UPDATED RISK ANALYSIS OF THE ORLEN UNIPETROL LITVÍNOV LANDFILL AREAS

Jiří Kamas
Zdeněk Vilhelm
Karel Waska
Lucie Hertlová
Boris Bodácz
Robert Hovorič
Miroslav Minařík

CONTAMINATED SITES 2022

The Prayer of the Flowers

…

Quite close were the glaring factories, and the sky above them wore the fearful look that it wears in dreams of fever. The flowers were right in the stride of that advancing city, and thence I heard them sending up their cry. And then I heard, beating musically up wind, the voice of Pan reproving them from Arcady—

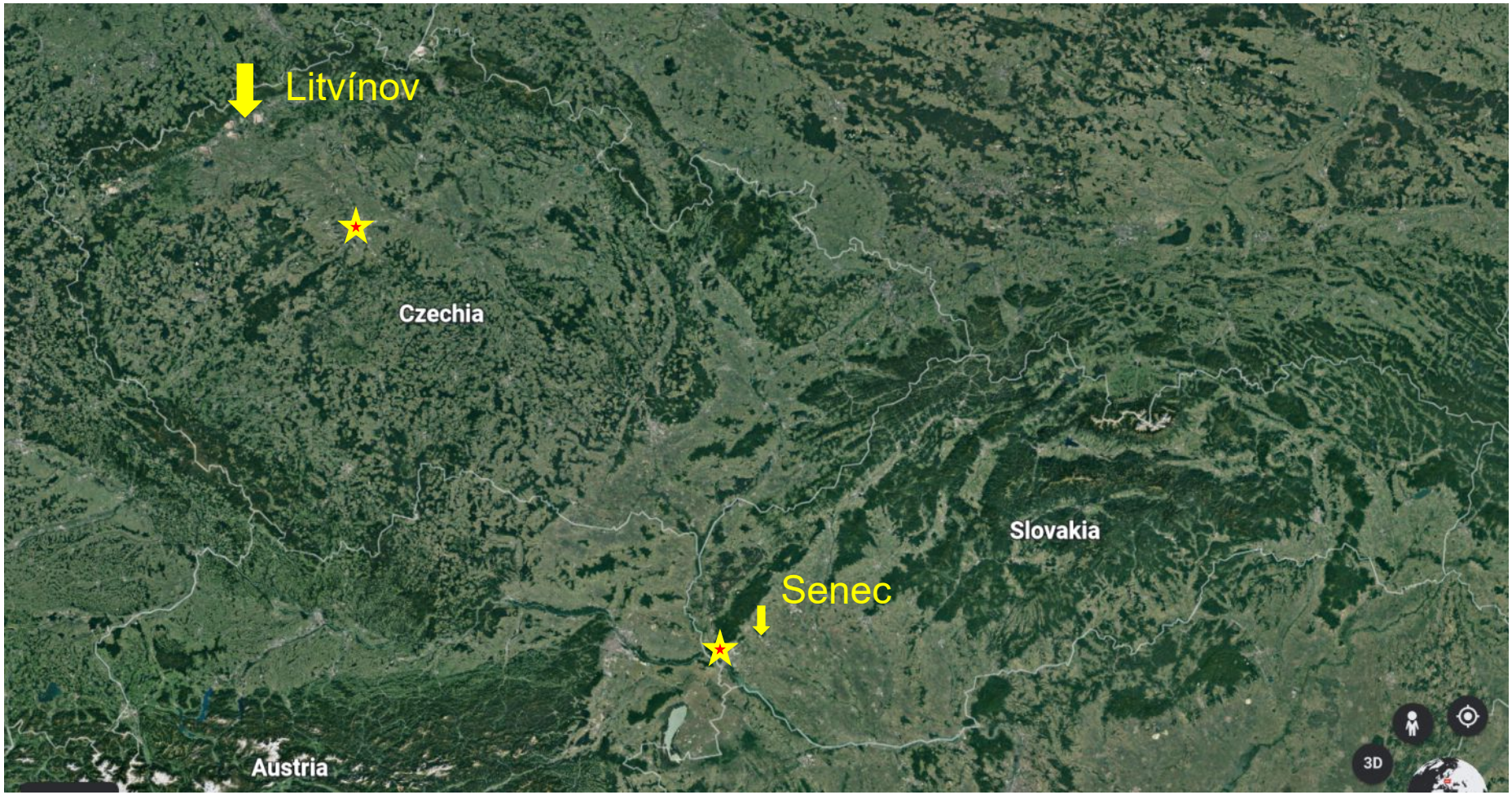
“Be patient a little, these things are not for long.”

