Analytical Methods for the Study of Trace Elements in Geologic Materials

SAMPLE COLLECTION & HANDLING

- Collection
  - -Cores
  - -Channels
  - -Grab
  - -Continuous samplers
  - -Washed
  - -Etc.

- Handling
  - -Minimize moisture loss
  - -Avoid oxidation
  - -Prevent contamination

Analytical Methods for Characterizing Geologic Materials

Chemical Analysis

- ***Bulk Sample**
  - -Inductively coupled Plasma (ICP) AES & MS
  - -Instrumental neutron Activation analysis (INAA)
  - -X-ray fluorescence (XRF)
  - -Atomic Absorption Spectroscopy (AAS)
- ***Micobeam**
  - -Electron microprobe
  - -Scanning electron microscope
  - -Ion microprobe
  - -Laser mass analyzer

Analytical Methods for Characterizing Geologic Materials

Mineralogical Analysis

- -X-ray diffraction (XRD)
- -DTA/TGA (MS)
- -Optical Petrography
- -Infrared &UV spectroscopy
- -Raman spectroscopy
- -Mössbauer spectroscopy

Speciation

- -Extended X-ray analysis fine structure (XAFS)
- -Wet chemistry

Summary of Some of the Characteristics of the Trace Element Analysis Techniques

Technique	Instrument Price[a]	Detection Limits[b]	Spectral Interference	Matrix Effects	Multi-elemental	Sample Type
INAA	+++	0.001-1	low	low	yes	solid
ED-XRF	+	1-10	high	medium	yes	solid
WD-XRF	++	0.1-1	low	medium	yes	solid
PIXE	+++	1-10	high	medium	yes	solid
ICP-AES	+ to ++	1-30	high	medium	yes	liquid
ETA-AAS	+	0.01-0.2	medium	high	no	liquid
ICP-MS	++ to +++	0.03-0.1	high	high	yes	liquid

[a] + less than $100,000 to $250,000; +++ more than $250,000.

[b] μg/g for solid sample type; ng/ml for liquid sample type

ANALYTICAL TECHNIQUES

For Coal Mineralogy

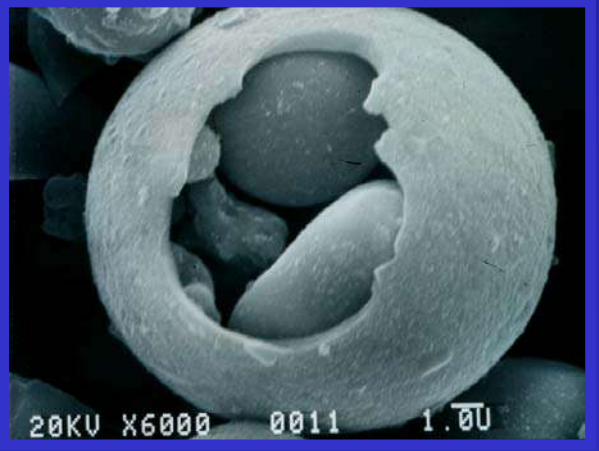
- X-Ray Diffraction (Semi-quant./Direct)
- Scanning Electron Microscopy (Qual.-Semi-quant)
  +Energy Dispersive X-Ray (Indirect)
- Infrared Spectroscopy (Qual.-Semi-quant./Indirect)
- Electron Microprobe Analysis (Qual/Indirect)
- Transmission Electron Microscopy (Qual/Indirect)
- Ion Microprobe (Qual/Indirect)
- Optical Microscopy (Qual-Semi-quant/Direct)
- Thermometric (DTA/TGA) (Semi-quant/Direct)
- Mossbauer Spectroscopy (Semi-quant/Direct)
- Others-Raman, EXAFS
- Normative Analysis (Quant/Indirect)

MODES OF OCCURRENCE

- Chemical form of the element
- Influences behavior during cleaning, combustion, conversion, leaching, weathering, etc.
- Determines environmental impact, technological behavior, by-product potential
- Examples:
  - Calcium-Calcite, organic salt, clay, sulfate, feldspar, phosphate, etc.
  - Zinc-Sulfide (sphalerite ZnS)

