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BANSKÁ BYSTRICA, SLOVAK REPUBLIC, 8 – 10 OCTOBER 2018

The activity has been implemented within the framework of national project
***Information and providing advice on improving the quality of environment in Slovakia**.*
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

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Methods of Contamination Spread Estimation on Nubarashen POPs Burial Site - Armenia

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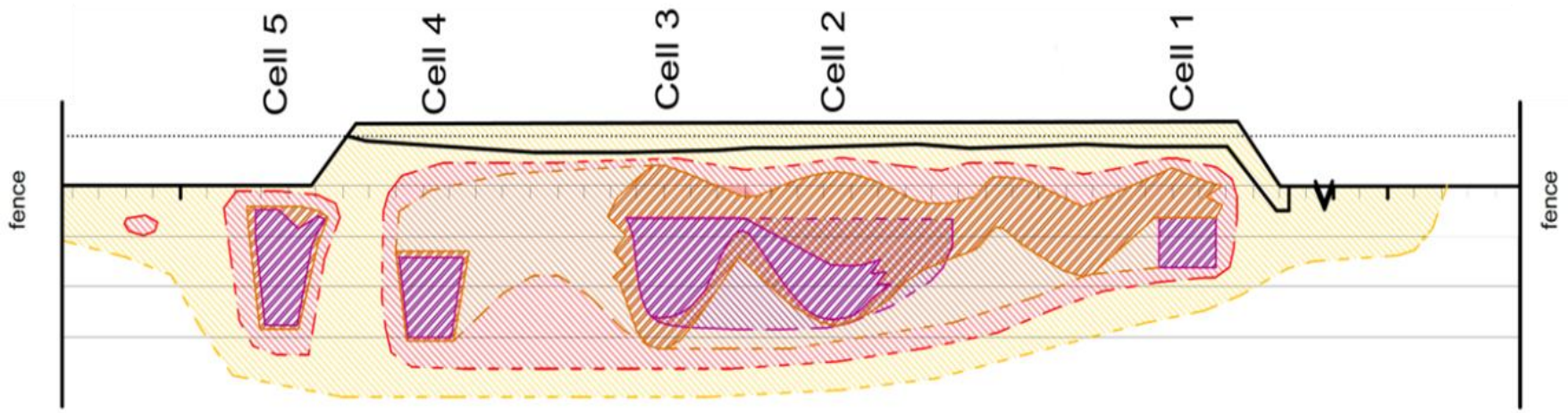
Introduction

1. What? – POPs burial site investigation
2. Where? – Armenia – Yerevan - Nubarashen
3. When? – 07 – 12/2017
4. With whom? – UNDP; DEKONTA
5. **Why? – to design remediation action**

Introduction



Conents

1. Extend of Investigation
2. Results of Investigation
3. Judgement methods as supplementary to direct and indirect methods
4. Contamination Quantification
5. Closing Remarks

The Extend of investigation

Contamination survey: based on the approved sampling plan, in total **30 probes, 5 trenched pits, 20 surface collection points were installed and ca 200 field XRF measurements** were conducted in the following scope:

- 15 probes into individual cells of the landfill to the depth 2.5 – 3.5 m from the landfill surface level (geological and contamination documentation, **sampling for screening analysis – 5 mixed samples and analysis, sampling for contamination spreading – 6 stratified samples and chemical analyses**);
- 15 probes in the close vicinity of the landfill to the depth 1.8 – 2.0 m (geological and contamination documentation, sampling for stratification of contamination – **57 stratified samples and chemical analyses**);
- 20 surface samples collected from the wider vicinity of the landfill body to the depth 0.1 m (contamination documentation and sampling for contamination spreading – **20 chemical analyses**);
- 5 trenched pits (geological and contamination documentation, sampling for further technological tests); and
- Field measurements using an X-ray Fluorescence (XRF) spectrometer instrument (contamination spreading and correlation of spectrometry and chemical analysis based on more than 200 measurements).





The Extend of investigation

The **engineering-geological and hydrogeological survey:**

- 13 boreholes drilled, a total depth of 180 m.
- 15 exploration trenched pits.
- Geological documentation of exploratory objects. 35 soil samples for soil mechanics analyses collected.
- Within the engineering-geological mapping of the site - 43 points documented.