Lord Dunsany – Fifty-one Tales, 1915

OUTLINE

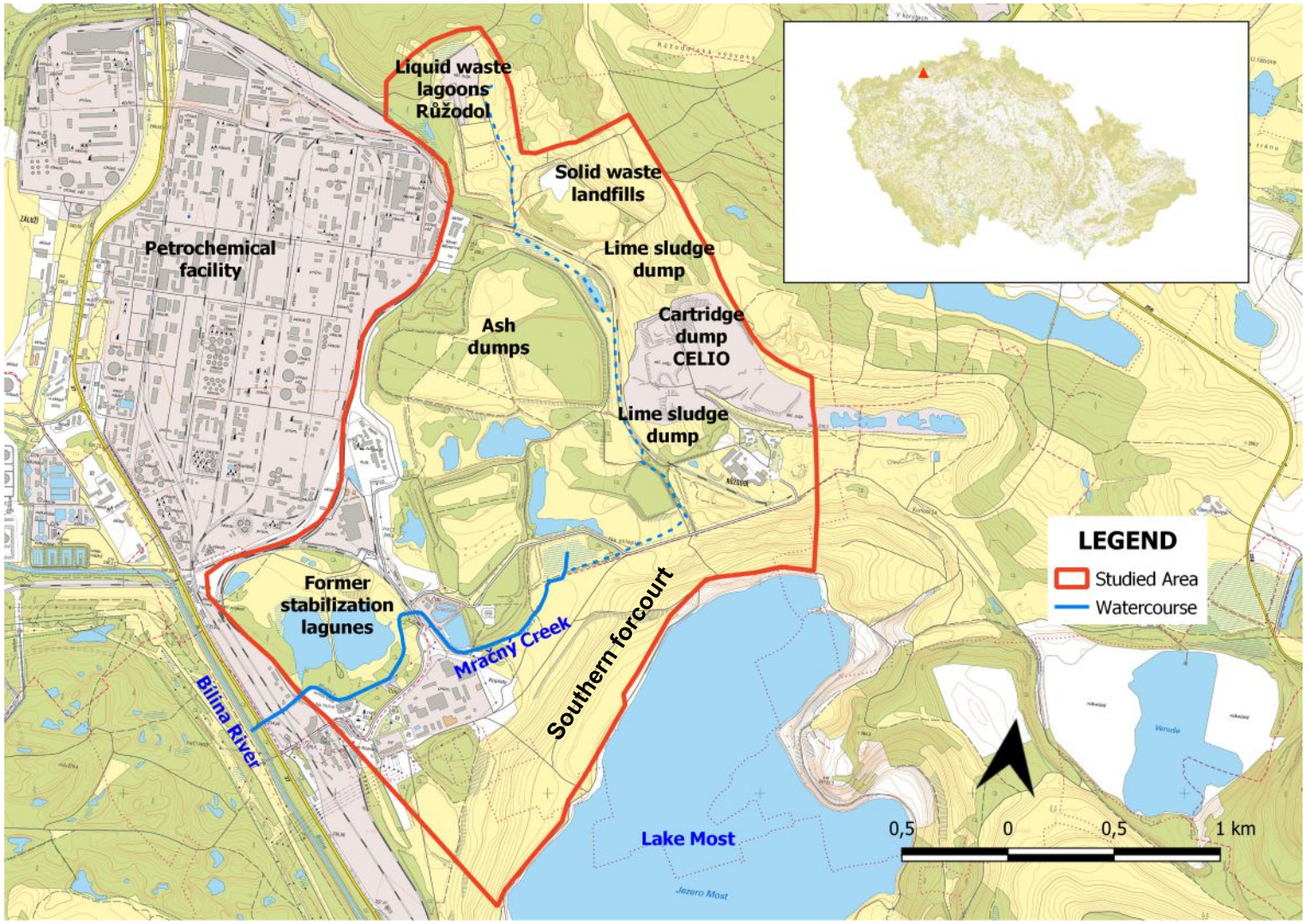
1. Introduction
2. History
3. Additional survey
4. Risk Assessment Actualization
5. Conclusion

