

Choice of substances, sites, matrixes for screening exercise



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About criteria for...

- Selection of hazardous substances
- Selection of sites
- Selection of matrixes



the goals...

- To prove occurrence/absence of HS
- To prove concentrations are less than set limits
- To detect the trends
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Selection of HS - criteria

- **limits** on concentrations in surface water set on European level (i.e. 33 priority substances and 8 other pollutants)
- **the biggest gaps** of information on occurrence of priority substances in the waste water and receiving environment
- the fact that certain substance or group of substances **occur on the market**
- the fact on occurrence of substances in the environment from **Finnish experience** (e.g. dibutylphthalate, butylbenzylphthalate)
- to narrow the scope → focus on **industrial and consumer chemicals** not agricultural pesticides
- cyanides, halogenated organic compounds (AOX) only in **specific** places, i.e. in Nemunas after Sovietsk (Kaliningrad region) → concern that they might be emitted directly to the river from metal processing (metal cutting) industry, mirror production (CN) and pulp and paper industry (AOX)



Selected HS

- **102 substances → 9 groups of substances:**
 - Metals (7)
 - Phenols and their ethoxylates (21)
 - PAH (8)
 - Chloroorganic pesticides (7)
 - VOC (7)
 - Organotin compounds (11)
 - Phtalates (18)
 - Brominated diphenylethers (18)
 - Other: C10-13 chlorinated parafins, pentachlorophenol, chlorpyrifos, cyanides, AOX (5)

Note: full list is provided in addition



Selection of sites - criteria

1st round

- **urban waste water treatment plants (WWTP)**
 - majority of industries discharge their effluent into the public sewer
 - WWTP of biggest cities were considered to contribute to the pollution most
 - smaller towns → 1) industry in the town; 2) higher pollution according previous results (metals, PAH, VOC)
- **transboundary rivers**
 - the sites in the rivers close to the border → HS inflowing/outflowing
- **rivers inflowing to the Curonian Lagoon/ Klaipėda Channel (Nemunas and Akmena)**
 - the sites at the estuary to check whether HS gets with the inland waters to BS
- **transitional waters to the Baltic Sea (harbour area, Maku bay)**
 - very high potential to occur specifically in this areas, e.g. organotin compounds, phenols and their ethoxylates in harbours area
 - it is the main way of the pollutants from inland activities to enter the Baltic Sea waters.



Selection of sites - criteria

2nd round

- some cities discharged highly polluted wastewater to the rivers → **rivers below the most polluting cities** have been added in order to check potential influence of the discharged wastewater to the quality of the surface waters
- repeating → sites with results “**of concern**”