Scanning Electron Microscope

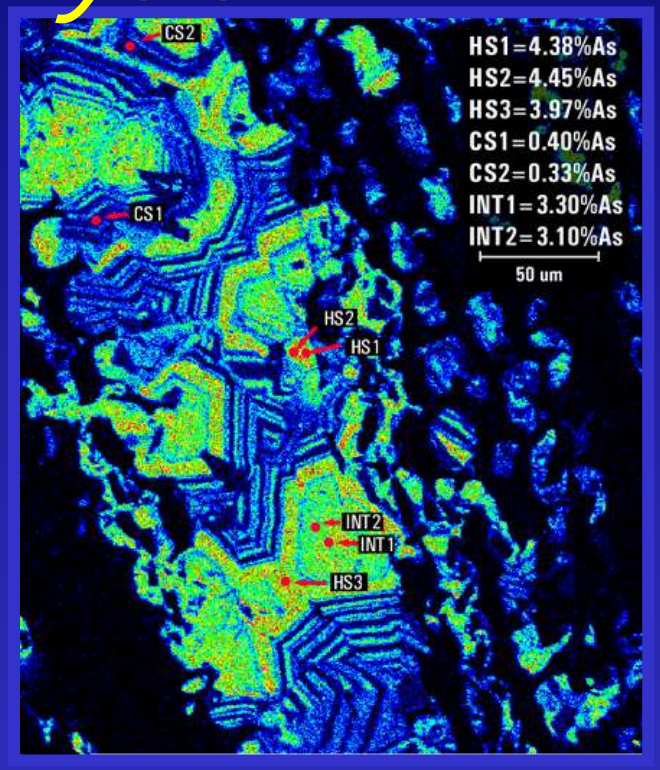
SEM Image of Fly Ash Particle



Electron Microprobe

Arsenic in Coal: Microanalysis

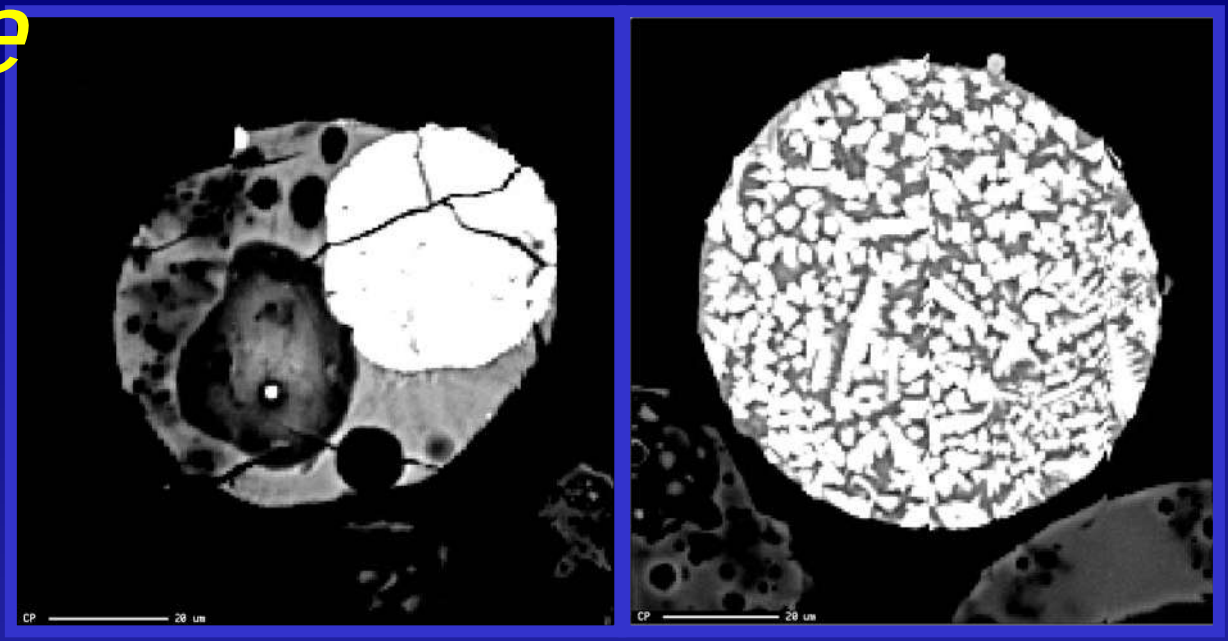
- *Arsenic is a trace to minor element in pyrite; concentrations ≥150 ppm can be determined using the electron microprobe.*
- *Direct confirmation of As residence indicated by other methods, but shows concentrations vary widely within and between grains.*