The Site of ORLEN Unipetrol chemical facility



Google Earth

The Site of ORLEN Unipetrol Landfills area



Q-Gis

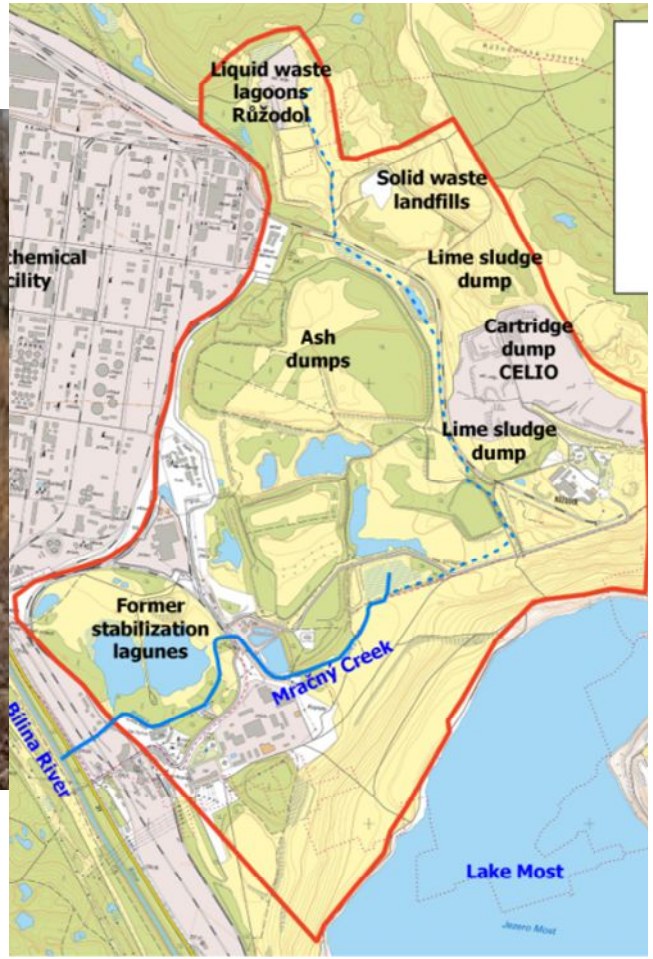
Risk assessment Actualization

Risk Recipients:
Mračný Creek (Bílina River), Lake Most

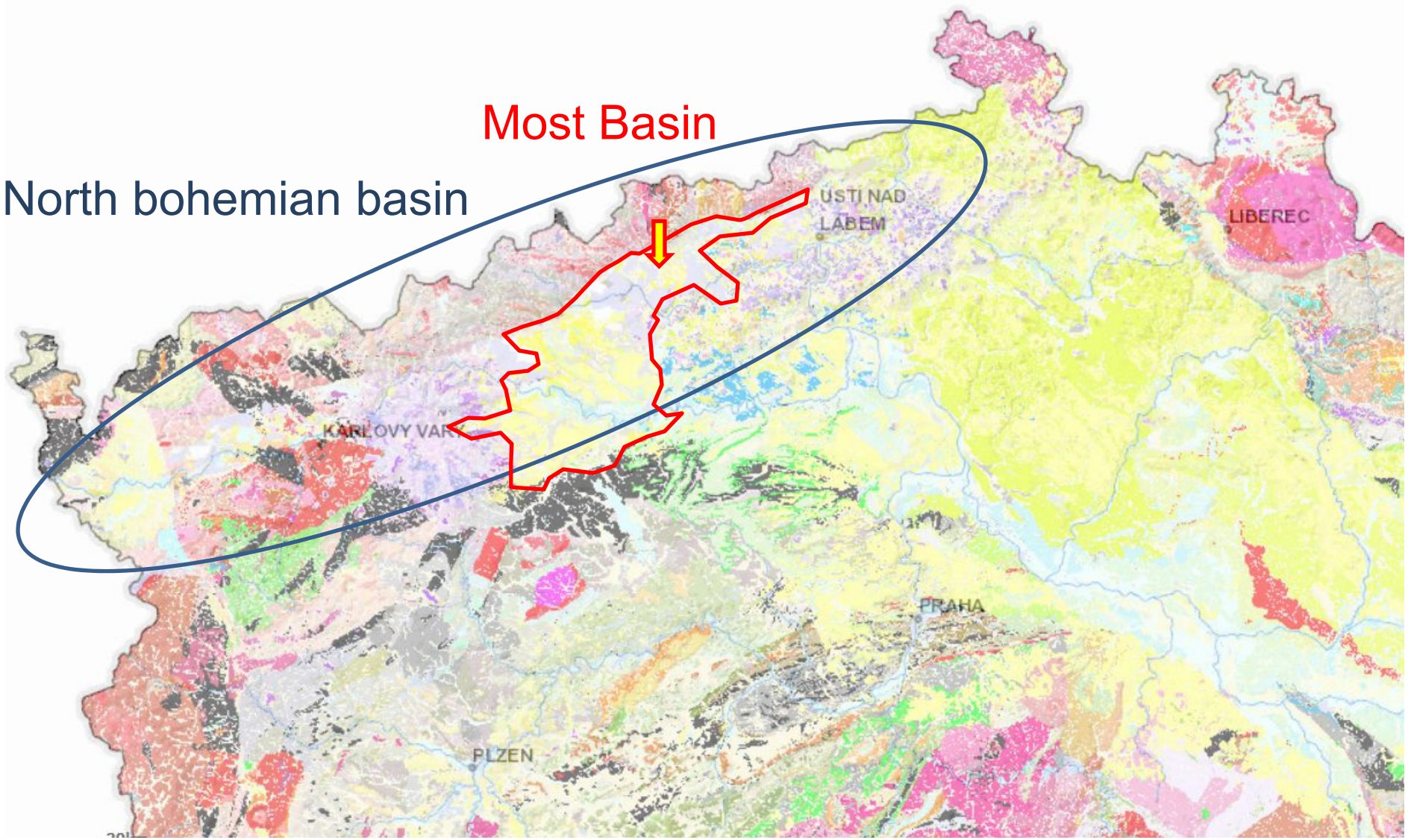
Geology:
Most basin, subpart of North-bohemian basin, with the Palaeozoic crystalline bedrock (orthogneiss) and Mesozoic and Tertiary sedimentary fill (conglomerates, quartzites, sandstones, marlstones, lignite, and clays), anthropogenic cover (wastes)

Hydrogeology:
1. Shallow aquifer in quaternary silty/sandy gravels, the upper zone of isolating clay, dumped mining tailings and landfilled wastes (ashes, soot, etc.).
2. Isolating unit of tertiary clays and siltstones (100 – 200 m thick), K = 10^{-10} - 10^{-11} m/s.
3. Deep aquifer containig deep coal mining strata. => RISK?!

Connection between the deep coal aquifer and surface waters



ORLEN Unipetrol Landfills



Coal-processing chemical facility

- In 1939 Nazi founded the chemical plant for coal hydrogenation using Winkler gasification, first synthetic gasoline for war-front needs was produced in late 1942.
- **Waste dumping ever since.**
- In 1944 and 1945 the allies bombed and destroyed ca 70% of the factory.
- From 1950s through 1972 the conversion to crude oil petrochemistry was finished and new production units were erected (urea, sulfur, oxo-acoholes etc.).
- The municipalities of Růžodol (1950s) and Kopisty (1970s) were demolished for coal mining and tailings / waste dumping.

Landfill areas surveying and risk assessments

- 1993-1994: first spatial survey and Czech Environment Inspection (CEI) Decision
- 1997: first Risk Assessment focused on separate parts => Only local contamination detected
  - Only local landfill-located ecosystems and migratory species defined to be in risk
  - Isolating cover, land reclammation, surface water drainage and monitoring were recommended
- 1999: Updated Risk Assessment of the area as a whole
  - Includes the area southern forecourt towards the inundated grounds of former Most-Ležáky surface coal mine => necessity to pump groundwater contaminated with ammonium ion (ammonia in pH>7) to prevent its migration from the fly-ash dumps towards the Lake Most
  - Several oil-residue lagoons identified and recommended for removal
- 2002: Addition and Addition Supplement to the 1999 URA
- 2016: URA for the petrochemical facility and Růžodol liquid-waste lagoons

Landfill areas surveying and risk assessments

- Substantial time period of monitoring (1993 – 2019)
- Comparable monitoring methodologies only after 2012
- Data review, analyses and synthesis and new conclusions inferred.