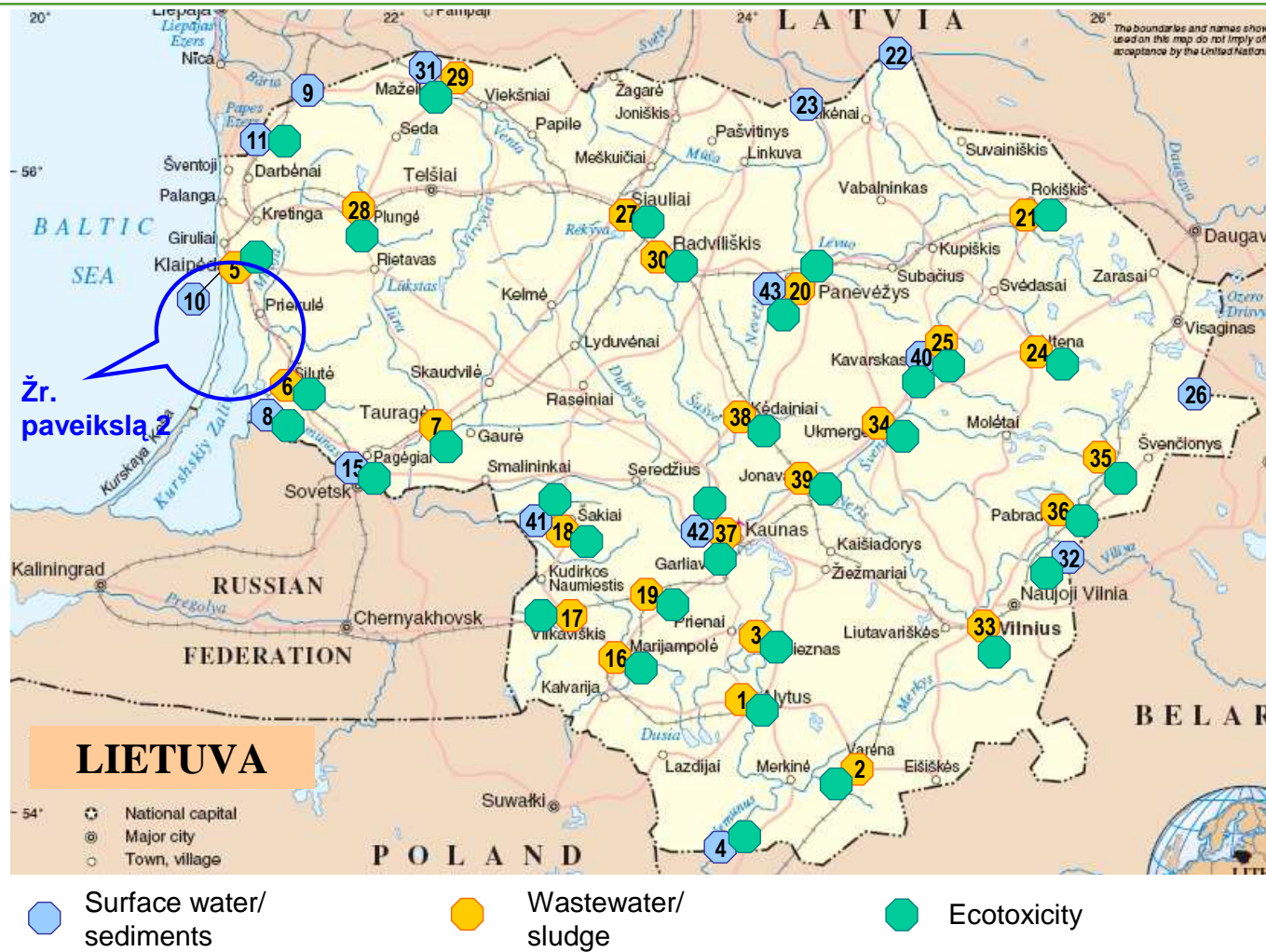
Selected sites

44 sites :

- 25 WWTP
- 8 sites on transboundary rivers at the border
- 2 sites on the rivers before inletting into the Curonian Lagoon and Klaipėda Channel
- 4 sites at the transitional waters of Klaipėda Channel
- 5 sites on the rivers after polluting cities

