The study of POPs contaminated sites in Danube River basin of Republic of Moldova for Risk Assessment and Remediation Action.

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The aim of the presentation is an Evaluation of Hazards and Environmental Risk Assessment from POPs polluted sites in Lower Danube River region of the Republic of Moldova on different levels (local and regional).

Objectives

- **inventory of potential polluted by toxic organic substances sites and site assessment procedure;**
- **soil sampling and determination of old pesticide pollution level in soil (hazard determination);**
- **regional risk assessment: ranking of polluted sites;**
- **detail risk assessment procedure for remediation actions design (case study).**

Danube River Basin District: Ecoregions

MAP 2

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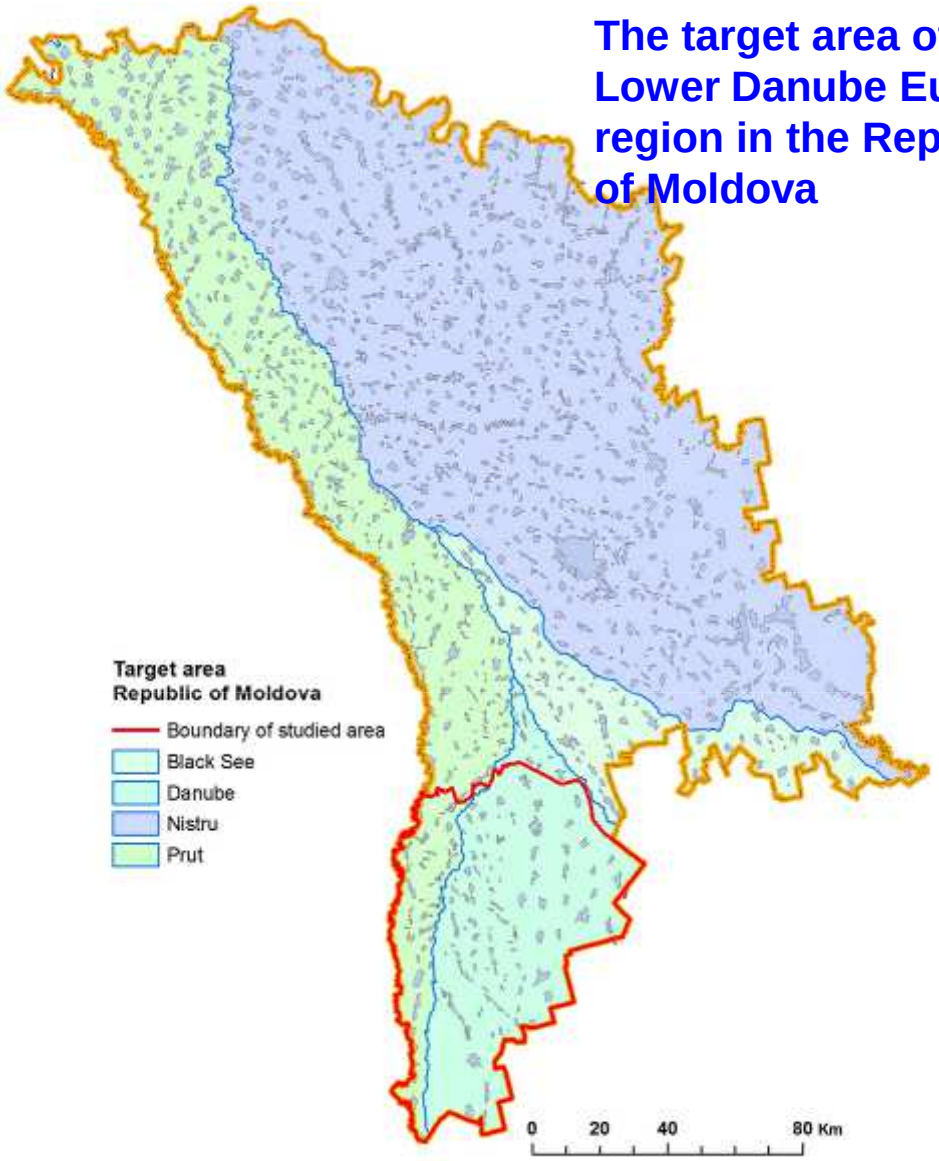
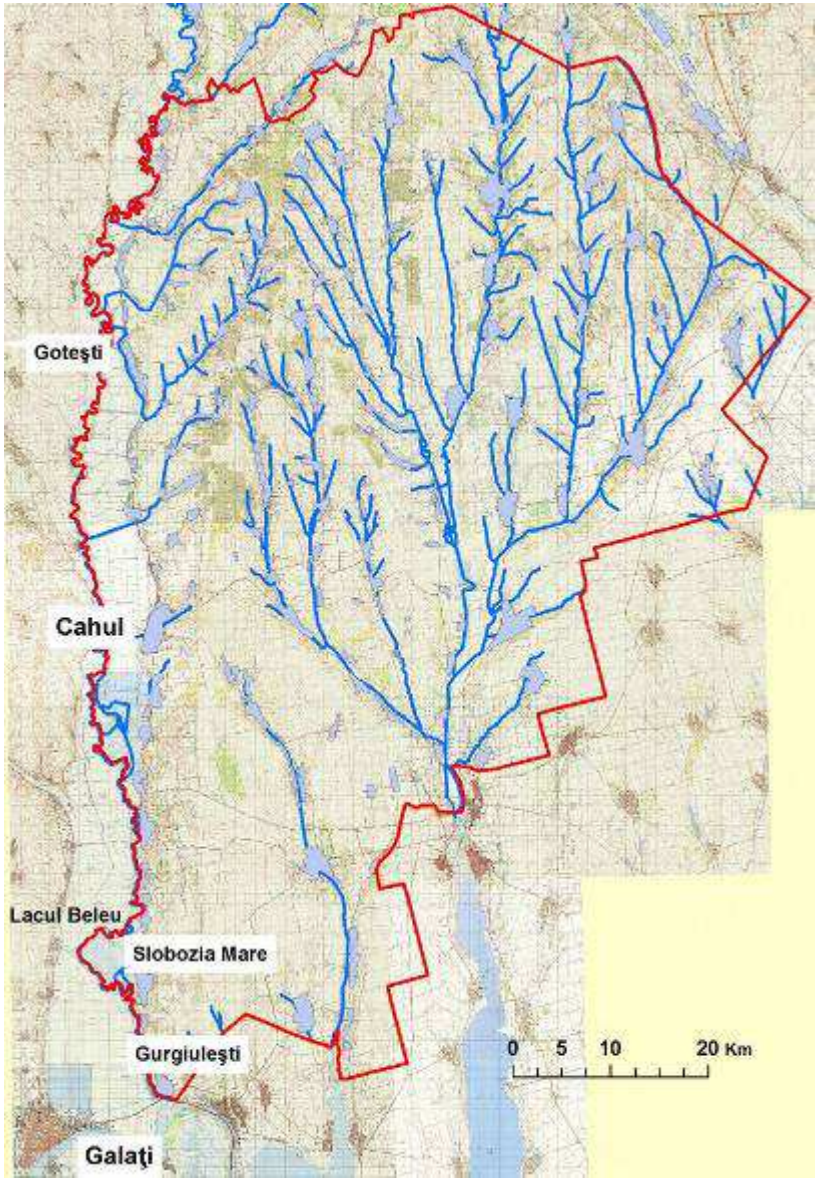
icpdr iksd

This ICPDR product is based on national information provided by the Contracting Parties to the ICPDR (AT, BA, BG, CZ, DE, HR, HU, MD, RO, RS, SI, SK, UA) and CH, except for the following: EuroGlobalMap v2.1 from EuroGeographics was used for national borders of AT, CZ, DE, HR, HU, MD, RO, SI, SK and UA; ESRI data was used for national borders of AL, ME, MK; Shuttle Radar Topography Mission (SRTM) from USGS Seamless Data Distribution System was used as topographic layer; data from the European Commission (Joint Research Center) was used for the outer border of the DRBD of AL, IT, ME and PL.

Vienna, December 2009

The target area of Lower Danube Euro region in the Republic of Moldova





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The inventory of POPs potential polluted sites was made in 2009 – 2010 by World Bank Project (Center of Environmental Study "ECOS")

(http://pops.mediu.gov.md/) and included:

- **interview of local authority, specialist and population about location and history of polluted sites;**
- **site visit, soil sampling and field study of actual situation at sites, competition of questionnaire with local coordinate fixation;**
- **analysis of toxic substances in complex soil samples;**
- **methodology elaboration for risk assessment of polluted sites;**
- **creation of geodatabase and GIS server application.**

Soil sampling and determination of toxic pollution in soil.

Random sampling (20 – 30 subsamples for complex sample)

Analyses were made in accredited by ISO 17025 laboratory “GEOLAB”

Gas Chromatograph Agilent6890 (2000)
equipped by μECD and FID detectors.
Gas Chromatograph with Mass Selective detector Agilent6890/5973

Site Assessment Procedure: site visit and sampling

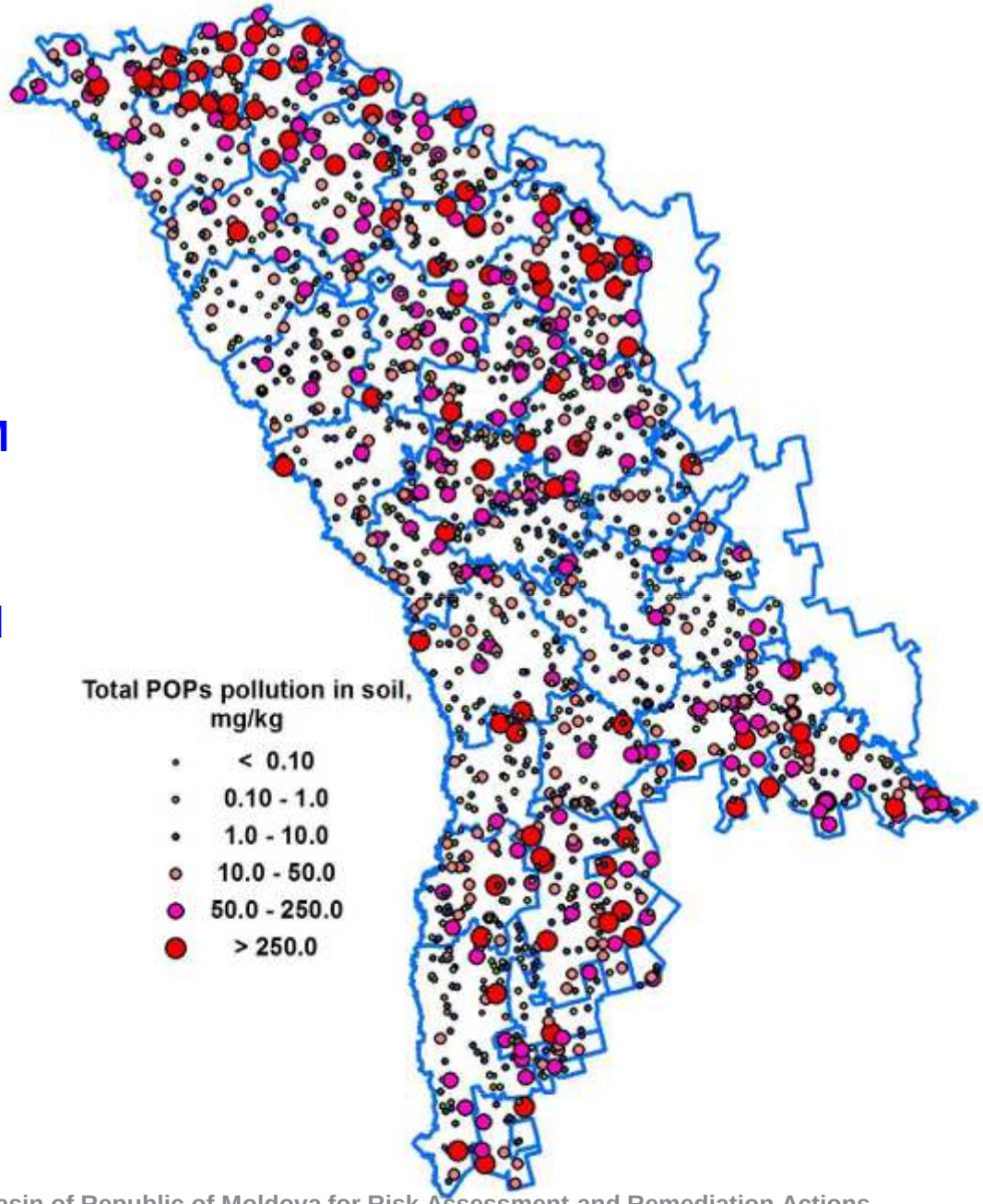
Spectrum and pollution level

10 POPs were monitored (no Dioxin and Furans) and only five POPs (groups of) compounds namely ∑ DDT, ∑ HCH, Chlordane, Heptachlor and Toxaphene have been found and included in database .

