations in water ($\mu g \cdot L^{-1}$) →

Cu – 0.09
Zn – 0.22
Cd – 0.005
Pb – 0.15

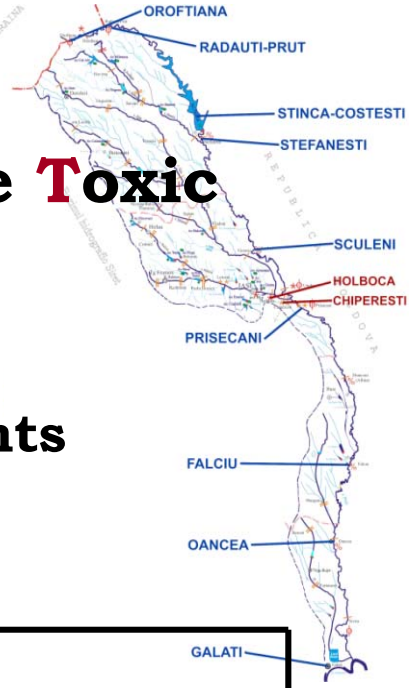
Concentrations in water ($\mu g \cdot L^{-1}$) →

Cu – 10
Zn – 20
Cd – 0.5
Pb – 3

Contribution from direct atmospheric deposition to the reservoir (%) →

Cu – 1
Zn – 1
Cd – 1
Pb – 5

PBT - POPs



Persistent Bioaccumulative Toxic
PBTs

↓

Persistent Organic Pollutants
POPs

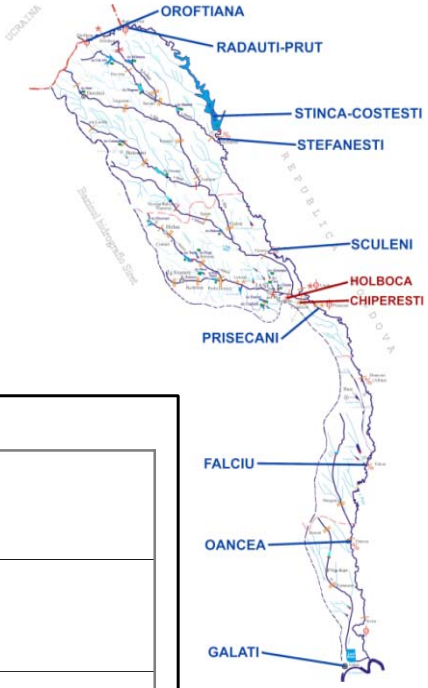
↓

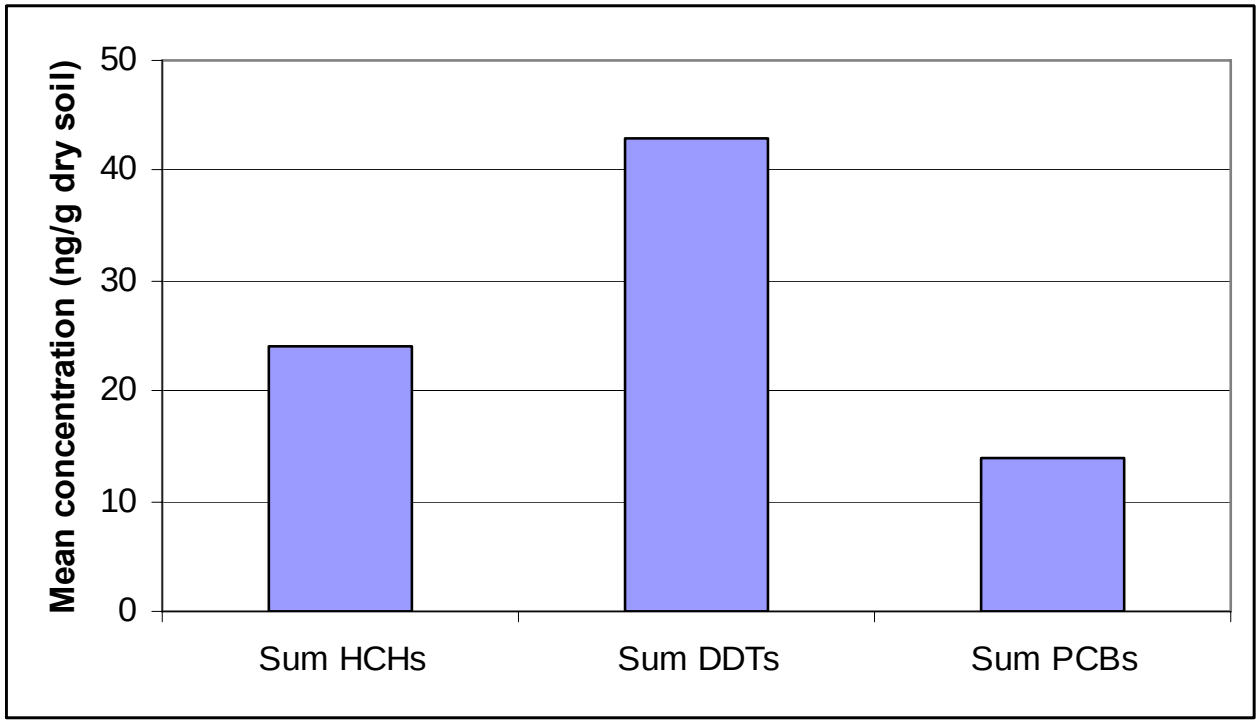
Pesticides → **Aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene**