The **geophysical survey:**

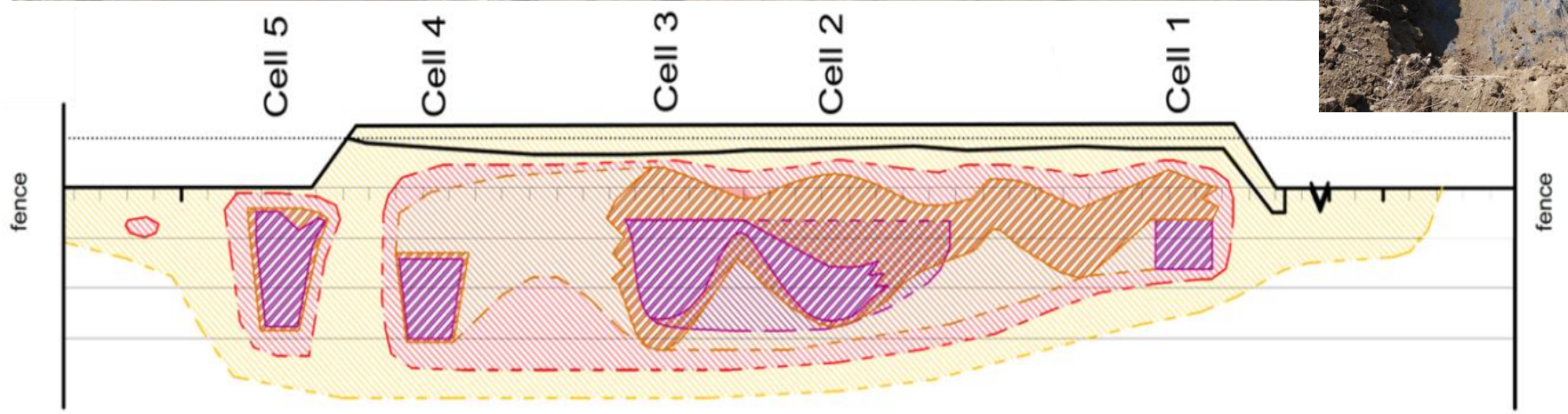
- shallow dipole electromagnetic profiling (DEMP)
- specify the location of burial cells and
- to identify the bedrock profile for future construction objects.
- within the fenced area, in total 3,660 m of transversal and longitudinal profiles.
- outside the fenced area, a total of 1,773 m of profiles.

Results of investigation direct and indirect methods

Results - Recent site contaminating operations

- The landfill was constructed in 1976 as a depository site for obsolete pesticides and other chemicals (POPs).
- The closest non-permanent housing is located ca 300 m at the western and south-western side of NBS.
- The area of the landfill body is ca 0.15 ha (105 x 15 m), maximal expected thickness is 4 m.
- **Unprofessional operations and release of deposited material due the vandalism and illegal excavation of pesticides done into the landfill body in 2009**.
- **The contamination spread is limited to water non-saturated zone, alternatively to creek sediments and surface water**
- The primary contamination is to be expected exclusively in the landfill cells.
- Most of the out-of-landfill contamination spread is a result of unauthorized manipulation with pesticides in 2009 and its reclamation attempts.

Results - Recent site contaminating operations



Recent site-cotaminating operations

	Agent	Weigh (t)	Weigh (%)		Agent	Weigh (t)	Weigh (%)
1	DDT	192.5	38.24	18	Trochlor sodium acetate	4.98	0.99
2	Hexachlorcyclohexane	48.396	9.61	19	Cosan	2.693	0.53
3	Calcium arsenate	42.640	8.47	20	Lissapol	1.878	0.37
4	Endobacterin	33.121	6.58	21	Sevin	1.846	0.37
5	Other pesticides containing arsenic, sulphur, phosphor, cyanides and mercury	App. 30t	5.96	22	Thovit	1.810	0.36
6	Simazine	18.117	3.60	23	Chlorophos	1.695	0.34
7	Colloid Sulphur	17.950	3.57	24	Cosan	1.498	0.30
8	Rezetopth	17.1	3.40	25	TUR	1.280	0.25
9	Dalapon	17.0	3.38	26	Hexachlor benzene	1.265	0.25
10	Cyneb	16.374	3.25	27	Dendrobacilin	0.890	0.18
11	Pentachlor phenol	8.715	1.73	28	DNOC	0.890	0.18
12	Granosan	8.402	1.67	29	Liquid soap	0.289	0.06
13	Vitriol	7.318	1.45	30	Paris Green	0.239	0.05
14	TMTD *	7.205	1.43	31	Dichol	0.168	0.03
15	Fenthiuram	6.765	1.34	32	Metaldehyde	0.1	0.02
16	BIP (biological insecticide preparation)	5.160	1.03	33	Cynox	0.096	0.02
17	Diamine phosphate	5.0	0.99	34	Fumigating box	5,494 boxes	?

Results - Geological patterns

Results - Geological patterns

Quaternary terrace deposits and alluvial accumulations are widespread in the area

Upper Pliocene and Quaternary lava flows cover different horizons of Voghjaberd formation and older rocks. The lava flows have originated in Gegham Volcanic Mountain range.

Lower – Middle Pliocene is represented with Volcanic formation, formed with various volcanic tuffs, breccias and lava flows, with lesser amounts of alluvial and lacustrine deposits, thickness 300 to 1,000 m.