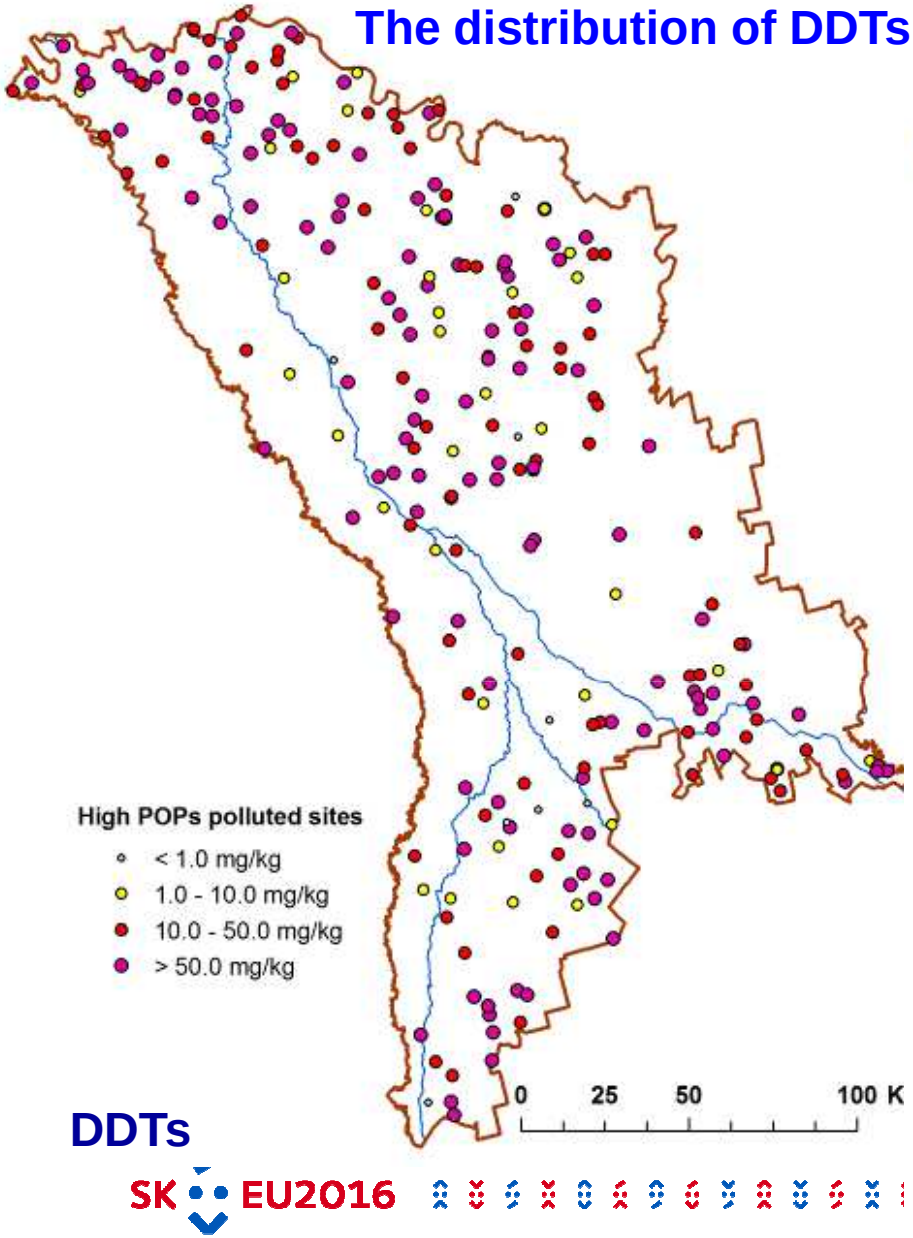
The inventory of all territory of RM showed a large quantity of potential polluted sites (1589).

252 sites (15.9%) were determined as very high polluted territory (POPs in soil more 50,0 mg/kg).

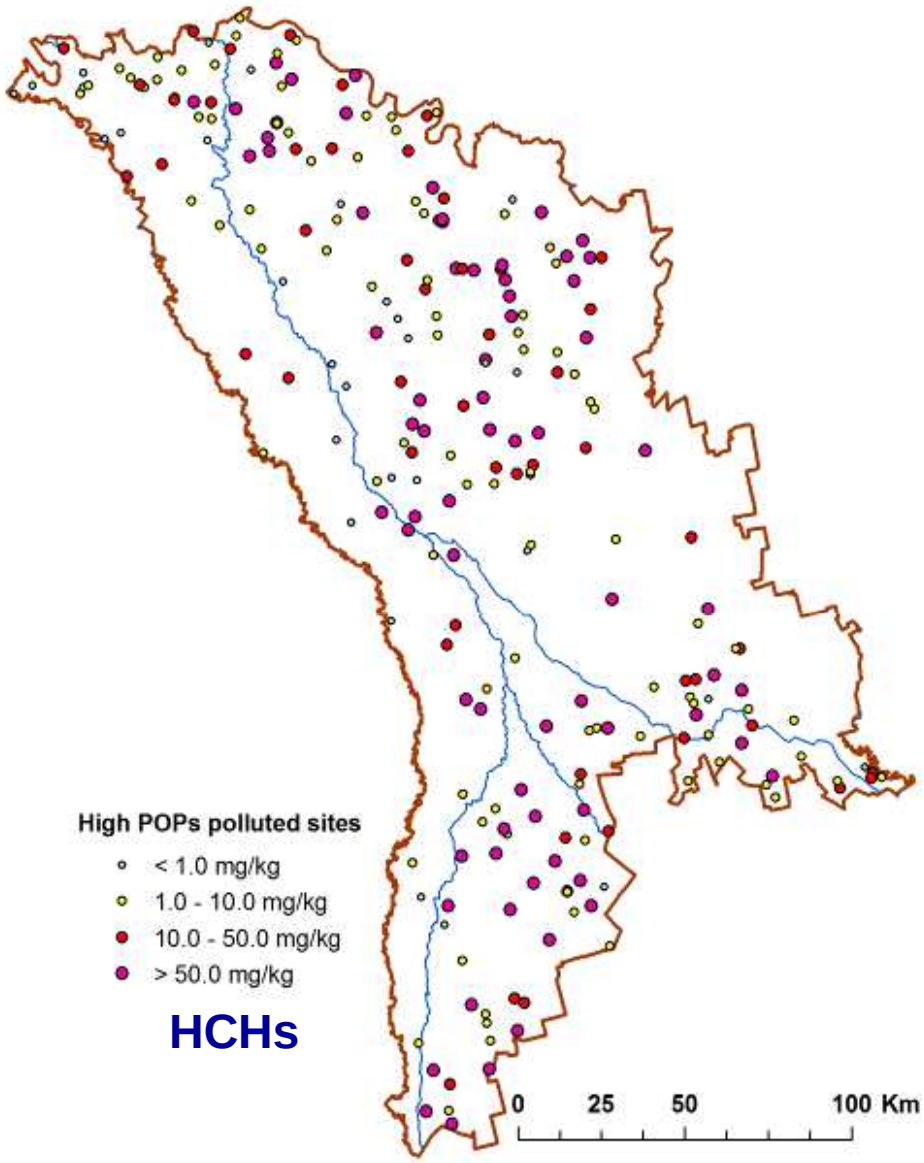
By river basins:
Danube – 39 sites (15,4 %);
Prut – 50 sites (19,9%);
Black Sea – 22 sites (8,7%);
Nistru – 141 sites (56 %).



The distribution of DDTs and HCHs at high POPs polluted sites.



DDTs



HCHs

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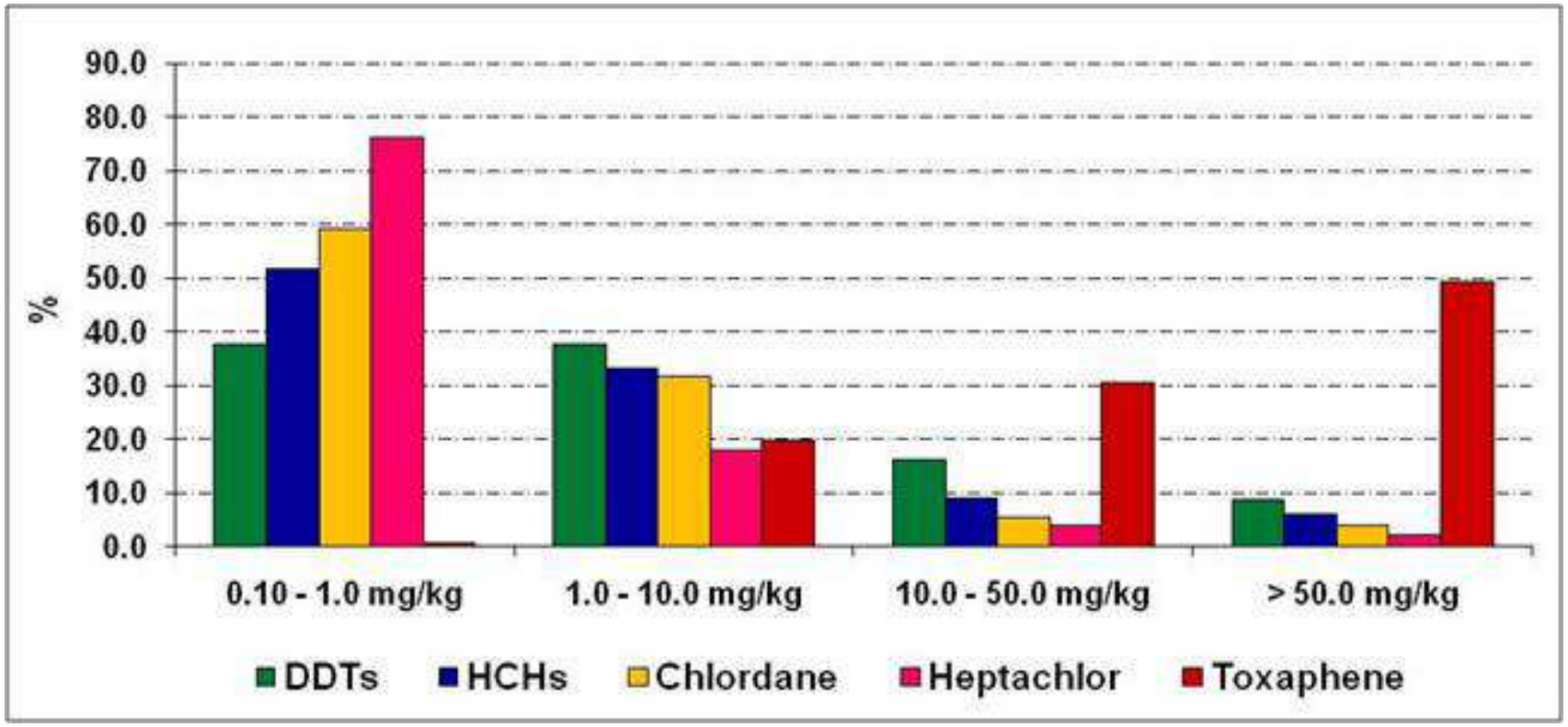
Spectrum and pollution level