Chemicals → **Hexachlorobenzen (HCB)**
Polychlorinated Biphenyls (PCBs)

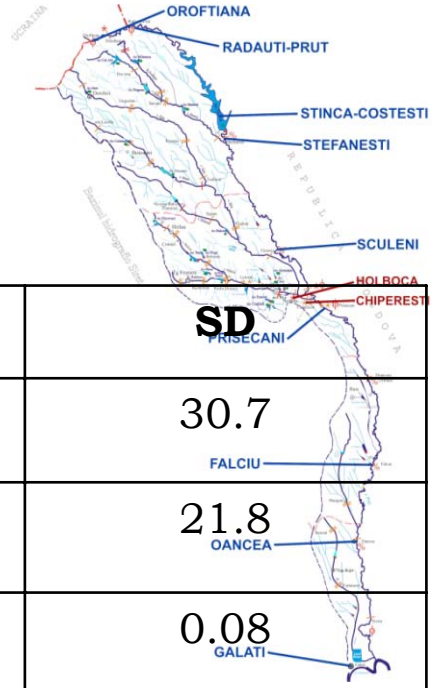
By-products → **Dioxins**
Furans

Mean levels of sum HCHs, DDTs and PCBs in soil samples.





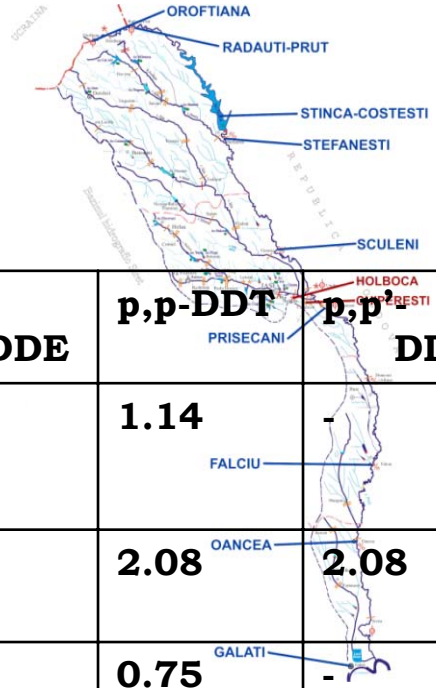
Range concentration, mean (ng/g dry wt.) and standard deviation of Sum HCHs, DDTs, HCB and Chlordane in moss samples.



OCPs	Range	Mean	SD
Sum HCHs	8.9 – 133.1	31	30.7
Sum DDTs	5.8 – 95.3	27.5	21.8
HCB	0.1 – 0.4	0.23	0.08
Sum Chlordane	nd* –0.4	0.03	0.09

*nd – not detected

Comparison of HCH isomers and DDT analogue (ng/g dry wt.) in moss in different countries.

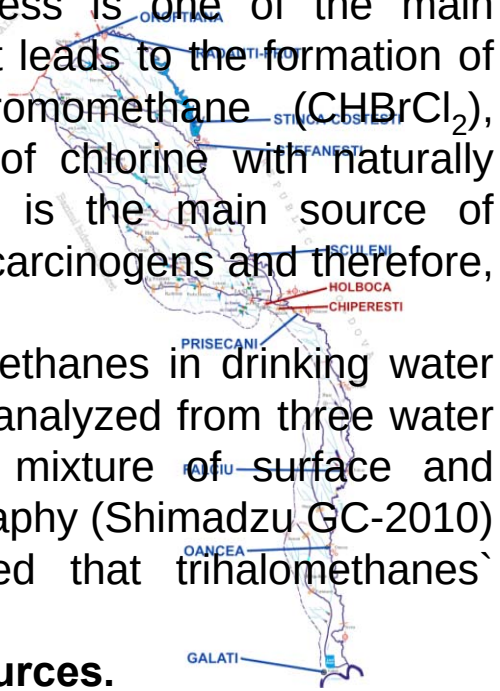


Country	a-HCH	b-HCH	g-HCH	d-HCH	p,p'-DDE	p,p-DDT	p,p'-DDD
Czech Republic 1988-1994	1.07	<0.1	1.28	<0.3	0.15	1.14	-
Singapore (2004)	0.65	21.19	bdl	0.574	1.86	2.08	2.08
Victoria Land (1999)	1.51	-	0.78	-	3.5	0.75	-
Eastern Romania (2005)	4.5	13	11.5	2.1	6	14.8	2.6

- bld – bellow detection limit.