Results - Geological patterns

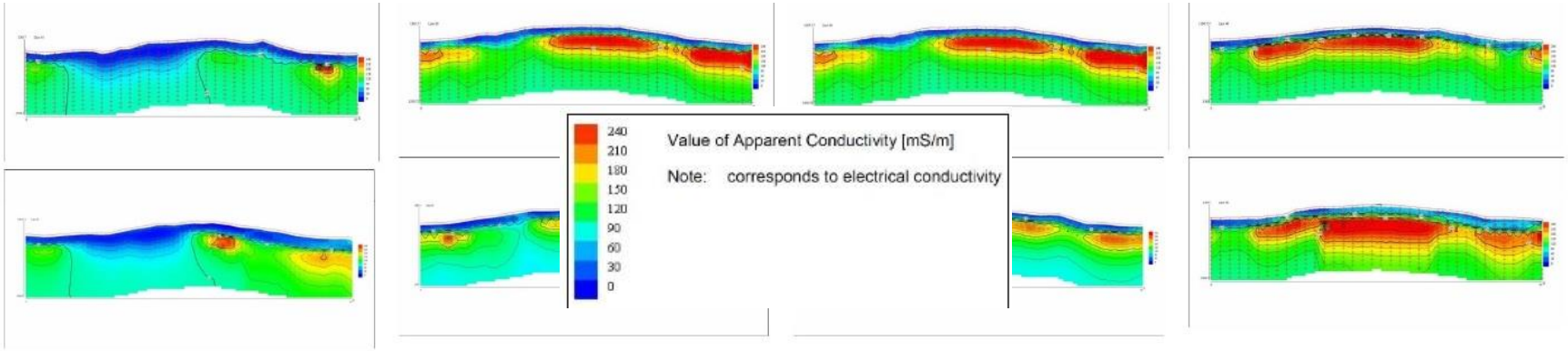
Upper Miocene: Hrazdan formation, clays and sandstones, thickness of 1,000 m.

Middle Miocene: gypsum-salt bearing formations, thickness > 1,200 m. + minor beds of carbonates and sandstones within it. The clays and salt form the lower half of the formation and gypsum with clays form the upper half.

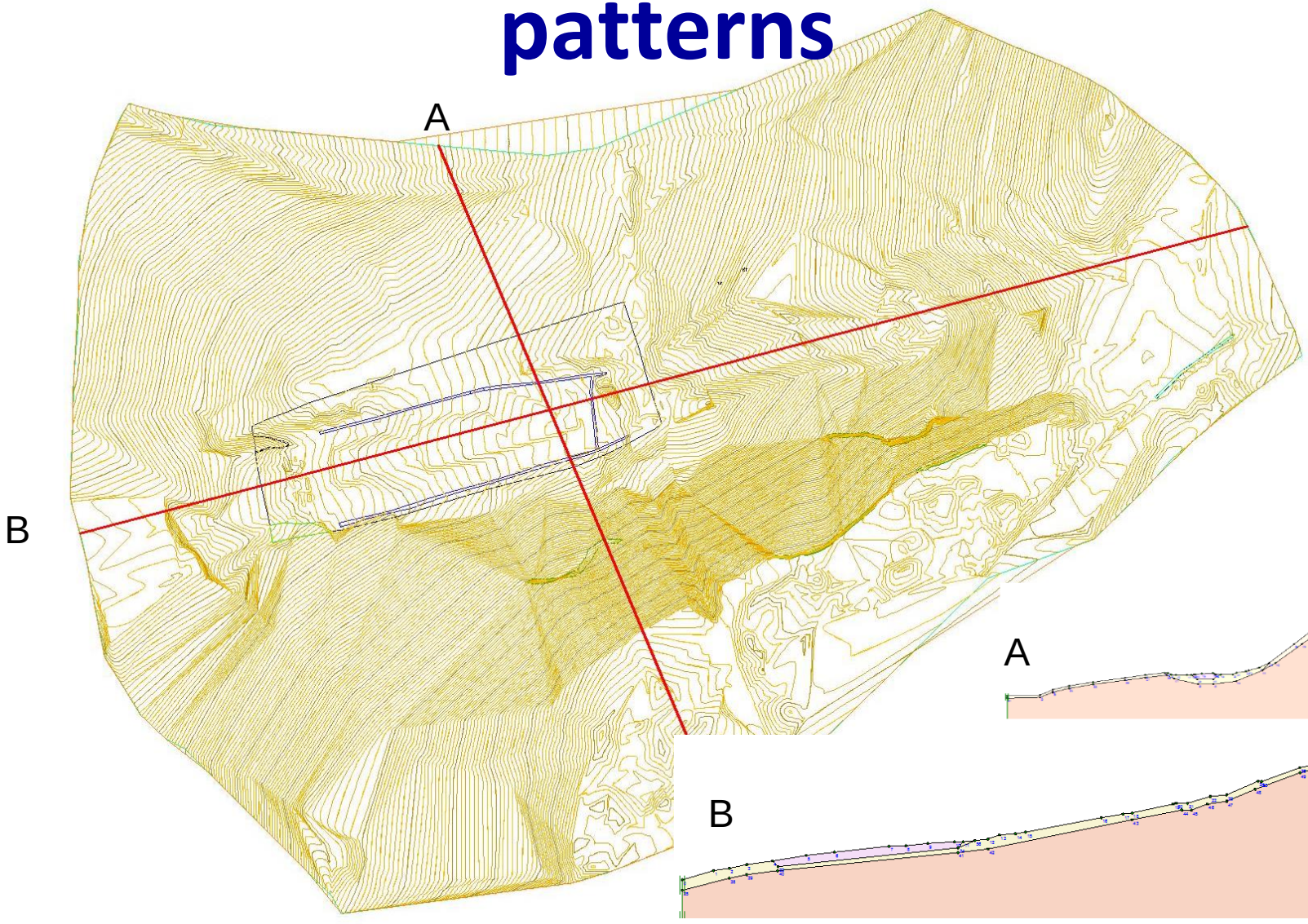
Upper Oligocene – Lower Miocene: Hatsavan formation, clays and continental terrigenous deposits, mostly conglomerates, thickness 430 m and unconformably overlaying the older formations. The conglomerates at the base of the formation.