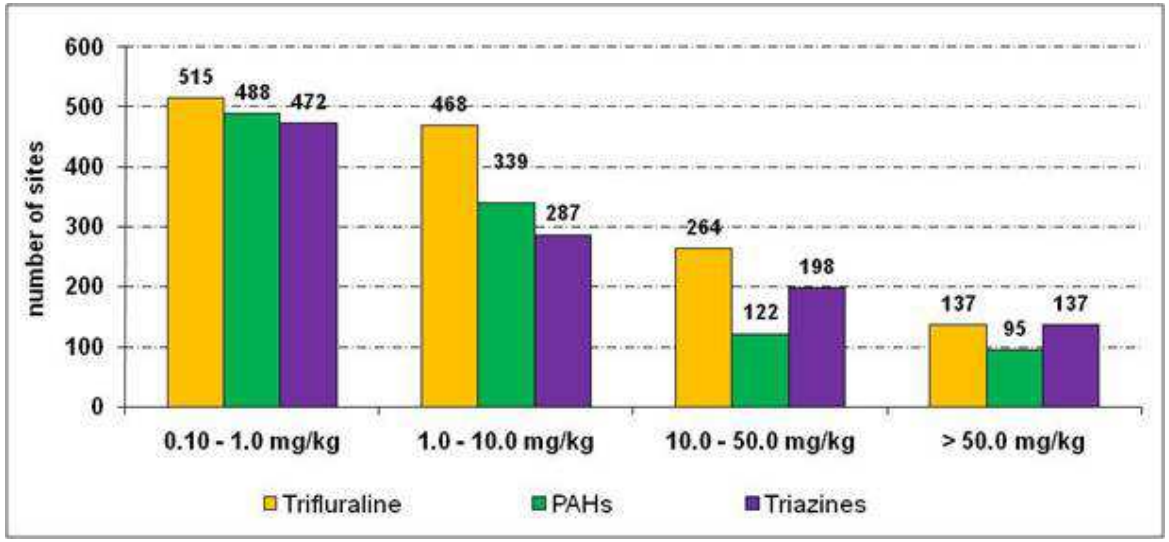
The distribution of POPs pollution by clusters (lognormal distribution): 0.10 – 1.0 mg/kg; 1.0 – 10.0 mg/kg; 10.0 – 50.0 mg/kg; and > 50.0 mg/kg.

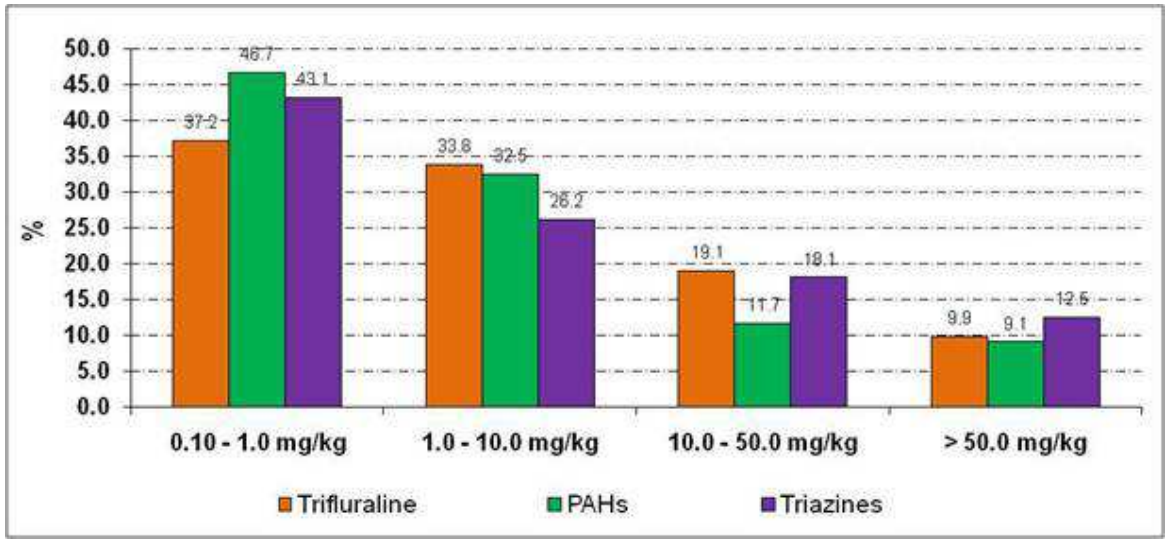
Spectrum and pollution level

High POPs polluted sites have a complex pollution by other toxic substances: Trifluraline (85%), triazines (64%), PAHs (33%)

Some sites with relative low POPs pollution have high concentration by other toxic substances.

The distribution of toxic pollutants by clusters: 0.10 – 1.0; 1.0 – 10.0; 10.0 – 50.0; and > 50.0 mg/kg.





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Methodology of ranking system

National Classification System for Contaminated Sites of Soil Quality Guidelines Task Group of CCME of Canada (http://www.ec.gc.ca/ceqg-rcqe) was used as Technical Basis for the Classification System.

This system was designed to evaluate the hazard, or hazard potential from studied sites by scoring site characteristics that can be grouped under three categories:

1. Contaminant Characteristics: level and spectrum of pollution; hazard and toxicity of contaminants; residence media;
2. Migration Potential to leave the original residency media and move to another media,
3. Exposure pathway and receptor analysis: groundwater, surface water, direct contact, and air transport to a receptor.

The methodology for the ranking of POPs contaminated sites

1. Contamination level

POPs pollution was assessed by two factors:

- **POPs contamination level;**
- **number of toxic substances (synergism effect).**

Pollution level	Pollution ratio	Risk index
No pollution	< Det. Limit	0
Marginal	Det. Limit < C < 0,9 MAC	2
low	1 MAC < C < 9,9 MAC	4
Middle	10 MAC < C < 99,9 MAC	6
High	100 MAC < C < 499,9 MAC	8
Very high	500 MAC < C < 4999,9 MAC	10
Extremal	C > 4999,9 MAC	14

POPs number	Variability index
1	1.0
2	1.1
3	1.2
4	1.3
5	1.4
6	1.5
7	1.6
8	1.7
9	1.8
10	1.9
11	2.0
12	2.1
13	2.2
14	2.3

$$HP_{total} = (HP_{aldrin} + HP_{dieldrin} + HP_{endrin} + HP_{chlordane} + HP_{DDTs} + HP_{toxaphene} + HP_{hexachlorbenzene} + HP_{heptachlor} + HP_{mirex} + HP_{alfa\text{-}HCH} + HP_{beta\text{-}HCH} + HP_{gama\text{-}HCH} + HP_{chlordecone} + HP_{pentachlorobenzene}) * k$$

HP – index for every pollutant by the ratio to MAC (0,1 mg/kg for soil); k – variability index.

2 Risk receptors

Contact zone	Distance to receptors, m	Risk index
Direct contact	0 - 24.9	14
Guaranted contact	25 - 49.9	10
Possible contact	50 - 99.9	8
Low contact	100 - 199.9	4
Very law contact	200 - 300	2

Risc receptors	Weight Index
Woods	1,2
Wetlands	1,1
Rivers and springs	1,2
Water supply points	1.4
Lakes	1,2
Unused lands	1,1
Agriculture lands	1,2
Vineyards and gardens	1,2
Pastures	1.3
Settlements	1,5
Workplaces	1,4

The desktop quality control of database was made by ortophoto images.

$$HR_{total} = HR_{forest}*w + HR_{wetland}*w + HR_{stream}*w + HR_{waterbody}*w + HR_{undevelopedland}*w + HR_{arable}*w + HR_{perennial}*w + HR_{settlement}*w + HR_{workingplace}*w + HR_{watersources}*w + HR_{pasture}*w,$$

HR – index obtained by the distance to every receptors; W – weight index.

3 Pollutants Distribution Potential

- Wind dispersion
- Infiltration
- Run-off
- Human related intended/non-intended dispersion

The balance between factors which contribute to the “increasing” or “decreasing” the pollution spreading potential of the individual site is taken into consideration in order to calculate respective sub-index value.

$$HD_{total} = HD_{vind}*m + HD_{infiltration}*m + HD_{runoff}*m + HD_{access}*m,$$

Distibution potential	Magnitude Index
Wind dispersion	8
Infiltration	3
Run-off	6
Human related dispersion	2

Where:

$$HD_{vind} = \sum HD_{vind\text{-}increase} - \sum HD_{vind\text{-}decrease}$$
$$HD_{infiltration} = \sum HD_{infiltration\text{-}increse} - \sum HD_{infiltration\text{-}decrease}$$
$$HD_{runoff} = \sum HD_{runoff\text{-}increase} - \sum HD_{runoff\text{-}decrese}$$
$$HD_{access} = \sum HD_{access\text{-}increase} - \sum HD_{access\text{-}decrease}$$

m – magnitude index

Example of site's ranking system implication

Center of Environmental Study "ECOS", TRIMETRICA http://www.trimetrica.com/

Site code	POPs infrastructure	Sub-index			Hazard Total Score	Site's Rank
		Level of Contamination	Risk Receptors	Distribution Potential"		
C-Colonita-01	Deposit, blending station	16,8	76,2	38,0	38,9	III
C-Truseni-01	Blending station	19,6	33,6	46,0	29,1	IV
C-Truseni-02	**Deposit, blending station**	**66,0**	**64,8**	**84,0**	**69,2**	**I**
C-Truseni-03	**Deposit**	**30,8**	**33,6**	**94,0**	**44,3**	**II**
C-Truseni-04	**Blending station**	**23,4**	**85,0**	**31,0**	**43,4**	**II**
C-Truseni-05	Blending station	25,2	53,8	42,0	37,1	III
C-Stauceni-01	Deposit, blending station	15,6	20,8	6,0	15,2	V
C-Bacioi-01	Deposit, blending station	19,6	66,4	0,0	29,7	IV
C-Gratiesti-01	**Deposit, blending station**	**15,6**	**77,2**	**117,0**	**54,4**	**I**
C-Gratiesti-02	**Blending station, helicopter ground**	**28,6**	**86,4**	**27,0**	**45,6**	**II**
C-Bubuieci-01	Deposit	22,4	35,2	44,0	30,6	III
C-Singera-01	**Deposit, blending station**	**39,0**	**16,8**	**103,0**	**45,1**	**II**
C-Tohatin-01	Deposit	7,2	31,6	9,0	14,9	V
C-Tohatin-02	**Deposit, blending station**	**15,6**	**55,0**	**88,0**	**41,9**	**II**
C-Durlesti-01	**Deposit, blending station**	**9,6**	**75,0**	**78,0**	**42,9**	**II**
C-Ghidighici-01	Blending station, helicopter ground	15,6	58,6	16,0	28,6	IV
C-Ghidighici-02	Deposit	9,6	39,2	6,0	17,8	V
C-Budesti-01	Deposit, blending station	18,2	64,4	0,0	28,4	IV
C-Budesti-02	Blending station, helicopter ground	12,0	20,2	19,0	15,9	V
C-Budesti-03	**Deposit**	**31,2**	**41,8**	**74,0**	**42,9**	**II**