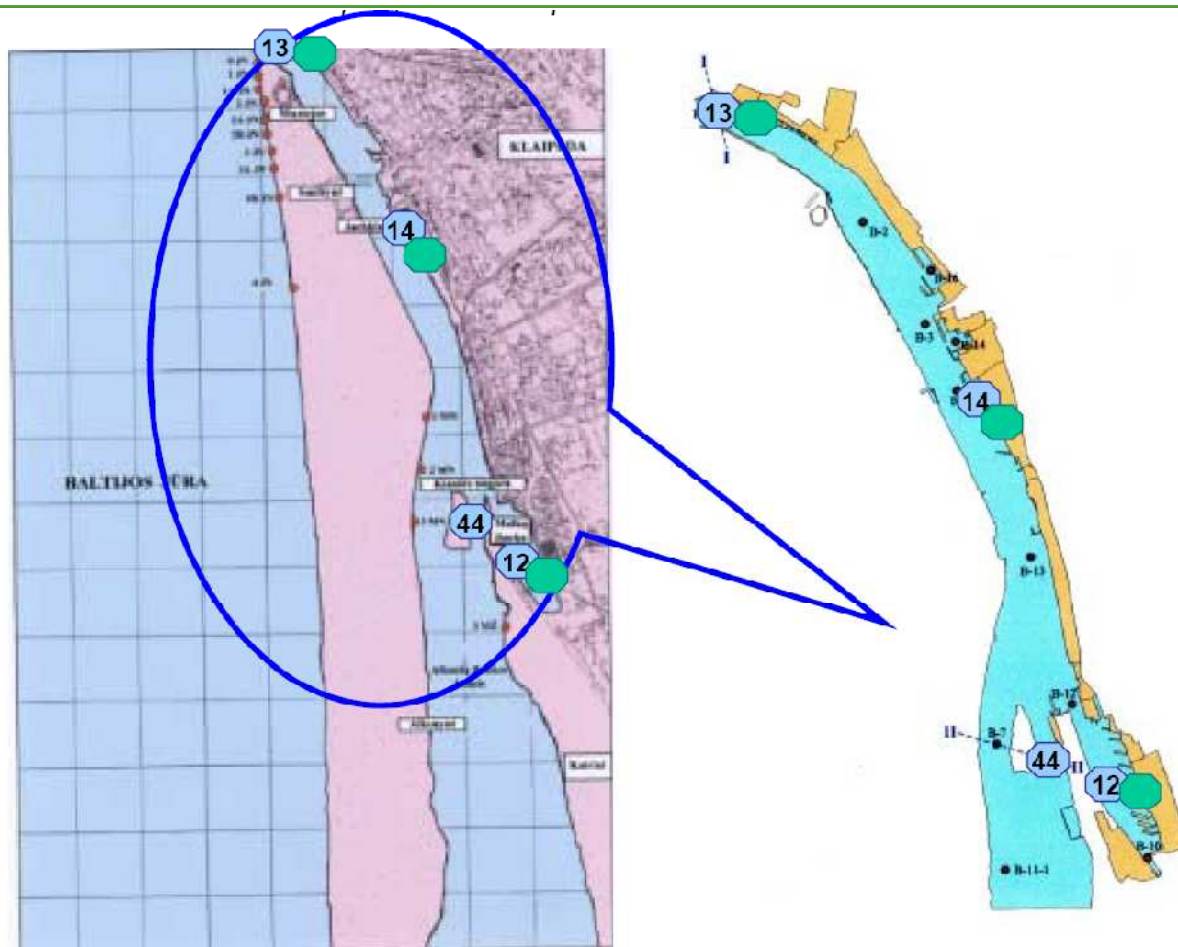


Screening of HS - sites





Screening of HS





Selection of matrixes - criteria

- potential occurrence of the substance in the specific matrix, i.e. particularly hydrophobic substances will not be found in significant concentrations in liquid phase → **limit analysis to the most relevant matrixes**
- relevant matrixes were determined based on different literature sources (*Report of the expert group on analysis and monitoring of priority substances*) and by the chemical-physical properties of the substances influencing their fate in the environment (solubility in water, partitioning, bioaccumulation etc.)



Selection of matrixes - criteria

Criteria	Meaning	Interpretation
$K_{oc} > 2700$ $\text{Log } K_{oc} > 3.5$	The partitioning coefficient between water and organic carbon. It indicates potential to adsorb to the soil/ sediments	<ul style="list-style-type: none">→ high potential of sorption of substance to soil/sediments→ higher K_{oc} values - less mobile organic chemicals→ $K_{oc} < 500$ no or little adsorption
$\text{BCF} > 2000$	Bioconcentration factor	<ul style="list-style-type: none">→ already starting from $\text{BCF} > 1300$ substance is liable to bioaccumulate in fatty tissue→ $\text{BCF} > 2000$ shows that substance bioaccumulates in fatty tissue→ $\text{BCF} > 5000$ shows that substance strongly bioaccumulates in the fatty tissue
$\text{Log } P_{ow} = 4.5-9$	Coefficient indicating partitioning of substance between octanol and water.	<ul style="list-style-type: none">→ liable to bioaccumulate in fatty tissue



Selection of matrixes – priority matrixes

Example

No.	CAS Nr.	Name	Priority matrixes where substances should be analysed				
			Waste water	Sew age sludge	Receiving water	Sediments	Biota
I. Metals and their compounds							
1.	7440-43-9	Cadmium and its compounds	H-M*	H-M	M	M	M
2.	7439-92-1	Lead and its compounds	H-M	M	M	M	M
3.	7440-02-0	Nickel and its compounds	H-M	M	M	M	M
4.	7440-66-6	Zinc and its compounds	H-M	M	M	H-M	M
5.	7440-38-2	Arsenic and its compounds	H-M	M	M	M	M
6.	7440-50-8	Copper and its compounds	H-M	M	M	H-M	M
7.	7439-97-6	Mercury and its compounds	H-M	M	M	M	H

Note: full table with ranking of matrixes provided separately



Selected matrixes

- Only matrixes with H-high/M-medium potential of HS occurrence
- Exception - chloroorganic pesticides (no WWTP)
 - Not anymore in use (hardly occur in WWTP)
 - Previous analysis proved their occurrence in WWTP in selected sites