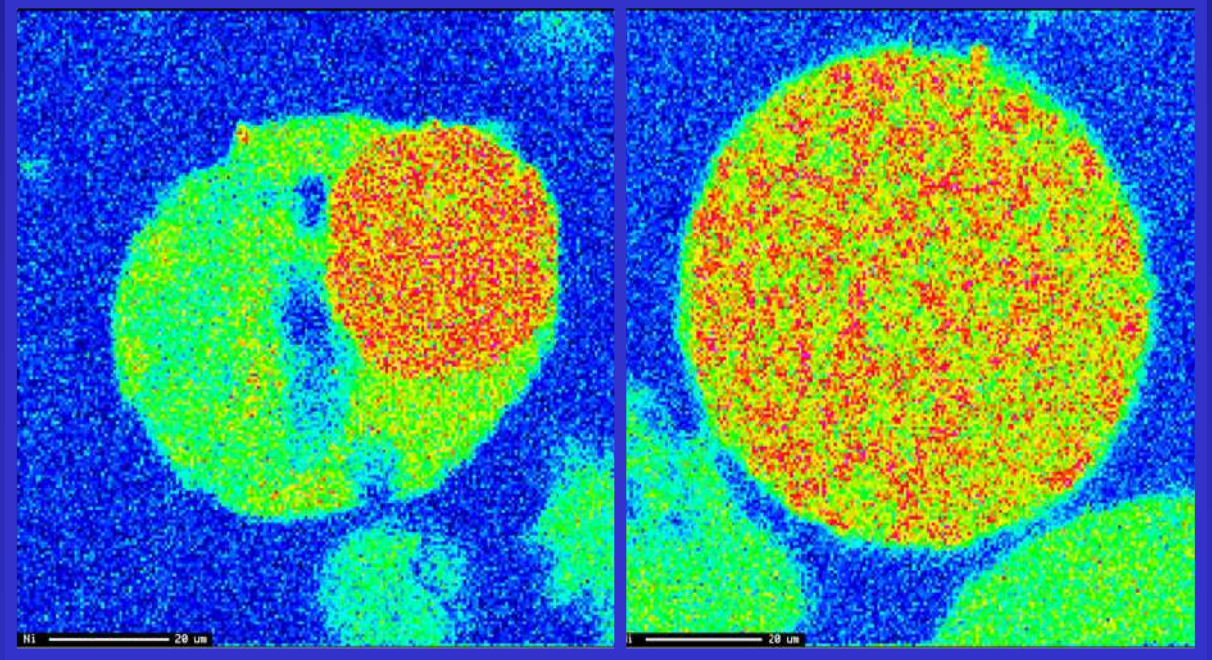
Arsenic-rich pyrite (to 4.5 wt. % As) with oscillatory zoning, Warrior Basin coal, Alabama.