Trihalomethanes in water

In many drinking water treatment plants, the chlorination process is one of the main techniques used for the disinfection of water. This disinfecting treatment leads to the formation of trihalomethanes (THMs) such as: chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), chlorodibromomethane ($CHClBr_2$), and bromoform ($CHBr_3$). Reaction of chlorine with naturally occurring organic matters, principally humic acid and fulvinic acid is the main source of trihalomethanes in the tap water. They are all considered to be possible carcinogens and therefore, human exposure to such compounds should be considered.



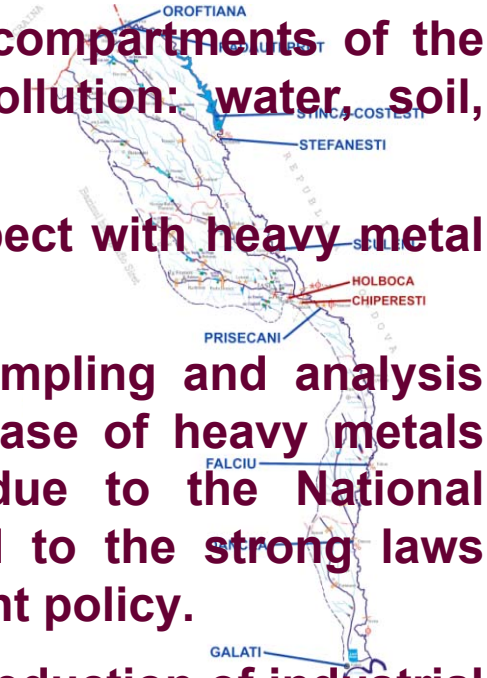
Purpose of this study was to investigate the presence of trihalomethanes in drinking water distribution systems of Iasi City. Tap water samples were collected and analyzed from three water distribution systems (surface water-Prut; groundwater-Timisesti and mixture of surface and groundwater). THMs concentrations were determined by gas chromatography (Shimadzu GC-2010) with an electron capture detector (ECD). Obtained results showed that trihalomethanes` concentration varies significantly according to drinking water source:

Table 1. Average THM values (µg/L) from different tap water sources.

Water source	$CHCl_3$	$CHBrCl_2$	$CHClBr_2$	$CHBr_3$	Total THM
Surface water	66,30	24,20	6,68	0,98	**98,16**
Groundwater	17,65	9,93	6,63	2,30	**36,51**
Mixture	23,32	11,03	6,10	1,87	**42,32**

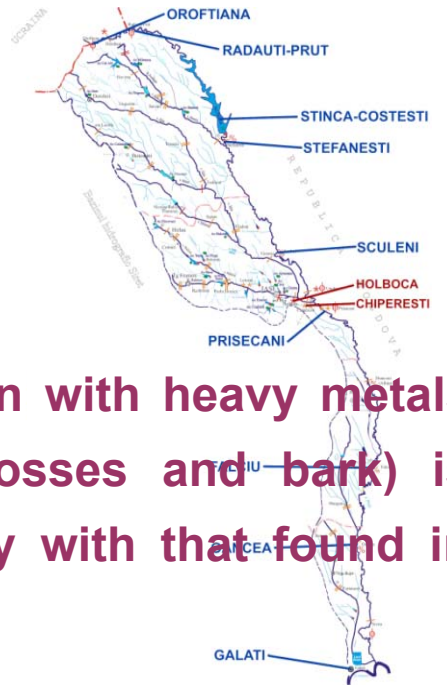
THMs concentrations are lower in groundwater source comparing with surface water source. Organic matters in groundwater source was found in a low concentration and consequently for disinfection process was used a lower chlorine quantity. The most dominant THM compounds are chloroform followed by dichlorobromomethane, chlorodibromomethane and bromoform.

CONCLUSIONS (HM)



- This work has approached all environmental compartments of the Prut River catchment submitted to metal pollution: water, soil, sediment and atmosphere.
- The main aim was the water monitoring in respect with heavy metal contamination
- During November 2000-April 2003 monthly sampling and analysis were done. In the last two years, small decrease of heavy metals concentration has been recorded partially due to the National Environmental Protection Agency activity and to the strong laws adopted by Romania concerning the environment policy.
- Another explanation of this trend is the strong reduction of industrial and agricultural activities.
- The main pollution sources of heavy metals of the Prut water are the river's tributaries; it is important to adjoin busy traffic, small contribution of long-range atmospheric pollutants as well as other water transboundary pollutants.
- Concerning the N and P content, it is possible a slow eutrophication is possible to arise in future, as some mesotrophic characteristics of water are present.

CONCLUSIONS



In Romania the level of air and water pollution with heavy metals (monitored chemically and by means of mosses and bark) is comparable in the eastern part of the country with that found in other European countries.

In studied area, as far as POP's concentration is concerned, the values are higher then admitted limits by international regulations.