$$H = (HP_{real} / HP_{max})*a + (HR_{real} / HR_{max})*b + (HD_{real} / HD_{max})*c$$

$$H = (HC_{real} / 100) * 50 + (HR_{real} / 100) * 30 + (HD_{real} / 100) * 20$$

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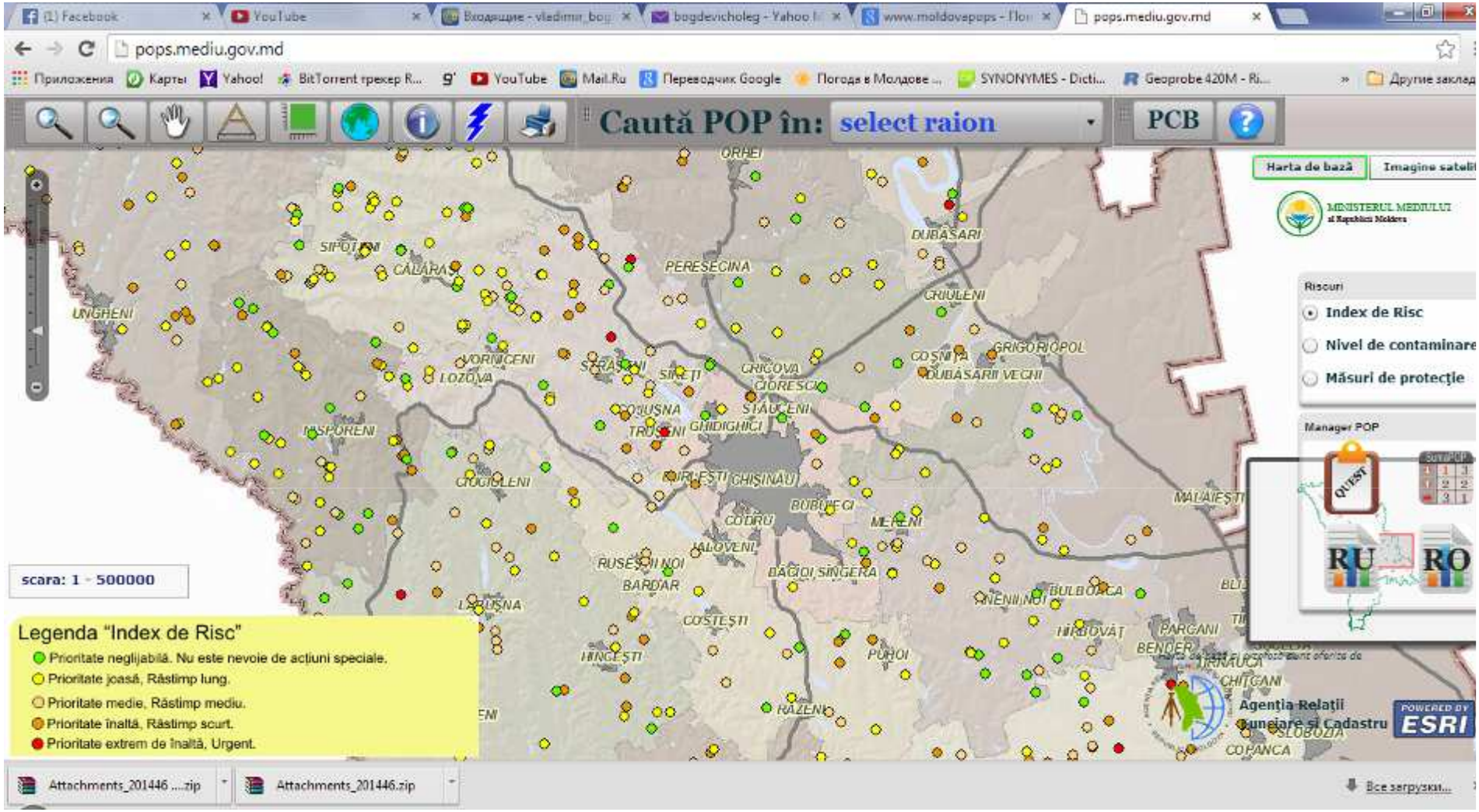
The realization of POPs information management system

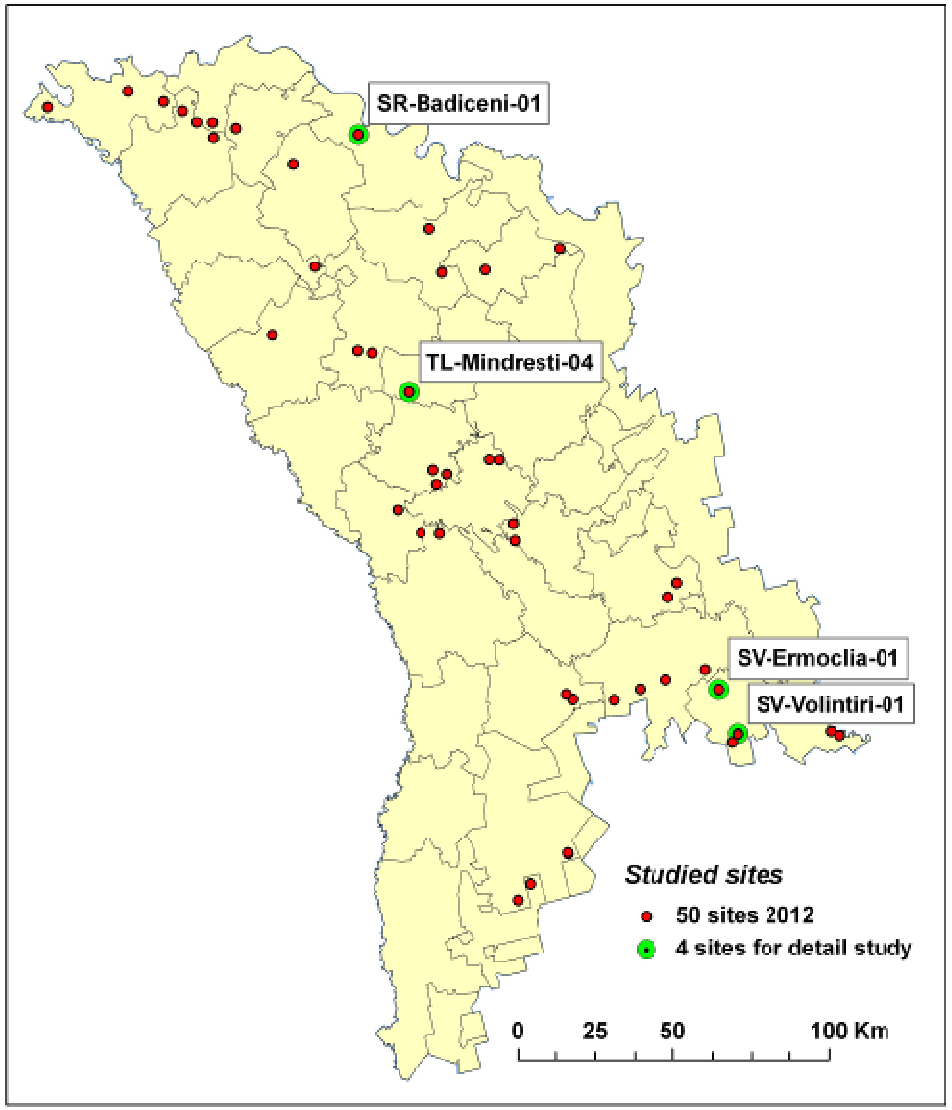


http://pops.mediu.gov.md

The project funded by the ”Green Cross Switzerland (GCCH)” under the FAO and GEF umbrellas was realized afterwards for the testing of the used methodology by The Center for Strategic Environmental Studies "ECOS" .

Four sites were selected among 50 priority contaminated sites for the detailed study which can provide available background information regarding the site as a part of preliminary Conceptual Site Model.

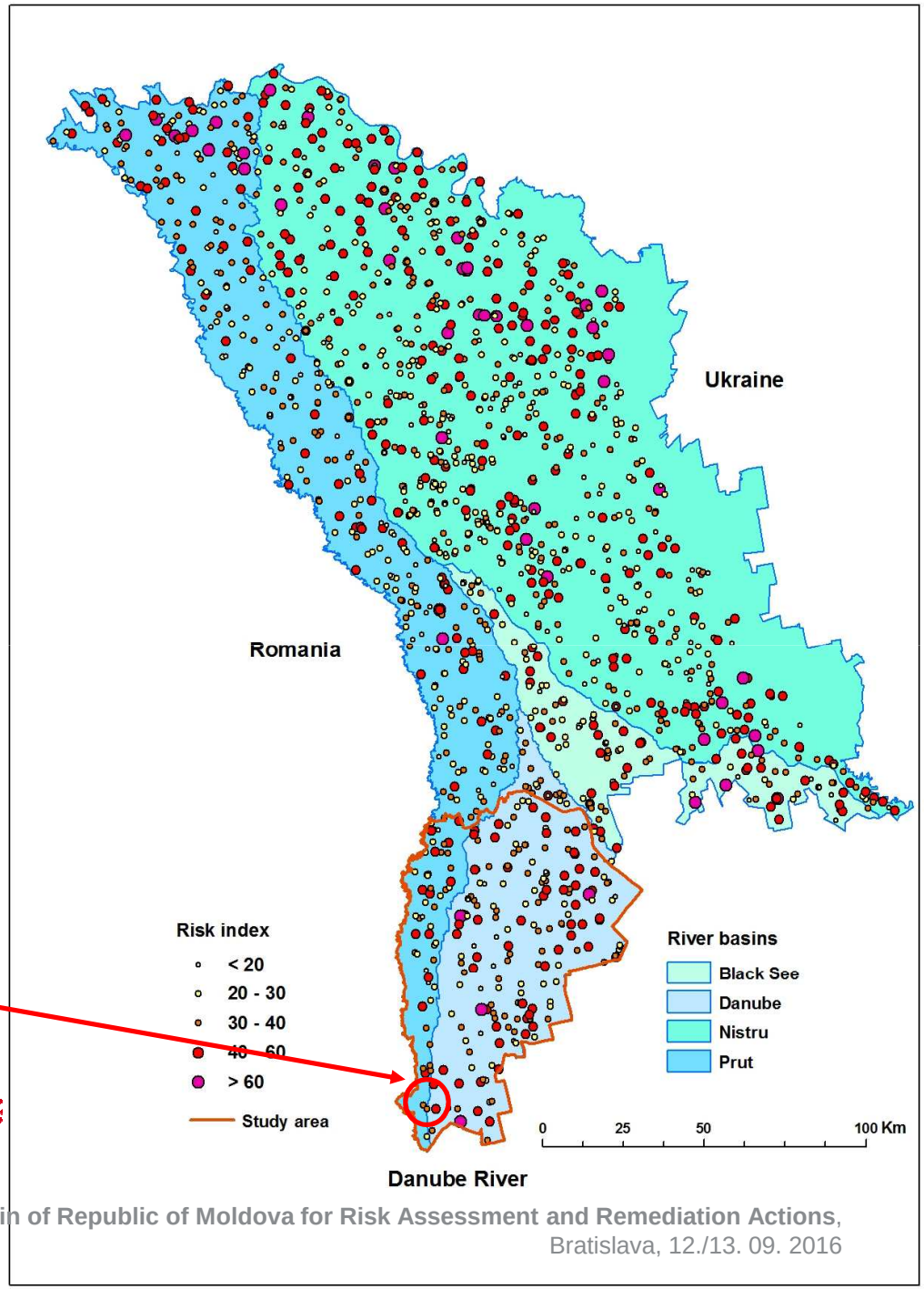
Proposed a cost- and time-efficient rapid assessment of contaminated sites showed a good results after this testing.