Waste types

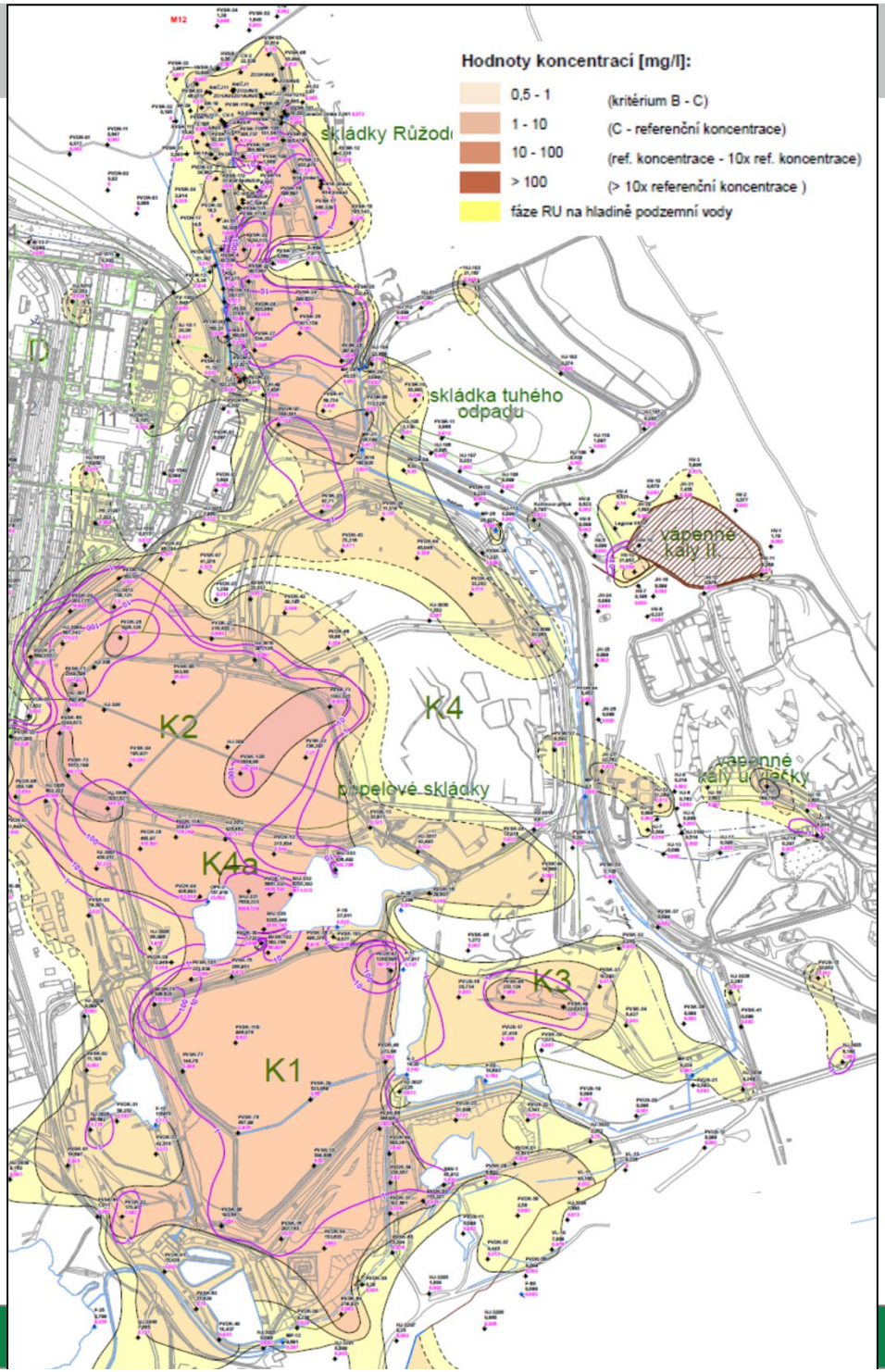
- Winkler (Coal) combustion residues
- Fly ashes, soot, slags (coal gasification)
- Lime sludge (phenol production)
- Petroleum sludges and residues
- Municipal & industrial wastes

Substances of potential interest

- **N_{amon}** – contaminant of widespread importance
  - NH_4^+, NH_3, & other forms of N (eg. NO_3^-)
  - High to extreme contamination: dissolved N_{amon} concetrations at 10^1 – 10^2 (10^3 at extremes) mg/L
  - Present at ash dumps and at Růžodol Liquid waste lagoons
  - Caused mainly by dumping of sulfide waste water onto the fly-ash
  - Highly mobile due to the NH_4^+ form
  - High concentrations of free NH3 found at gw. pH > 9
  - Recent findings indicate natural attenuation of N_{amon} and limited migration due to great sorption capacity of the fly-ash
  - Approx 1/30 (!!) of contamination is dissolved in gw., reminder is sorbed => impacts the projected remediation economy

N_{amon}

State as of
Oct-2017



Substances of potential interest

- **Petroleum hydrocarbons** – partially widespread importance

1. Spatially substantial is the remnant contamination at the Růžodol liquid waste lagoons => NAPL intruding the gw. table – dissolving and potentially migrating
- Wide spectrum of hydrocarbon chains with addition of other pollutants (aromatic hydrocarbons, phenols etc.)

2. Scattered in 5 detected hot-spots: Petroleum sludge lagoons

- Asphalt- or paste-like character, low leachability
- Higher hydrocarbon chains, accompanied by polyaromatic hydrocarbons and phenols
- Suggested for excavating and enrgetic use (combustion) in future

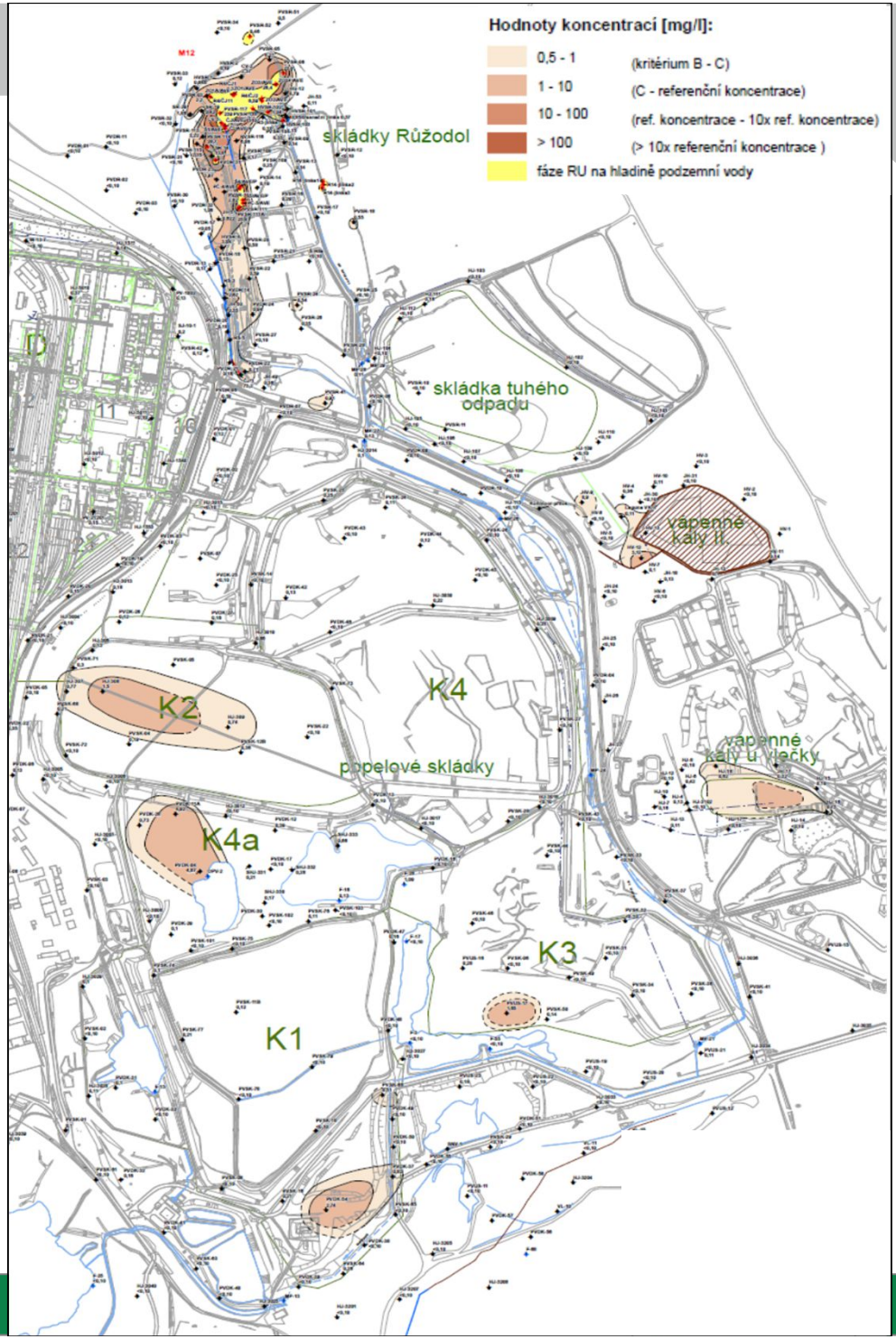
- **Aromatic hydrocarbons** – local (hot-spot) importance
- Majorly benzene and ethylbenzene
- Accompany petroleum hydrocarbons