Results – Elecrical conductivity field investigation

- EC is a geophysical method revealing materials with a different EC than the one of a natural soil. In a natural environment, the increased conductivity can be represented by materials with high content of water with dissolved ions, for instance. Clean water does not increase EC substantially.
- **This method is an indirect method not capable of specific detection of pesticides location**.
- **Results in line with previous GF survey (Tauw, 2013 - georadar)**
- Based on on-site measurement of the EC natural background, it can be identified which material differs from natural state. While EC of 100 – 150 mS/m can be assessed as natural, the values higher than 150 mS/m indicate anomalous situation. Values of EC were generated as an average value of conductivity in the given depth layer.



Results - Geomorphological patterns



Results - Field measurements by portable X-ray fluorescence analyser

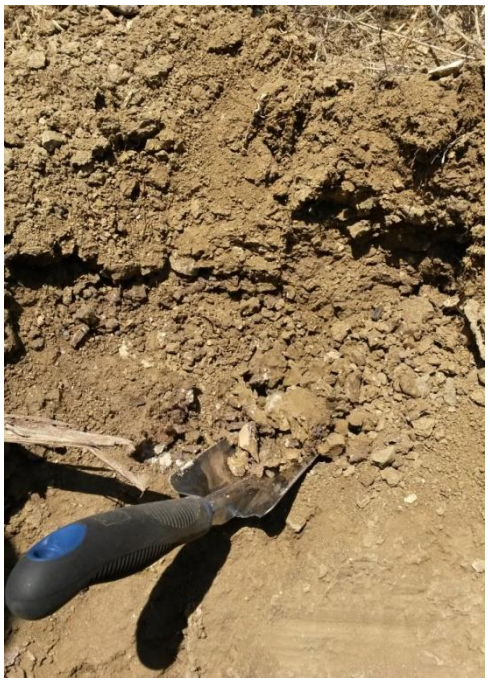
- **Verification of presence of contamination on surface, in probes and trenched pits based on correlation with quorum concentrations**.
- The results of measurements were correlated with results of natural background measurements and later used for the operational field contamination identification and its rough quantification.

- With knowledge of natural chemical composition of soil on site (quorum), trenched pits between the fence and the landfill body were examined with the portable X-ray fluorescence analyzer Delta Premium (Innov-X).
- Results from X-R measurement were compared with results of chemical analyses - potential correlation was evaluated.

Judgement methods as supplement to direct and indirect investigation methods

Site-contaminating operations

- Most of the out-of-landfill secondary contamination spread is a result of unauthorized manipulation with pesticides in 2009 and its reclamation attempts.
- **Mayor amount of POPs deposited show low solubility in water**
- **As a result of such activities, the out-of-the-landfill subsurface contamination is formed by a mixture of various types of pesticides and soil (proved by chemical analyses)**.
- **Potential surface contamination as result of air/water/human transport.**



Geological patterns

- The **original geological environment** on site is formed by marine/lacustrine sediments with abundant presence of natural gypsum. Clays in its natural state are hard with typical brownish coatings of Fe oxides and gypsum crystals (up to 3 mm). When doing the primary documentation of all survey probes, boreholes and trenched pits, the presence of these indicators were tracked in order to identify the original geological environment.
- This knowledge was later used for delineation of contamination on places with lower density of analytical data implying that the presence of original undisturbed geological profile excludes the possibility of contamination presence.
- Another typical geological feature on the site was a **presence of vertical fractures** formed from the surface of terrain to variable depth levels (2 – 4 m), where **absence of cracks prevent further contamination spreading**. In deeper horizons migration of contamination in natural environment is not expectable because of low solubility of pesticides and low permeability of clays-silts.
- **Therefore, where the analytical data on contamination were missing and the presence of natural geological profile without vertical fractures was documented, the presence of contamination by pesticides was excluded** (supported by X-Ray measurements).