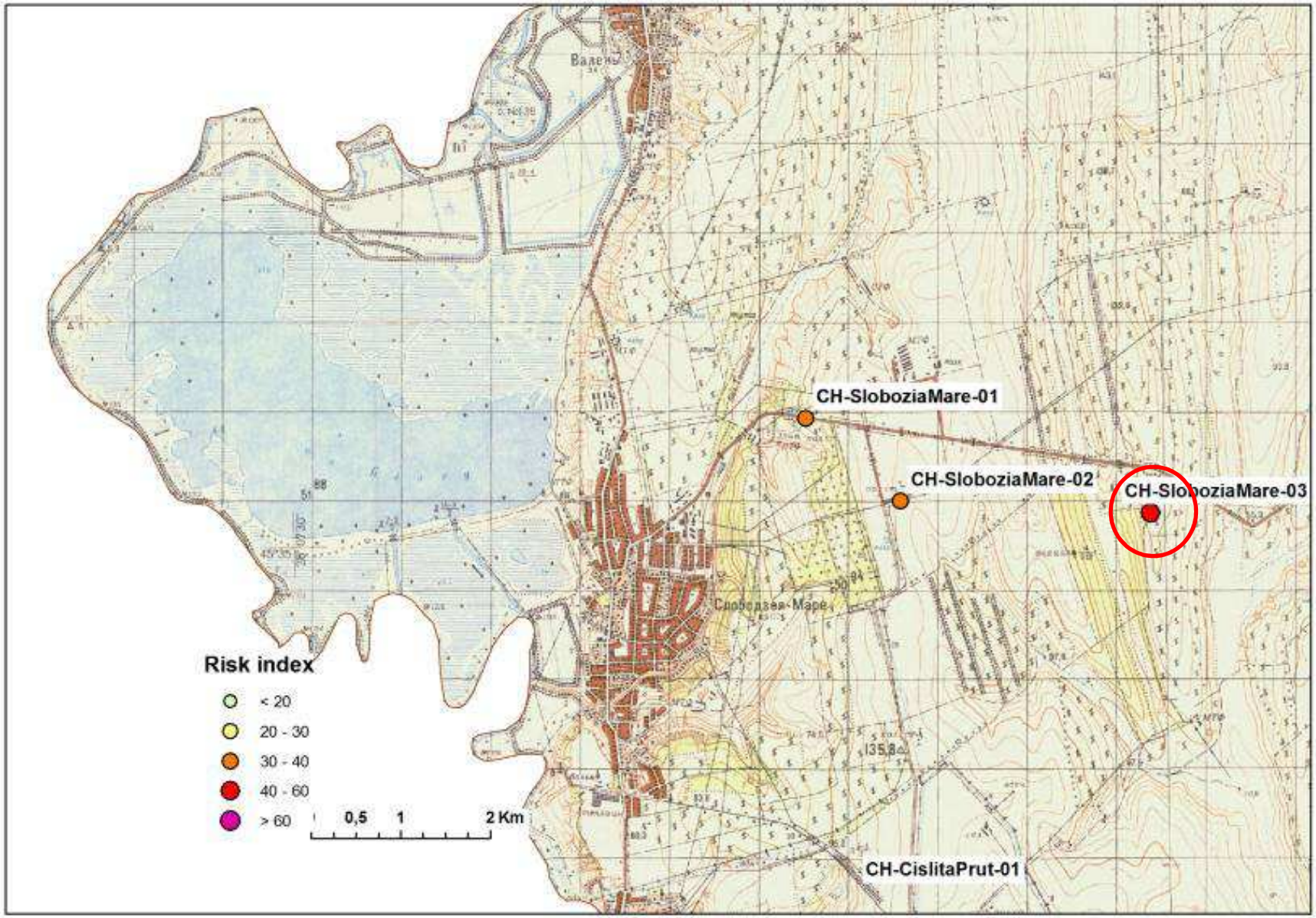
Rapid Environmental Risk Assessment at regional level showed a distribution of polluted sites and which should to be remediated first.

It is important for the decision makers and elaboration of the politic in this field.

Ch-Slobozia Mare-03



Case study: polluted sites at Slobozia Mare village



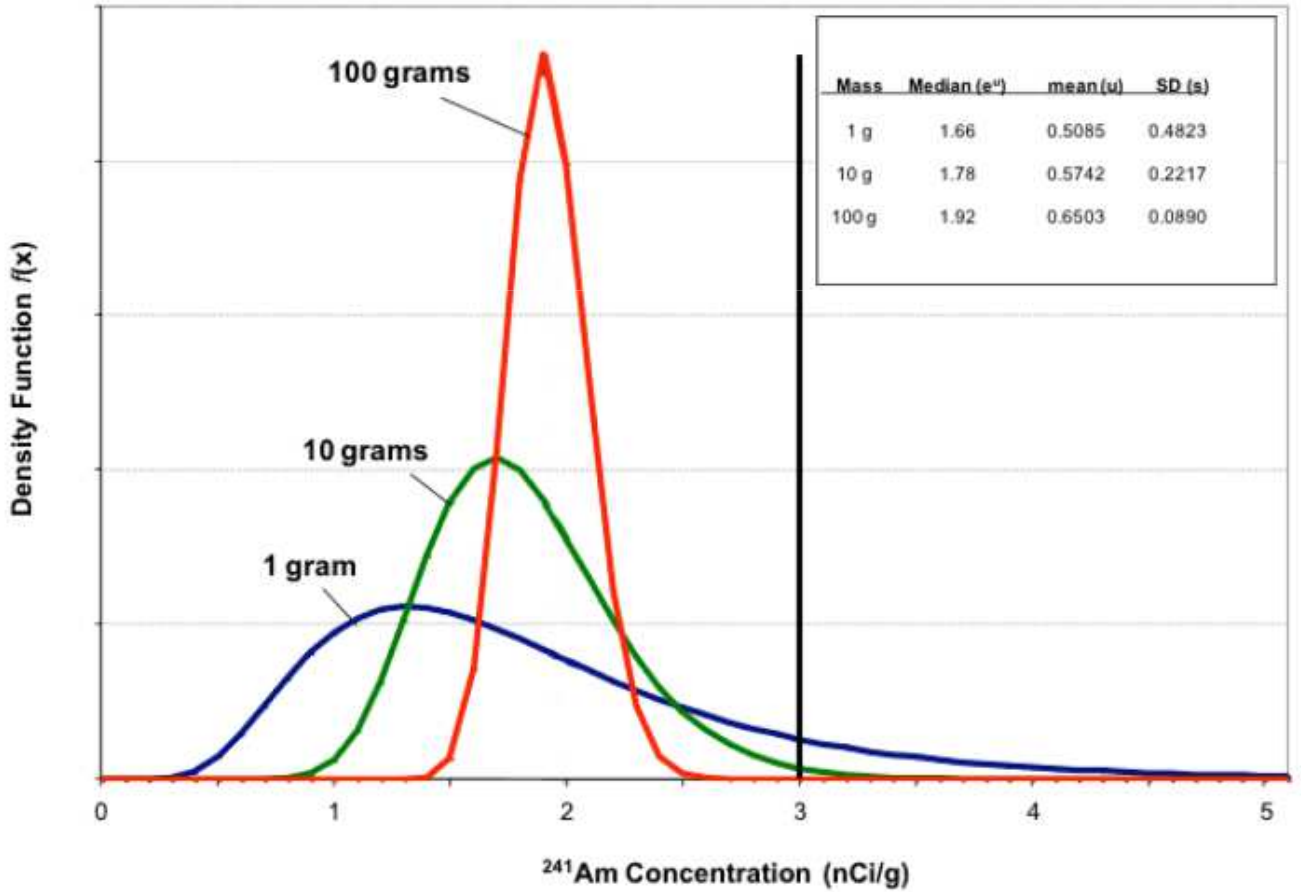
Design of sampling program

The detailed study of polluted sites needs to use Incremental Sampling Methodology (ISM): number of sub-samples and sample volume are key aspects.

<u>Sample quantity:</u> at least 500 g of soil, 5 L of water sample.

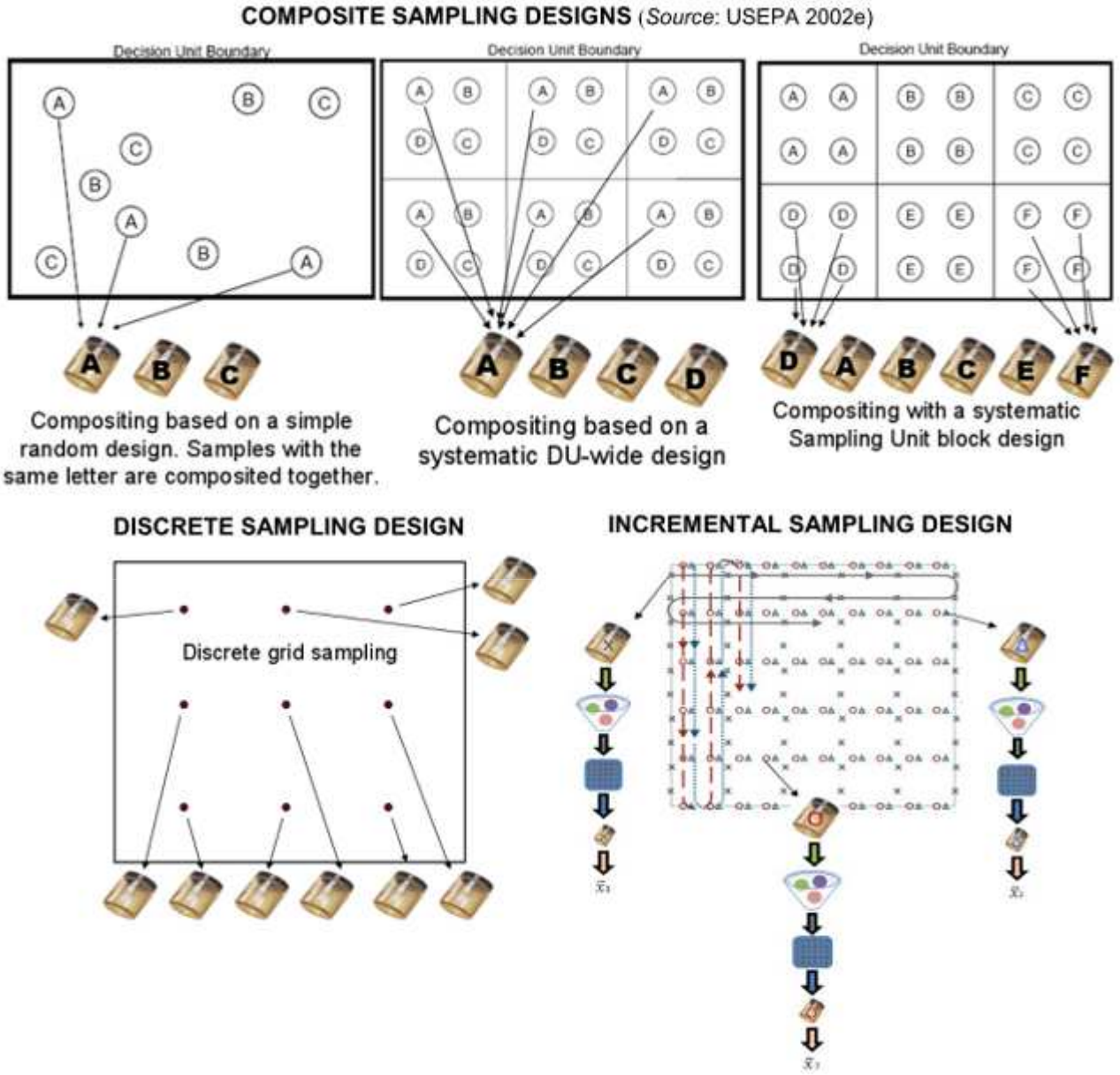
Collected composite samples - at least 25 number of increments (ISO 10381-4)

Smaller analytical masses contribute to high data variability (Gilbert and Doctor 1985).