Non-polar extractables

$(C_{10} – C_{40})$

Petroleum & aromatic hydrocarbons

State as of 2016



Substances of potential interest

- **Phenols** – local (hot-spot) importance
- Closely related to liquid waste dumping at Růžodol and lime sludge dumping

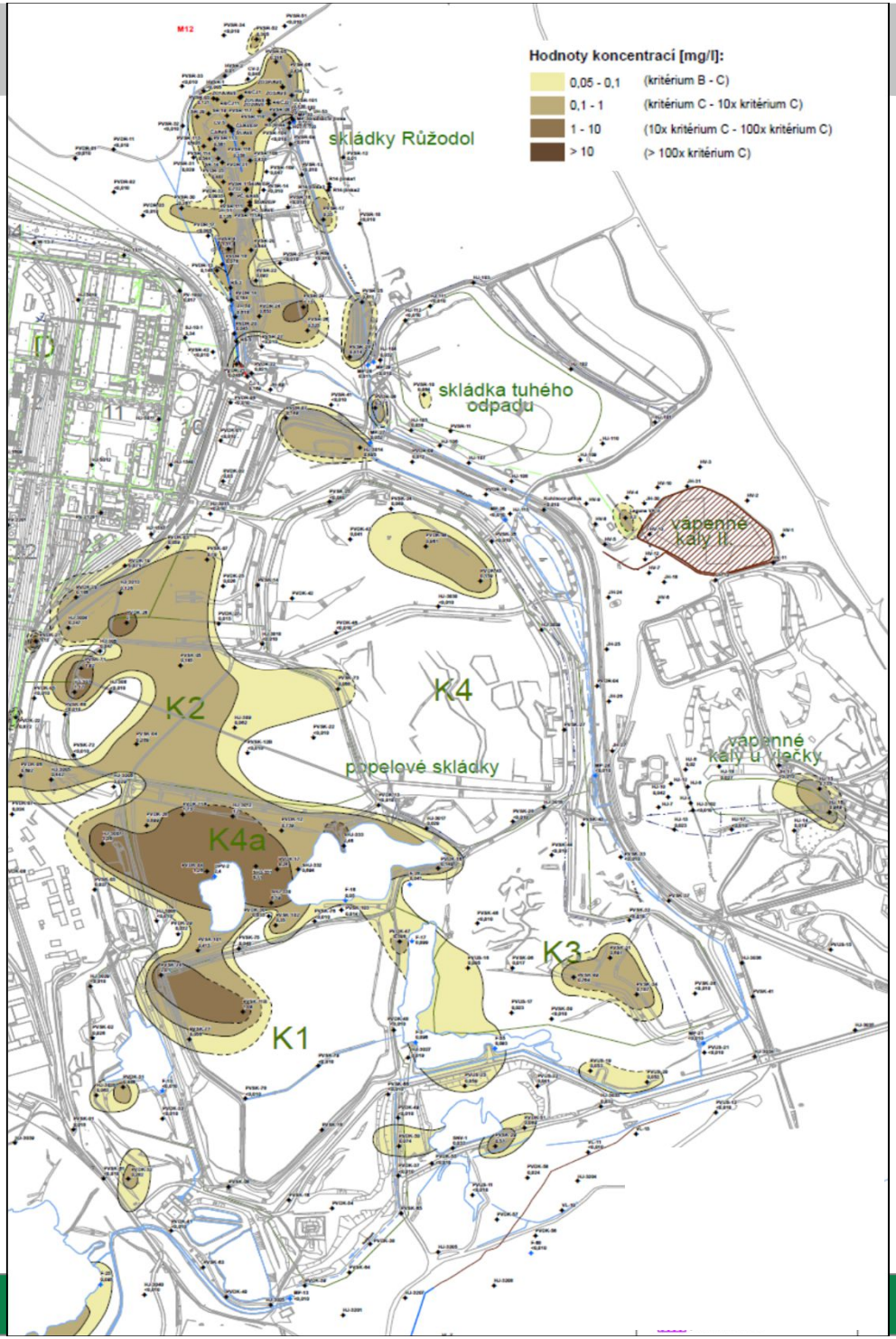
- **Arsene** – partially widespread importance
- Accompanying local hot-spots of high pH waters with N_{amon} contamination
- Complex geochemical processes of sorption/dissolution on the fly-ash, detected concentrations of 10^0 – 10^1 mg/L
- Globally present due to naturally high soil-content, atmospheric deposition (lignite combustion), and industrial activities in the region

- **Fluoride** – present in high pH gw. with N_{amon} (fly-ash),
- 10^1 – 200 mg/L

- **Sodium** – local importance
- Deposited lime sludges contain portions of lye
- Commonly 10^2 mg/L, occasionally 10^3 – 10^4 mg/L (hot-spots)