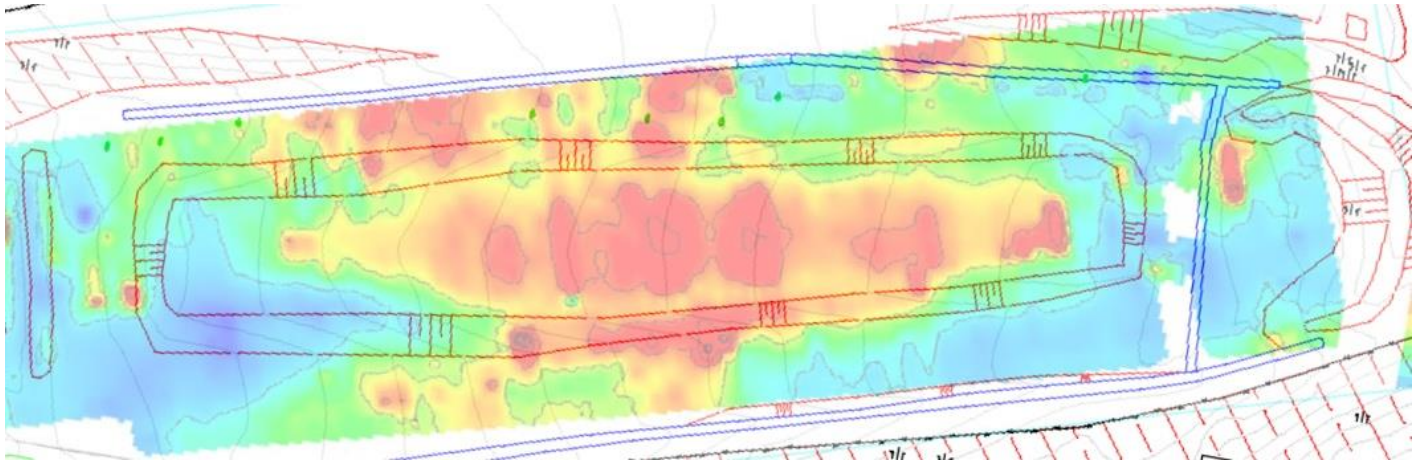
Geological patterns

Elecrical conductivity field investigation

This method enables to distinguish between the natural geological background and anthropogenicaly affected geological environment (typically fill material).

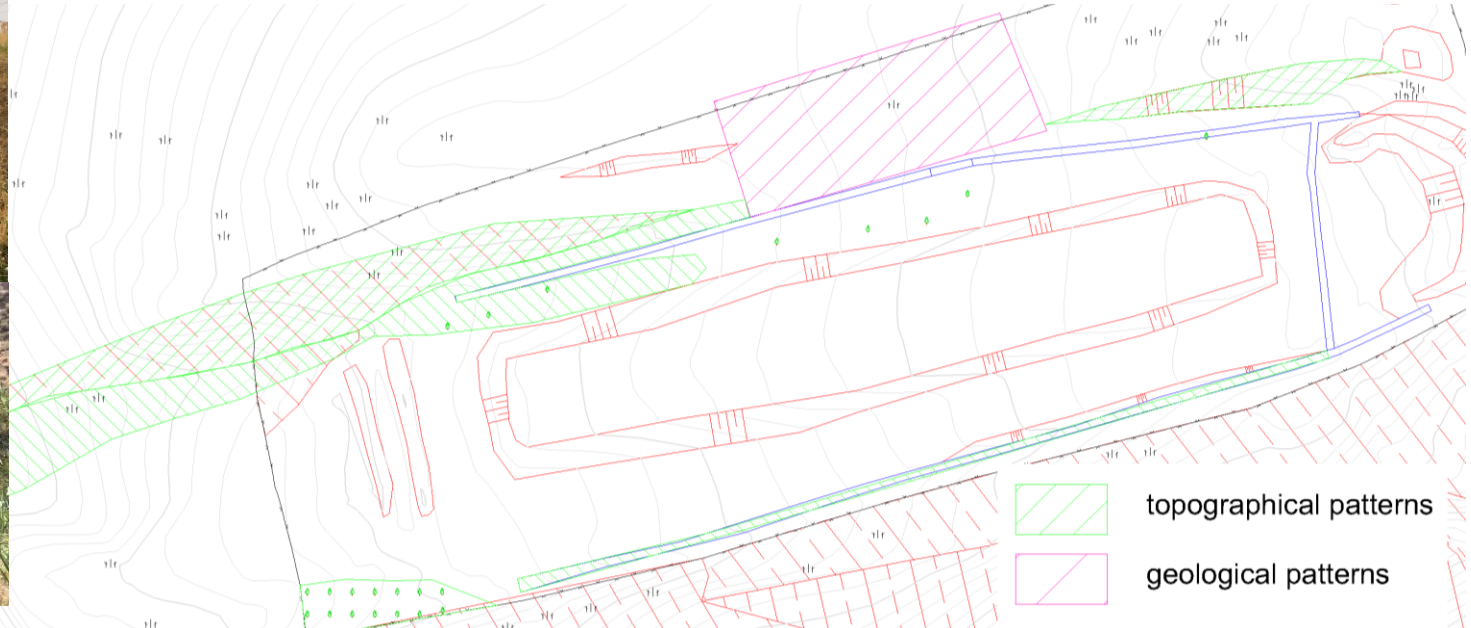
The value of EC detected on place with available analytical data was considered as indicating the contamination of analogical intensity in places where:

- the analytical data on contamination were not available, but contamination was indicated by chemical analyses in adjacent place (in vertical or horizontal manner) or
- the analytical data on contamination were not available, but contamination was indicated by X ray measurement in that particular place or in adjacent place,
- and the intensity of EC was comparable on both places



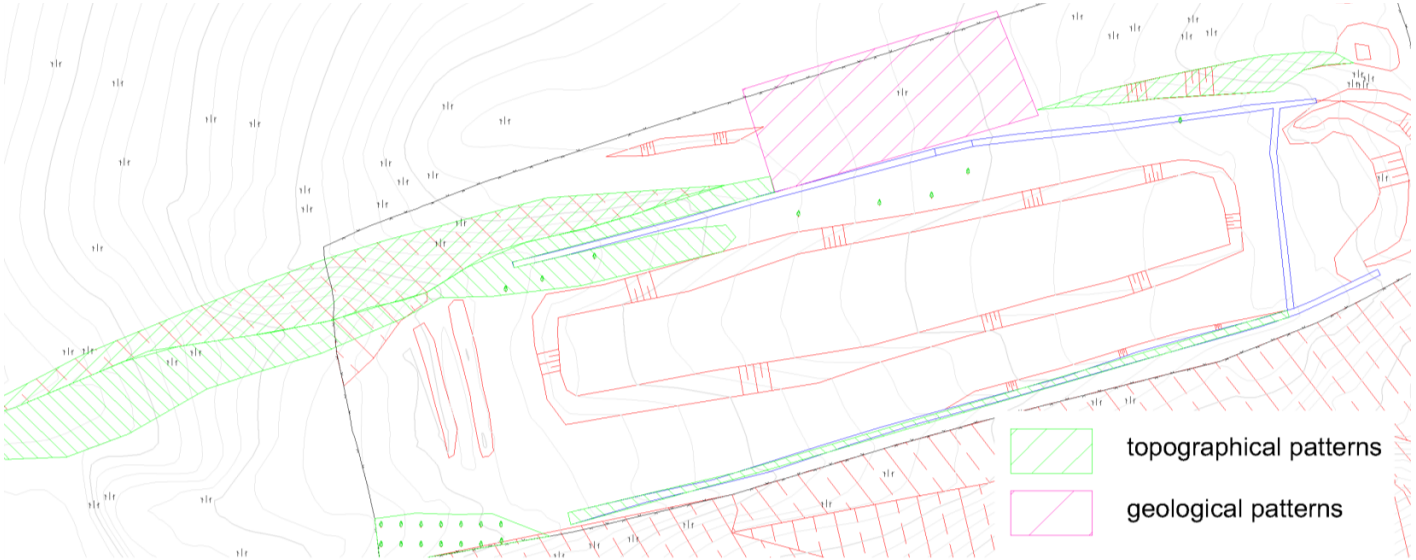
Geomorphological patterns

1. In areas of steep slopes between the northern fence and the landfill body, it was presumed that no subsurface contamination (no deeper than ca 0.5 m below ground level) could be present because:
   - no fractures and fissures were documented on the slope (i.e. spreading of contamination by infiltration of surface water is limited because of the quality of soil, also considering a limited solubility of typical pesticides in water),
   - no subsurface contamination was detected on the above-laying plateaus and
   - steep slopes are inaccessible for heavy machinery.