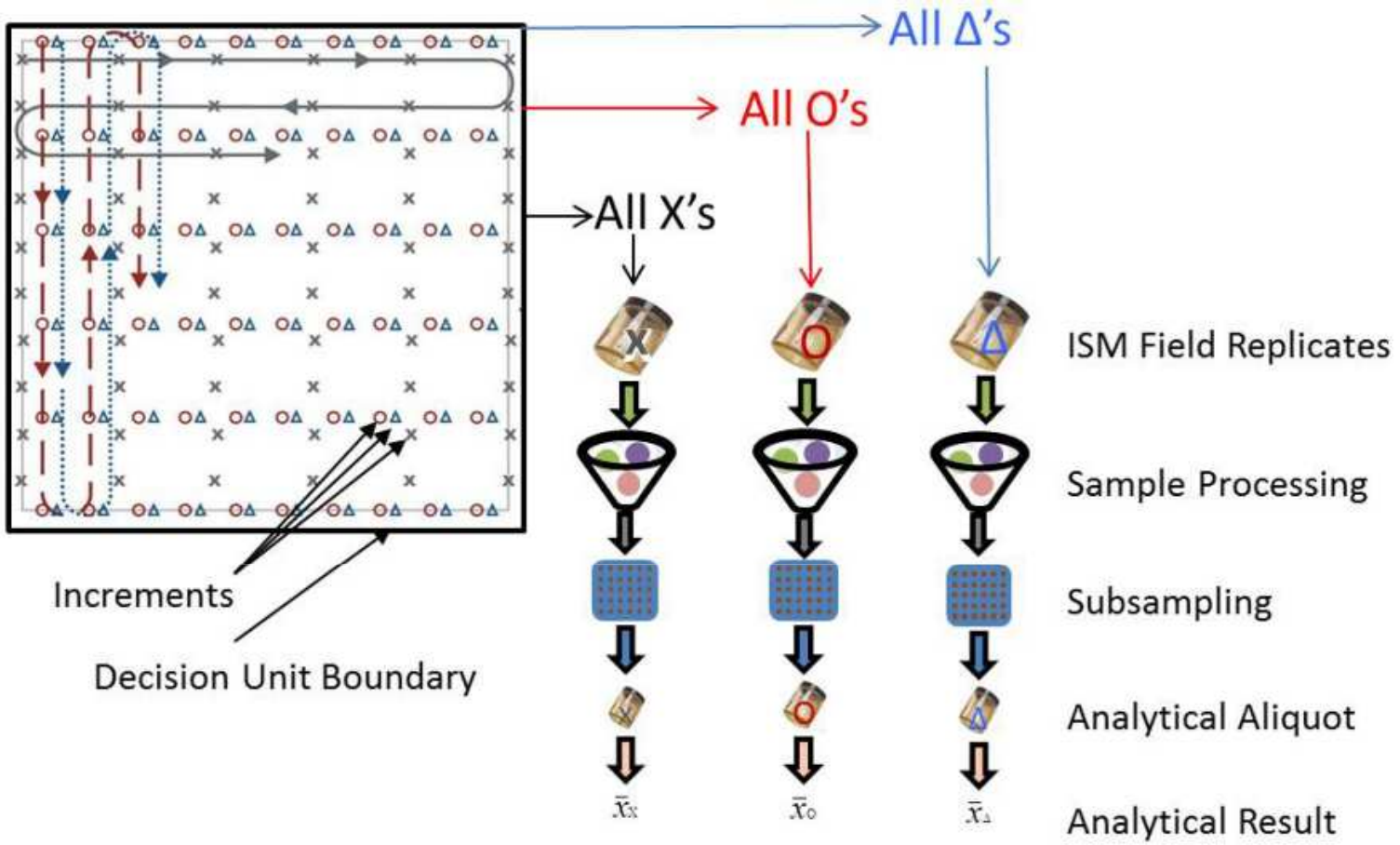


The three key components of ISM are:

1. **systematic planning,**
2. **field sample collection,**
3. **laboratory processing and analysis.**



Key steps of ISM process.

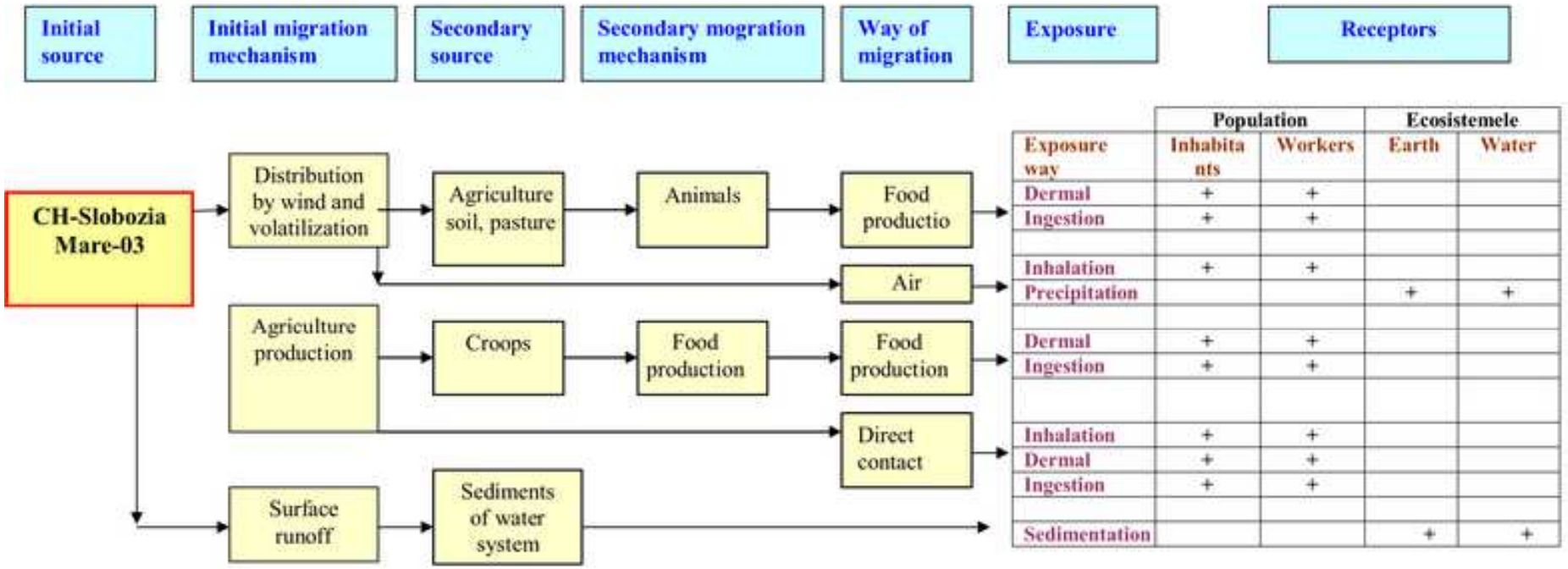


Sampling program for selected Ch-Slobozia Mare-03 site included 14 areas with three incremental soil samples for every site and three boreholes at hot spot of studied site.

Results of the analysis of soil pollution.

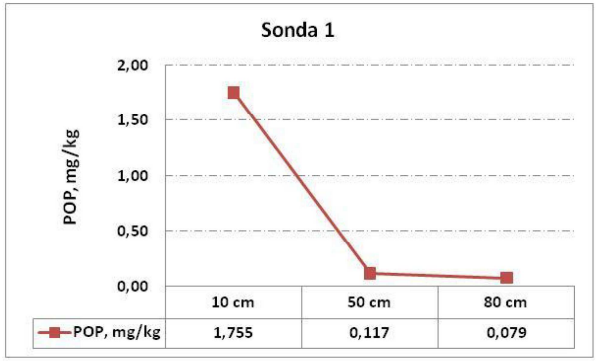
The conceptual model for environmental risk assessment and recommendation for possible remediation actions were elaborated for CH-Slobozia Mare-03 site

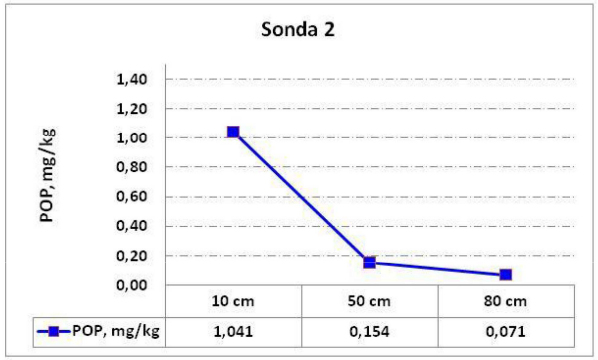
Site CH-Slobozia Mare – 03. Conceptual model (initial)

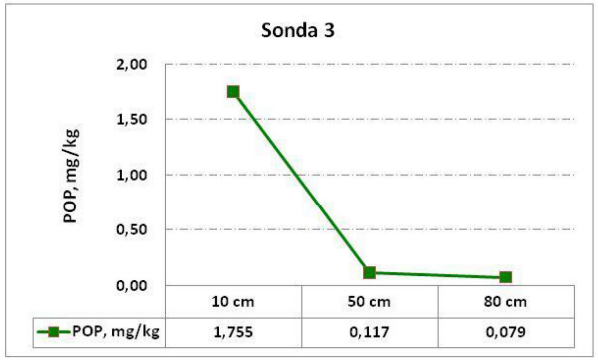


	Population		Ecosistemele	
Exposure way	Inhabitants	Workers	Earth	Water
Dermal	+	+		
Ingestion	+	+		
Inhalation	+	+		
Precipitation			+	+
Dermal	+	+		
Ingestion	+	+		
Inhalation	+	+		
Dermal	+	+		
Ingestion	+	+		
Sedimentation			+	+

The site is situated in arid, water deficiency area.
Ground water is on the depth more than 30 m and clay rocks protect it from the pollution.







The principal pollution is situated in top soil layer (approximately 0,3 m)

Example of polluted soil volume calculation

Nr of lots	POPs, mg/kg	Surface, m^2	Volume, m^3
1	12,76	1140	342,0
2	6,54	1642	492,6
3	2,05	1522	456,6
4	1,42	959	287,7
5	1,18	1112	333,6
6	1,15	4363	1308,9
7	0,59	1462	438,6
8	0,55	5969	1790.7
9	0,39	4363	1308,9
Total		**22532**	**6759,6**

This type of land is used for agriculture production and remediation is required ASAP.

SR-Badiceni-01

The results of toxic organic pollutant determination in complex soil sample:

incremental sampling strategy.