Arsene

State as of
Oct-2017



Phenols – gw. column zonality

- Sampling at different depths:
  - At gw. table, and than w/ fixed interval (5 m) to the bottom
  - Order of magnitude differences in concentrations

Remedial work to date

- Not deployed in the area as a whole, but targeted into particular hot-spots according to the extent of contamination:
  - **Liquid waste lagoons Růžodol:** liquid wastes were removed, the land surface was reclaimed; contaminated gw. is drained hydraulically above risk recipients
  - **Ash dumps:** partly caped and reclaimed, pumping system for the removal of the highly N_{amon} contaminated gw. was projected during the URA composition, but the intention was abandoned after the URA.
  - **Solid Waste dump:** In 1970 founded as wild, unsecured landfill, partly covered with soil in the past; gw. contamination negligible.
  - **Lime sludge dumps:** secured landfills with the used parts caped and reclaimed; major contaminant is phenol; northern dump reclaimed incompletely with parts of the waste left outside the reclammation area; separated from its southern neighborhoods by underground sealing wall and drainage system; drained groundwater collected and treated

Collection of most up-to-date data (2019)

- Drilling works
- Field leachate tests
- Soil and drill-core sampling & analyses
- Granulometric analyses of lime sludge
- Petroleum sludge hot-spot survey
- Groundwater level measurement and NAPL detection
- Hydrologic measurements
- Groundwater sampling and analyses
- Zoology survey

Results summary

Contaminant migration in the vadose zone is negligible:

- N_{amon}: specific geochemical behavior at the solid-liquid-gaseous phase interface
- As: mobile under rather abnormal condition (high pH)
- Petroleum sludges exhibit limited leaching properties to cause the contamination transport toward the saturated zone

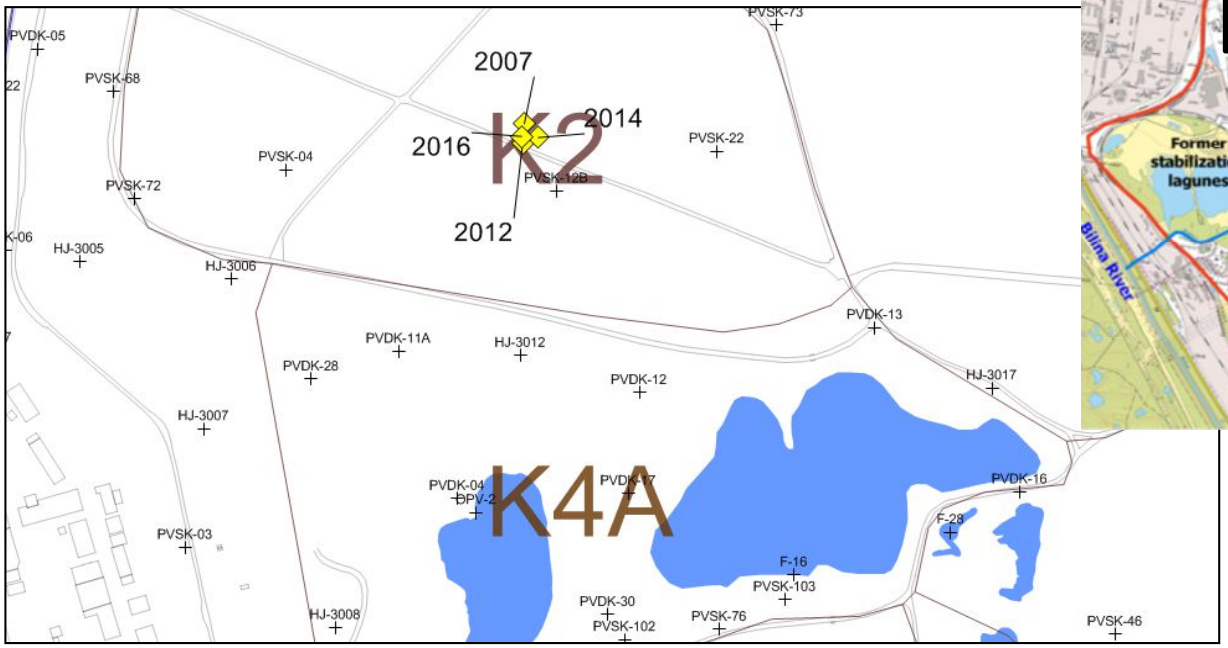
Contamination migration in the saturated zone:

- Groundwater flow and contaminant transport models were composed based on recent findings
- Previous analysis of the N_{amon} contamination plume center of gravity movement revealed that the plume center of gravity moved only about 20 m between 2008 and 2016. The plume center of gravity movement is lesser than the variance error of N_{amon} concentrations in particular wells during particular monitoring campaigns =>

the plume movement is smaller than the methodology accuracy

Results summary

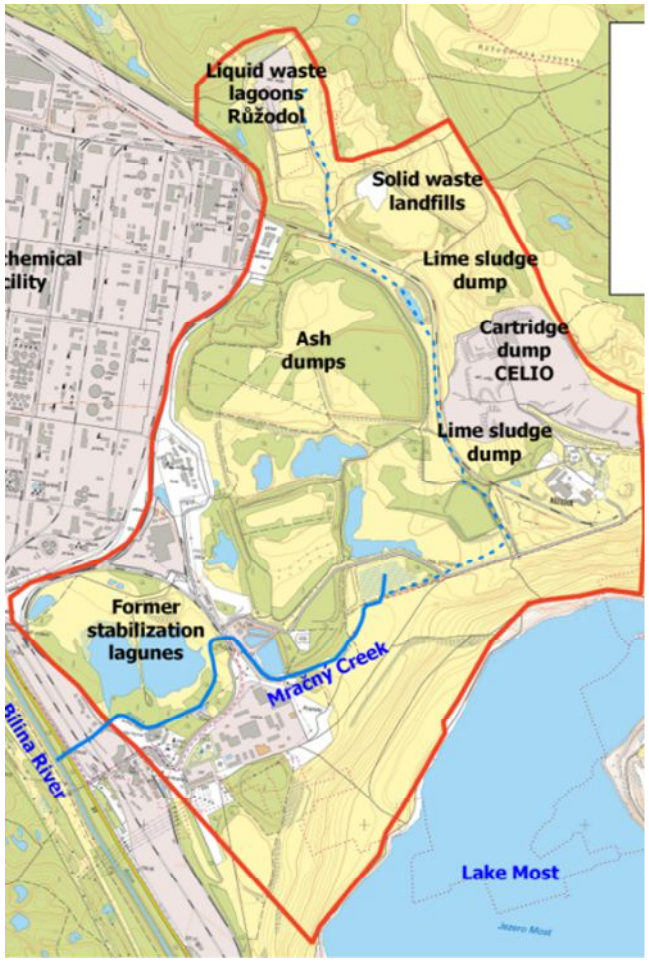
- N_{amon} plume center of gravity movement