Geomorphological patterns

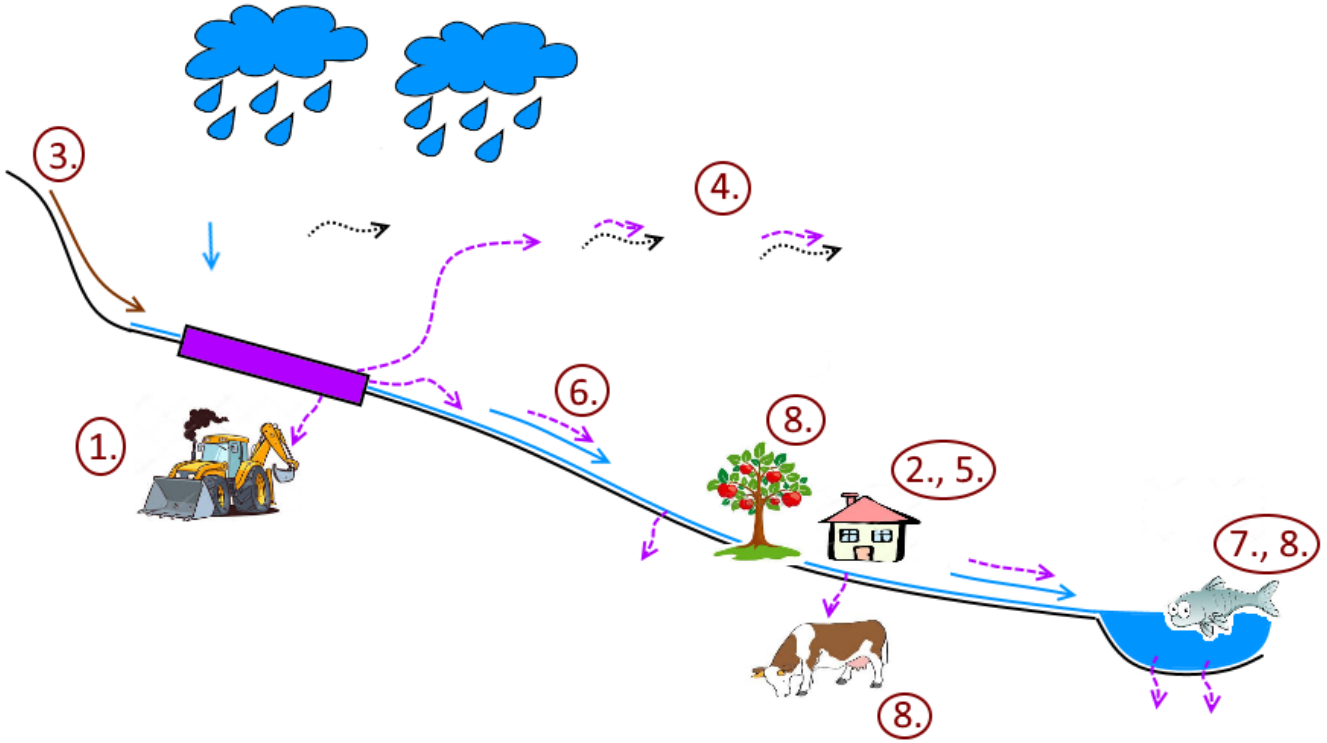
2. The area between the southern edge of the landfill body and trench running along the foot of the unstable slope. In this area it was assumed that the > 50 ppm contamination did not spread behind the surface water drainage trench in depth > than 0.1 m. The depth of the trench differs in its length varying from 1.0 to ca 2.5 m. This presents geomorphological barrier for potential spreading of contamination either natural or anthropological.
3. In case of surface water creek beds in the N-W edge of the site that are periodically run through during rain and snow-melting seasons the horizontal spread of contamination was assumed to be limited to the width of the creek bed.