Chemicals/ group of chemicals	CAS	Sample 2011, mg/kg	Stringent threshold limit in soil, mg/kg	Country	WHO hazard class
2-4 DDE	3424-82-6	3,518	0,1	Moldova, Russia	II
4-4 DDE	72-55-9	13,190	0,01	Spain (terrestrial org)	II
2-4 DDD	53-19-0	2,545	0,1	Moldova, Russia	II
4-4 DDD	72-54-8	3,557	0,02	Check Republic (precautionary)	II
2-4 DDT	789-02-6	4,868	0,1	Moldova, Russia	II
4-4 DDT	50-29-3	14,208	0,01	Spain (terrestrial org)	II
A-HCH	319-84-6	0,613	0,01	Spain (natural zones), Italy (park zones)	II
B-HCH	608-73-1	1,904	0,01	Spain (natural zones), Italy (park zones)	II
G-HCH	58-89-9	0,359	0,01	Finland (threshold), Spain (natural zones, soil and terrestrial org), Italy (park zones)	II
Trifluraline	1582-09-8	2,046	0,1	Russia	U
Prometone	1610-18-0	0,939	-	-	U
Atrazine	1912-24-9	2,069	0,01	Italy (park zones), Russia	U
Ametryne	834-12-8	1,057	-	-	III
Prometryne	7287-19-6	1,206	0,5	Moldova, Russia	U
Acenaphtylene	208-96-8	0,017	0,1	Canada	-
Acenaphtene	83-32-9	0,003	0,1	Canada	-
Fluorene	86-73-7	0,057	0,1	Canada	-
Phenanthrene	85-01-8	1,777	0,1	Canada	-
Anthracene	120-12-7	0,348	0,1	Canada	-
Fluoranthene	206-44-0	5,115	0,1	Canada	-
Pyrene	129-00-0	4,267	0,1	Canada	-
Chrysene	218-01-9	2,316	0,1	Canada	-
Benz[a]anthracene	56-55-3	2,675	0,1	Canada	-
Benzo[k]fluoranthene	205-99-2	2,406	0,1	Canada	-
Benz[a]pyrene	207-08-9	2,450	0,02	Moldova	-
Benz[b]fluoranthene	50-32-8	2,651	0,1	Canada	-
Indeno[1,2,3,cd]pyrene	191-24-2	2,360	0,1	Canada	-
Dibenz[ah]anthracene	53-70-3	ND $_{0,01}$	0,1	Canada	-
Benz[ghi]]perylene	193-39-5	0,844	0,1	Canada	-
4_4_Dichlorbenzophenone	90-98-2	36,003	-	-	-
Cooper	N/A	588,87	55	Moldova	-
Zinc	N/A	1255,17	100	Moldova	-
Lead	N/A	6,50	32	Moldova	-
Nickel	N/A	0,29	85	Moldova	-
Crom	N/A	110,01	100	Moldova	-

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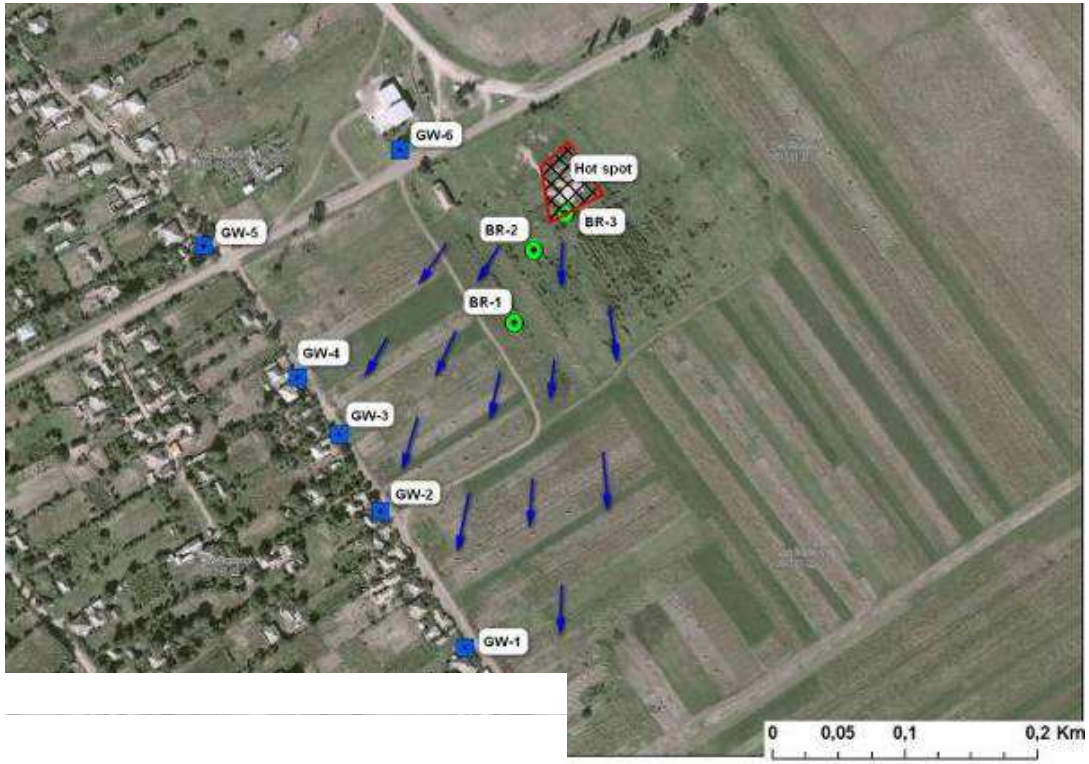
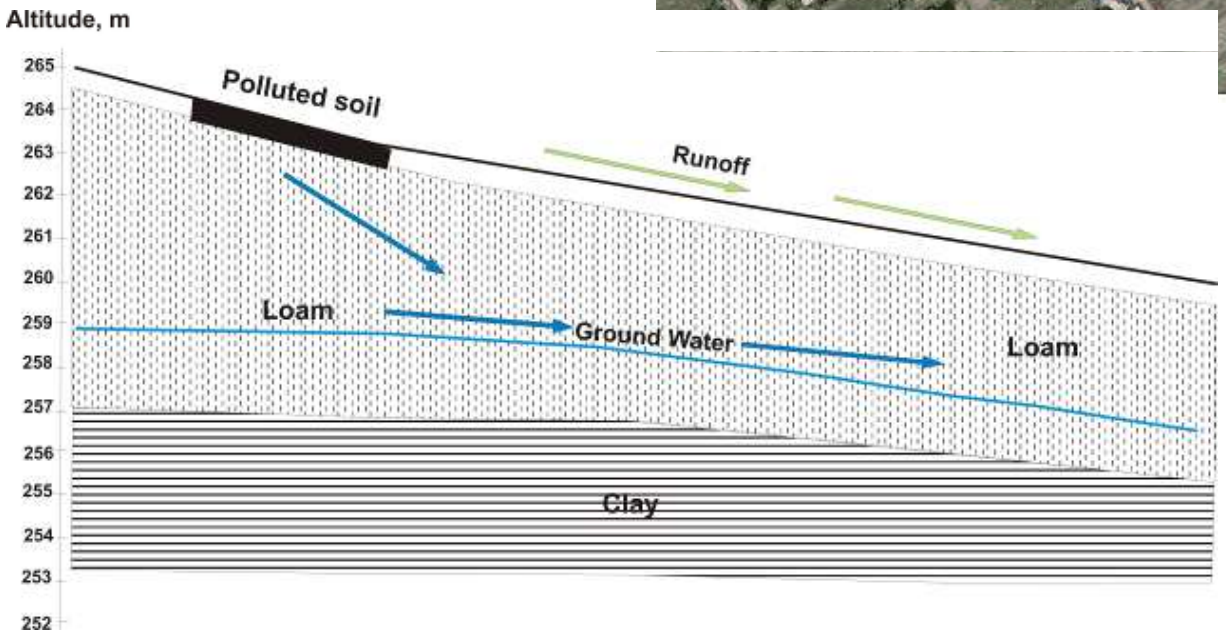
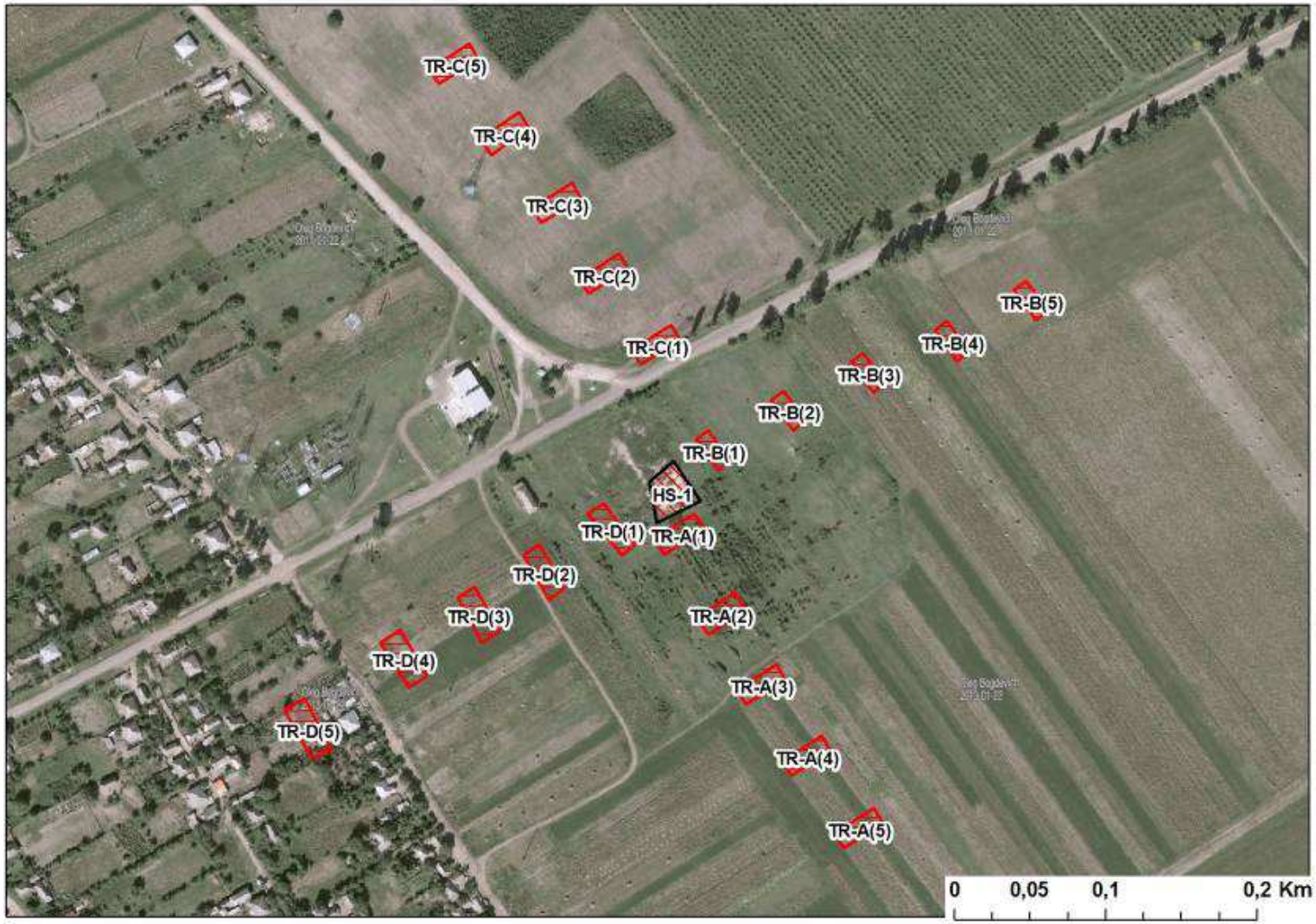
Possible way of pollution migration from site by runoff





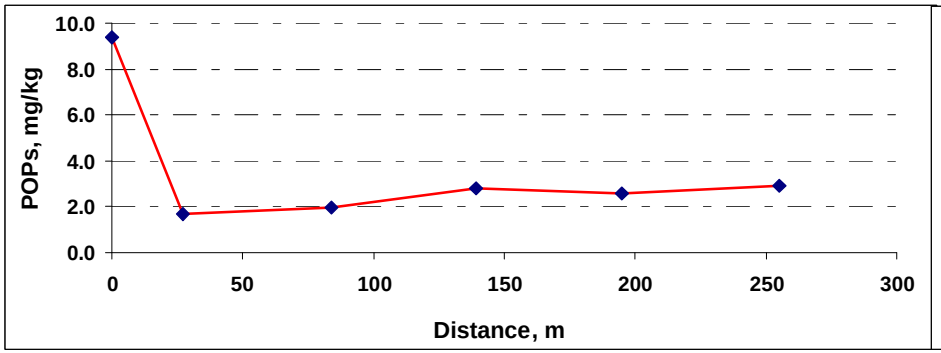
The scheme of geological section

Sampling schema for detailed risk study of Badiceni site

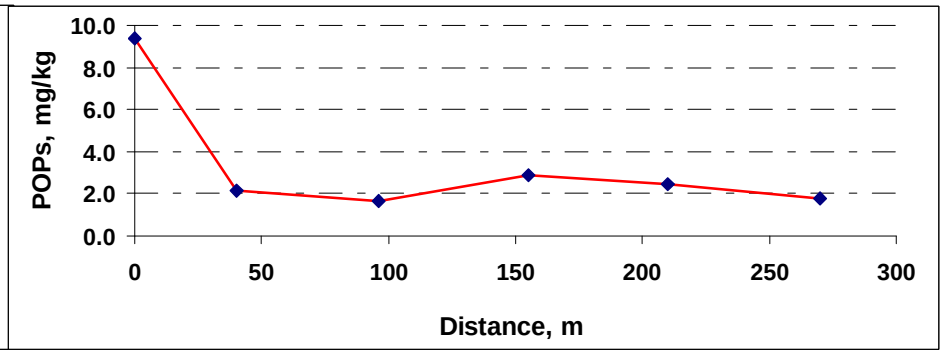


Results of SR-Badiceni study: soil samples.