Results summary

Contamination in the saturated zone:

- Dissolved **petroleum hydrocarbons** are mainly present at the reclaimed liquid waste lagoons in Růžodol and have been subject to several remedial actions => their risk potential is slowly decreasing with time
- **Phenols** have high solubility in gw., thus exhibit great migration potential. However, the contaminant plumes, present mainly at the lime-sludge dumps, are significantly retarded by attenuation processes.
- **Arsene** pollution plumes at Růžodol lagoons and at fly-ash dumps exhibit only limited migration



Results summary

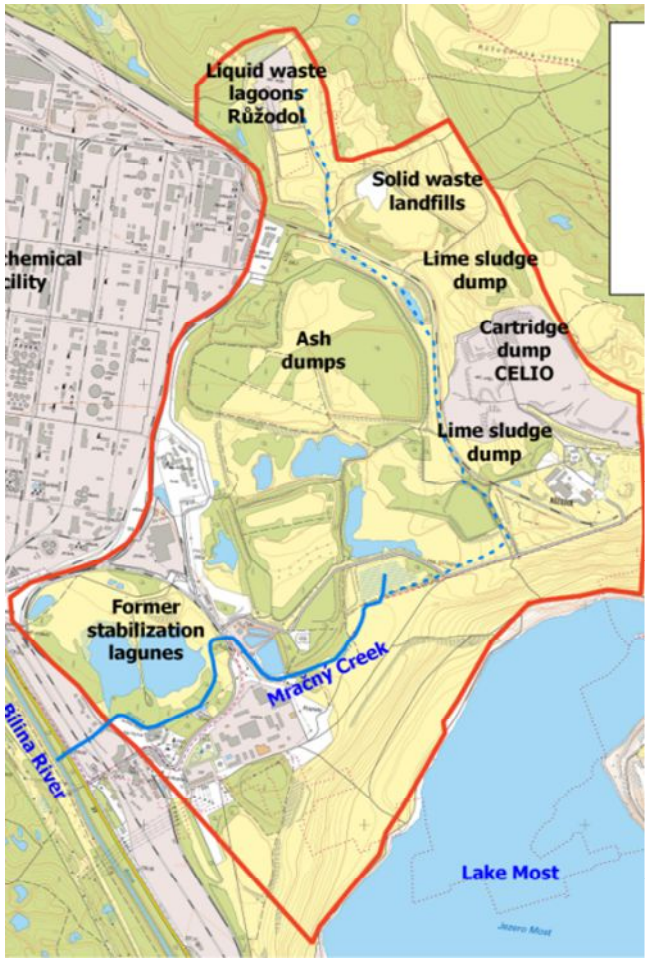
Contamination in the surface waters:

- Significantly influenced by the input of contaminated gw. and by the actual hydrological conditions.

Natural attenuation processes

Aerobic denitrification

Results limitations and uncertainties



Contaminant mass-balance

Aquifer		* N_{amon}	benzene	ethylbenzene	+ phenols	As
		kg	kg	kg	kg	kg
Quaternary	Dissolved	** 576 000	22	8	1 453	119
	Sorbed	8 578 000	252	286	56 624	
Ashes	Dissolved		30	18	191	317
	Sorbed	8 338 000	203	381	4 332	
Vadose zone		3 926 000	Globally insufficient data and geochemical characteristics			
Total		**21 418 000**	**506**	**694**	**62 600**	**436**

* N_{amon} mass balance acquired from former studies.
** Mass balance dissolved in groundwater was determined together for quaternary and ash aquifer.
+ Phenol mass balance does not include the lime sludge underlying strata, where no monitorable aquifer exists (the dumps are founded directly on clay izolator).

Risk conceptual model (Risc5 software)

Risk recipients identified:

1) workers and employees conducting the remediation works;
2) public (the area is transected by local bicycle path);
3) surface watercourses, rain sewers, and drainage systems;
4) water ecosystems, terrestrial ecosystems, and wildlife.

Transport pathways defined:

1) volatilization and inhalation (BTEX, ammonia);
2) direct dermal contact, accidental ingestion or inhalation by human;
3) rain water infiltration and groundwater flushing at surface effluents and lagoons.

Exposure scenarios (doses) for health and environmental risk defined…

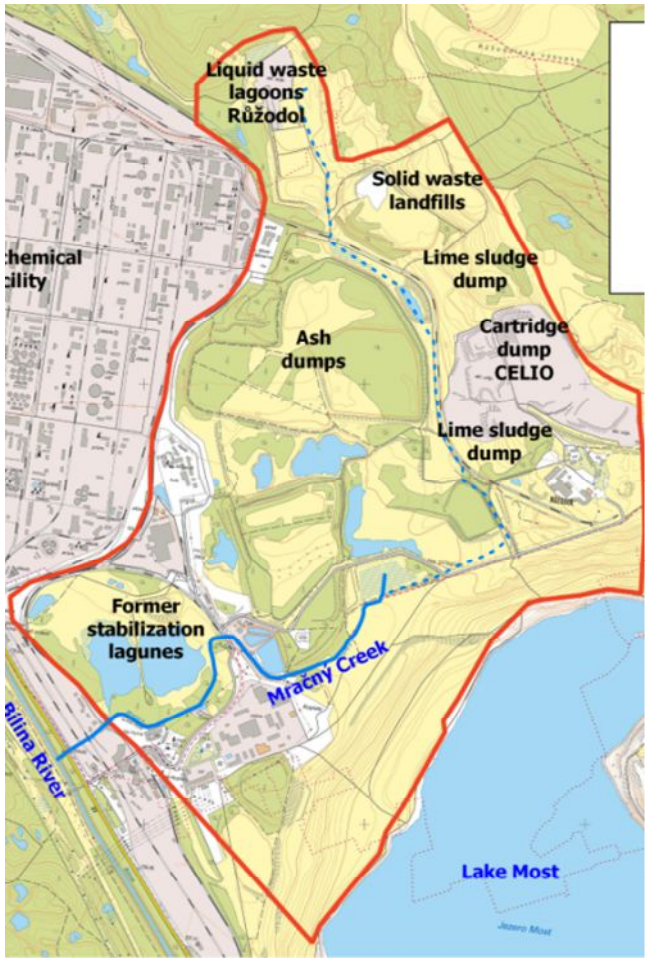
Uncertainties and weaknesses of the assessment were discussed…