Field measurements by portable X-ray fluorescence analyser

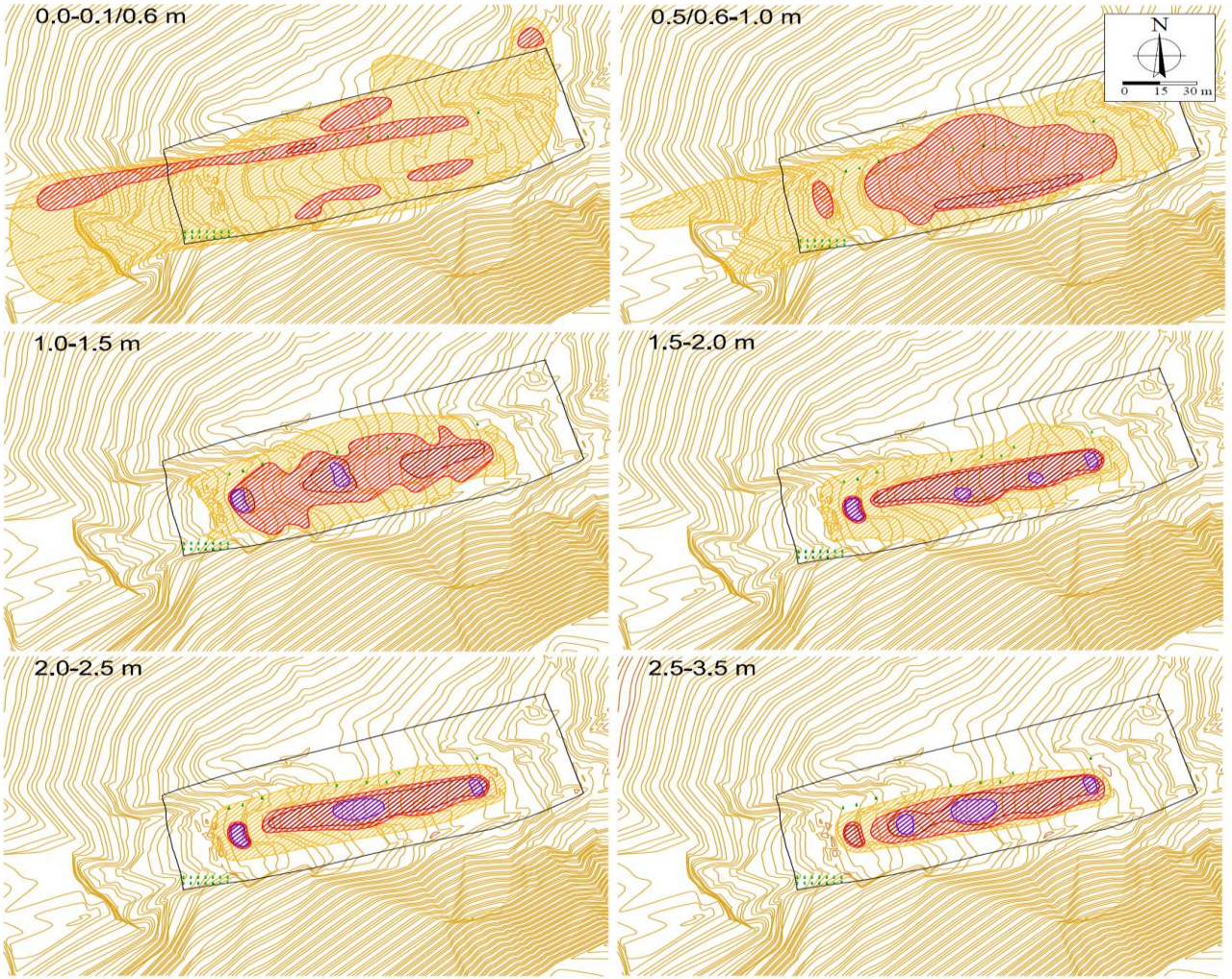
Supportive instrument for verification of previous assessment approaches.

•After correlation with results of natural background measurements later used for identification of presence of contamination on surface, in probes and trenched pits and its rough quantification.



Contamination quantification results

Contamination quantification



Contamination quantification results

Depth level	Average Thickness	Category 1		Category 2		Category 3			
		>30 % pure pesticides		<30% pure pesticides - 1,500 mg/kg d.m.		1,500 - 50 mg/kg d.m.		1,500 – 0.7 mg/kg d.m.	
[m]	[m]	[m^2]	[m^3]	[m^2]	[m^3]	[m^2]	[m^3]	[m^2]	[m^3]
0.0-0.5/0.6	0,55	-	-	32	18	2,034	1,119	13,423	5,105
0.5/0.6-1.0	0,45	-	-	270	122	3,408	1,534	9,297	4,184
1.0-1.5	0,50	120	60	602	301	2,066	1,033	4,550	2,275
1.5-2.0	0,50	145	73	1,002	501	313	157	3,257	1,629
2.0-2.5	0,50	258	129	795	398	390	195	2,408	1,204
2.5-3.5 *	1,00	262	262	786	786	652	652	1,603	1,603
>3.5 **	1,00	150	150	300	300	300	300	800	800
Total volume			674		2,425		4,989		16,799
Specific gravity (t/m^3)			1.5		1,7		1,7		1,7
Estimated weight (t)			1051,5***		4,122,5		8,481		28,558

Closing remarks

- Because modern contaminated land management generates increasing demand for sophisticated investigation methods contaminated sites deserve nature-based approaches.
- As site remediation costs play vital role in CS management the greatest pressure is, in paradox, put on reduction of site investigation and project design costs. In this context “down-to-earth” contamination investigation approach may present a sustainable strategy.
- In this context down-to-earth approach refers to assessment of geological-operational patterns used, in combination with data on contamination from direct/indirect investigation methods, as input data for evaluation and interpretation of contamination spread.
- Although careful considerations of geomorphological, geological, hydrogeological and operational patterns of each contaminated sites have always been considered as a part of a contamination site puzzle assessment, these should be approached with even higher respect nowadays.
- Nubarashen burial site (Armenia) is a good example of a contaminated site where nature-based approach had been implemented within site investigation phase.

In geology we trust!