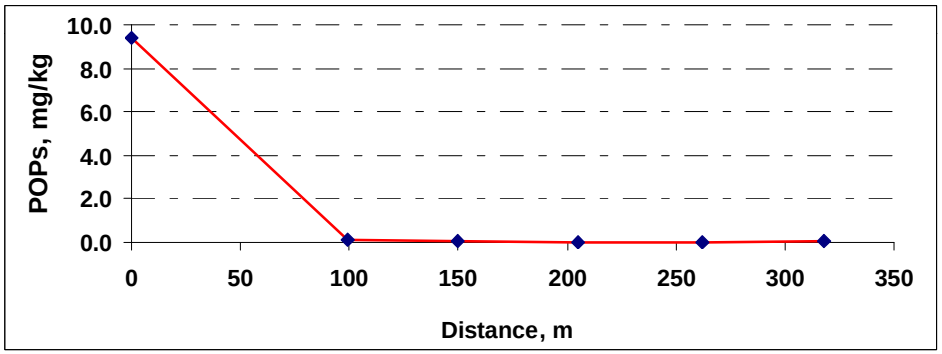
Transect A



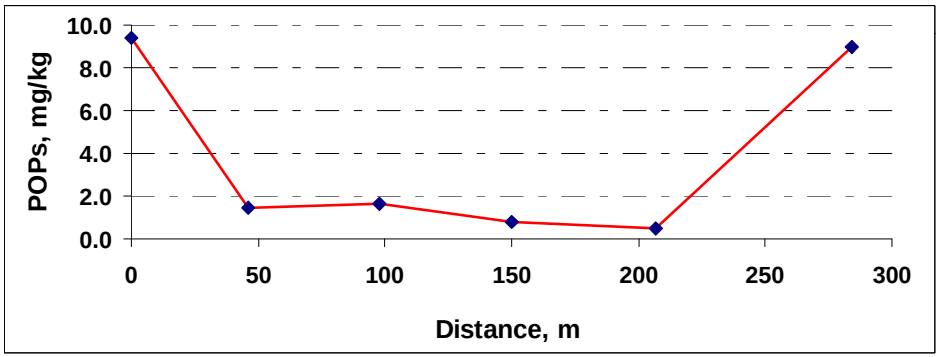
Transect B



Transect C

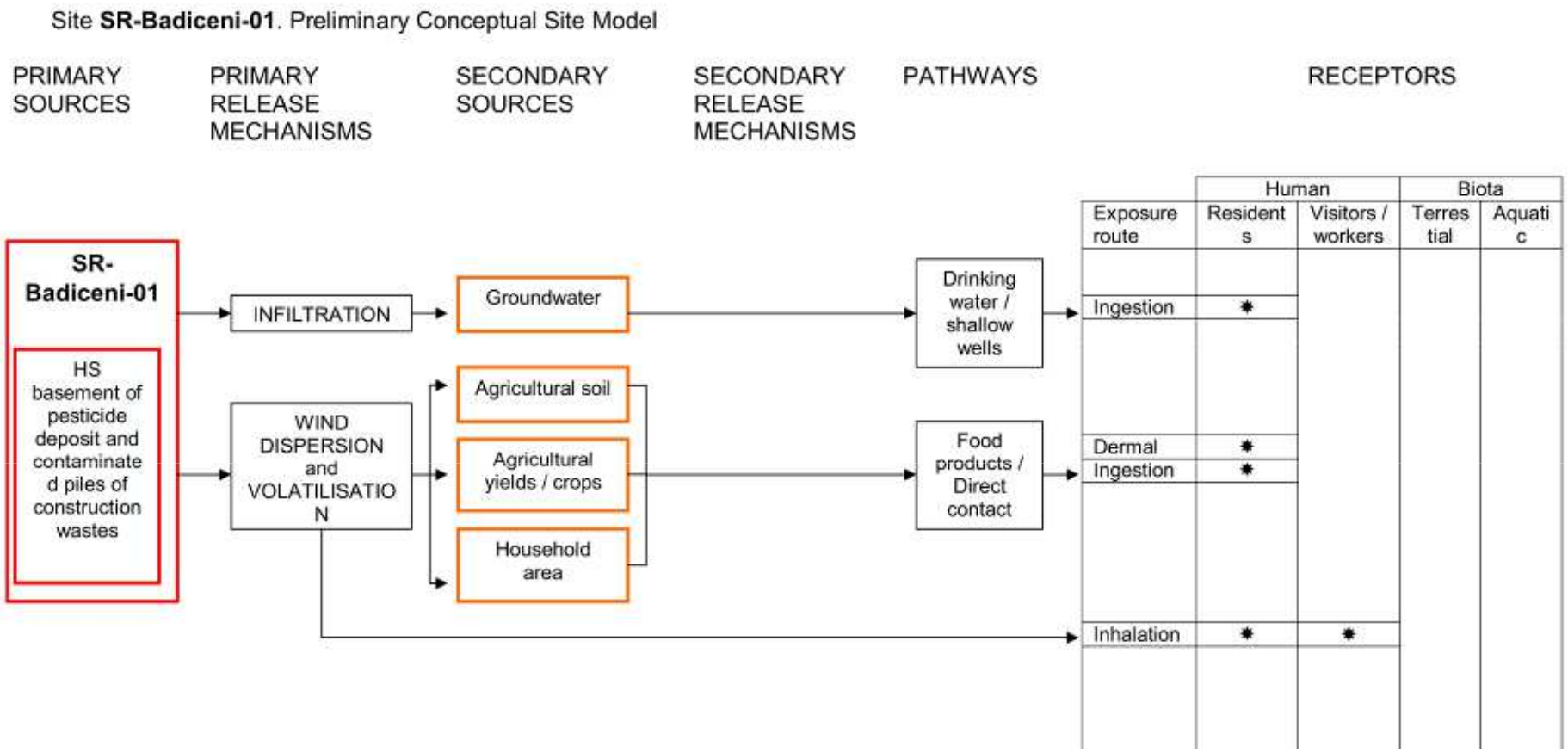


Transect D



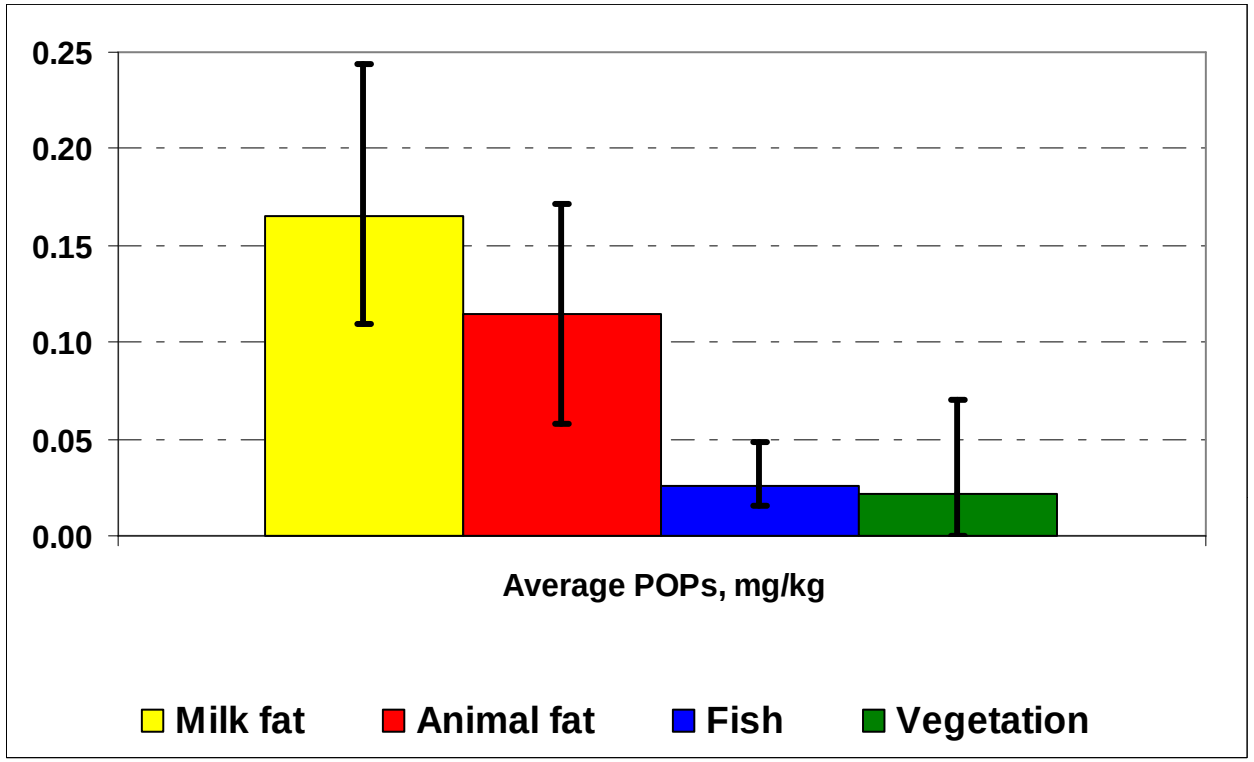
Soil sampling strategy – incremental sampling, which includes tree soil samples from every zones around of polluted sites.

Conceptual site model of Badiceni site



Center for Strategic Environmental Studies "ECOS" "Moldova contaminated land site prioritisation project" FAO, 2012

Results of SR-Badiceni study: biological samples.



The principal pollutant is 2-4-DDE isomer.

Conclusions

1. **the inventory of POPs polluted sites was made and information system is realized at the moment for environmental hazard (pollution level and spectrum) and environmental risk assessment (rapid risk assessment by screening of all territory);**
2. **the several projects were made for the testing of detailed environmental risk assessment procedure for selected sites;**
3. **the bioremediation technology is the most reliable approach for the remediation of agriculture sites in the case of land use and potential huge volume of polluted soil**
4. **the practice of the management of polluted sites is different and depends mostly on local authorities which act without detail site investigation and individual remediation projects;**
5. **the legislation and normative acts don't exist on the national level which are needed for the development of the remediation action for POPs polluted sites.**

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Thank you for the attention!

SK EU2016