Risks identified

Due to actual and envisioned land use practices…

- HUMAN HEALTH:
- No real risk identified

- ENVIRONMENT:
- Risk identified mainly for the global contaminants (Namon, As, Petroleum hydrocarbons) migrating from Růžodol, and fly-ash dumps to the surface waters (Mračný Creek, Bílina River, Lake Most) and partly for the phenols



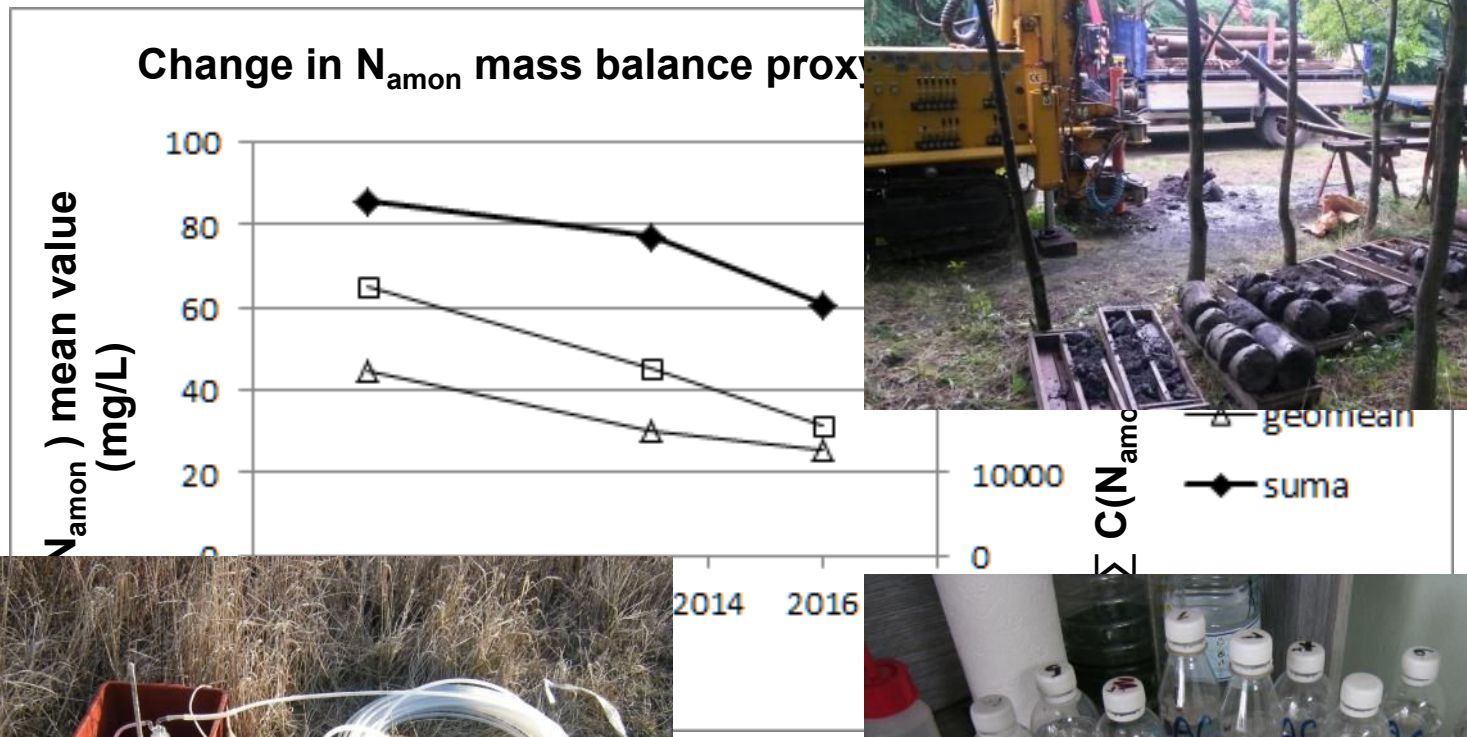
The area of incurred risk exceeds 2 km^2; great anthropogenic influence, yet, robust wildlife populations detetced!

Remedy recommendations

The area comprises number of contamination hot-spots (sub-localities) of historically significant anthropogenic influence

- Prevent new contamination of gw. and surface waters
- Prevent further aerial/spatial spread of contamination form the actual plume limits
- Prevent vadose zone flushing where the impact is negative, BUT no isolating coverage where the outcome compromises positive development (since 1999, the fly-ash dumps were projected for sealing coverage and gw. pumping to prevent plume transport to the Lake Most)

N_{amon} contaminant plume development



- S… ne aqu…
- M…
- V…

Remedy recommendations

The area comprises number of contamination hot-spots (sub-localities) of historically significant anthropogenic influence

- Prevent new contamination of gw. and surface waters
- Prevent further aerial/spatial spread of contamination form the actual plume limits
- Prevent vadose zone flushing where the impact is negative, BUT no isolating coverage where the outcome compromises positive development (since 1999, the fly-ash dumps were projected for sealing coverage and gw. pumping to prevent plume transport to the Lake Most)
  - => the intention was abandoned
  - Saving ca €40 milion in remedy costs

- Restrict public entry
- Maintain regular monitoring of present contaminants and risk recipients

- Economic use for petroleum and lime sludges

Remediation target limits

- Merely recomended.

- Respecting the outcomes of the Assessment, the remaining contaminant mass balance, and the level of uncertainty, the URA did not define remediation target limits,

THANK YOU FOR YOUR ATTENTION

"Be patient a little, these things are not for long."