Selected matrixes

Matrixes	MET	Ph&E	PAH	COP	VOC	OT	BDPE	Pht	SCCP	PCP
Wastewater	X	X	X		X	X	X	X	X	X
Sludge	X	X	X			X	X	X	X	X
Surface water	X	X	X	X	X			X		X
Sediments	X	X	X	X		X	X	X	X	X



Ecotoxicity

- biota (fish) → microbiotests
- **difficult to interpret and evaluate the results** of biota (fish) analysis gained within such project
- in rivers fish is **highly migrating**, therefore it is very difficult to correlate the occurrence of hazardous substances in the fish to any specific source of hazardous substances
- due to limited resources only very **random samples** could be taken and analysed what leads to even more complicated **interpretation of the results and decrease the added value** to the general results of the project and their practical applicability

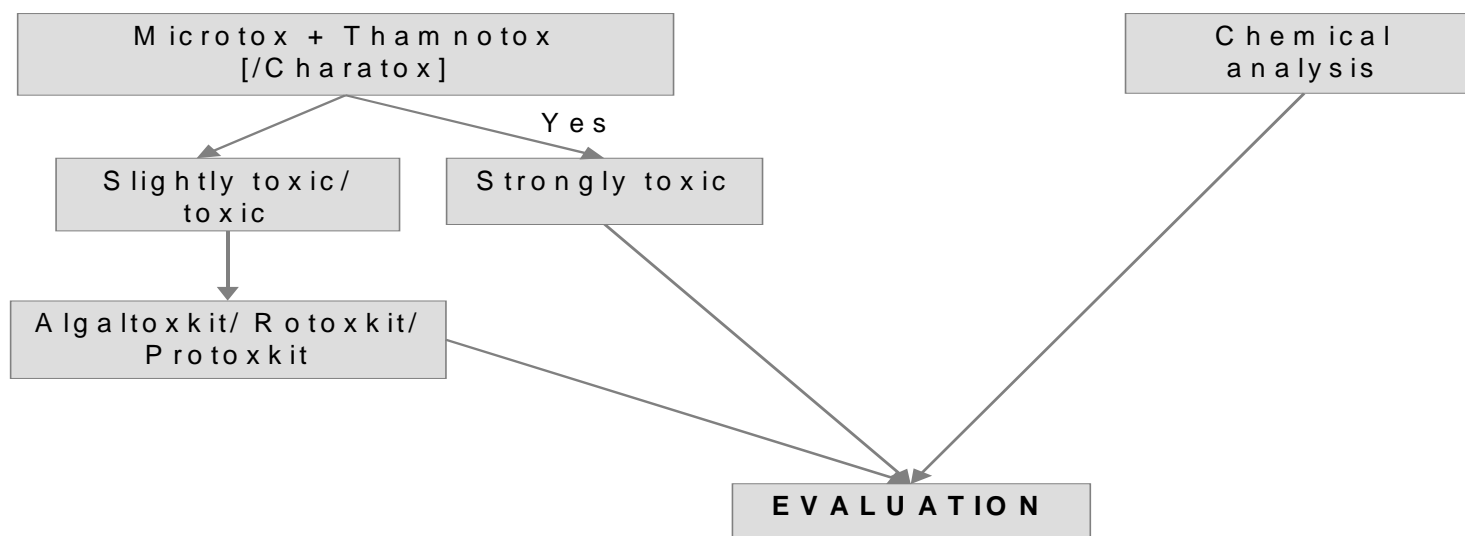


Ecotoxicity – Why?

- chemical tests alone are not sufficient to assess potential effects of complex wastes mixtures on aquatic environment because of difficulties to screen all possible chemicals in water and limited knowledge on chemicals toxicity and their interactions
- the complete chemical composition of water is not known, some other toxic substances may have great negative influence on the aquatic organisms, therefore the measurement of ecotoxicity in addition to chemical analysis in the same sites should give more complete view on the status of toxicity of waste water and status of surface water and lead to the better evaluation of the results
- due to the reason that not all species respond identically to different type of pollutants, it was decided to choose series of biotests with different organisms to get more valuable results



Ecotoxicity





Ecotoxicity

Why to limit current HS screening only to chemical analysis?

- Limited resources
- Correlation between chemical analysis and biotests principally not possible
- Toxicity caused by HS or other (BOD, nitrates...)