Microprobe Results

Back-scattered Electron Images



Nickel Elemental Maps



SHRIMP-RG Ion Microprobe

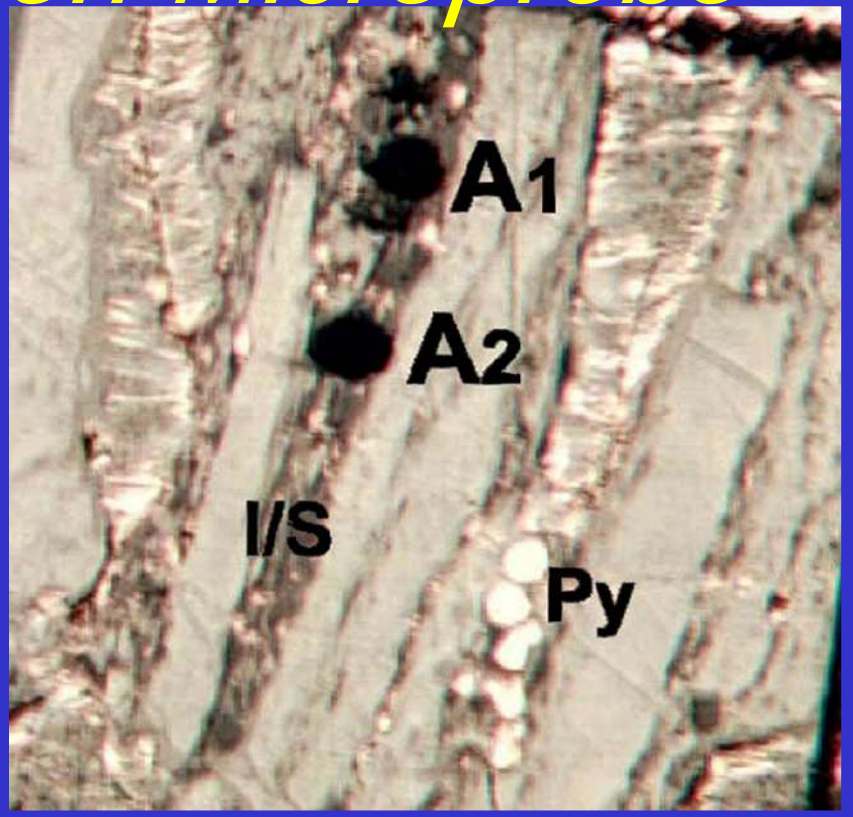
Sensitive High-Resolution Ion Microprobe Reverse Geometry

- Primary beam of O_2^- or Cs^+ ions
- Detection in the ppm range
- 10-15 micron spot size
- determine isotope ratios

Cr in Illite/Smectite in Coal: SHRIMP-RG Ion Microprobe

- *Quantitative results for silicate-hosted Cr using Stanford-USGS SHRIMP-RG ion microprobe.*
- *Concentration ranges:*

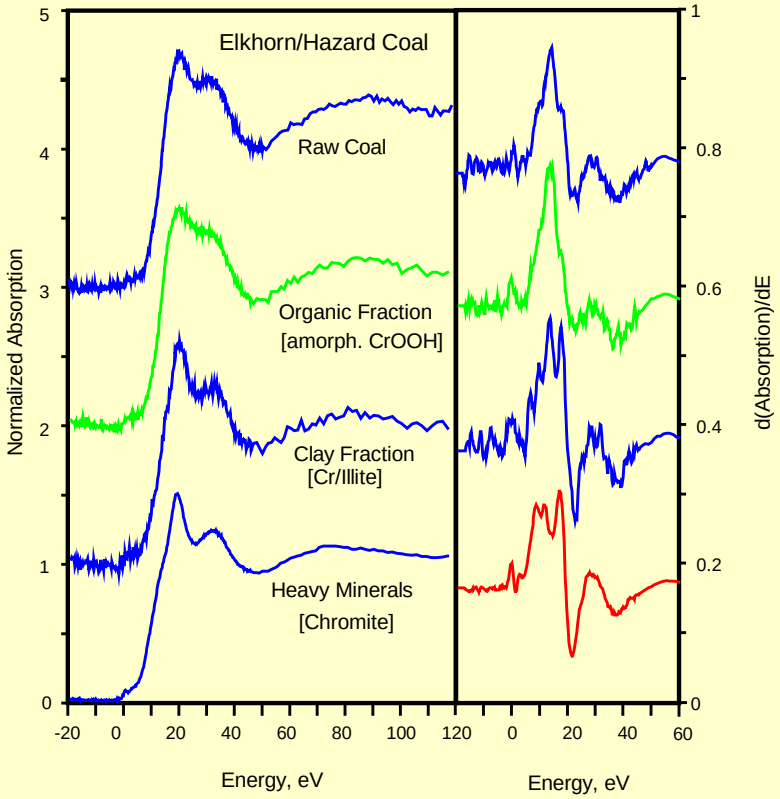
  Cr = 11 to 176 ppm
  Mn = 2 to 149 ppm
  V = 23 to 248 ppm
- *Confirms leaching results and electron microprobe data.*



Reflected-light image of illite band and SHRIMP-RG analysis points.

Chromium in Coal: XAFS

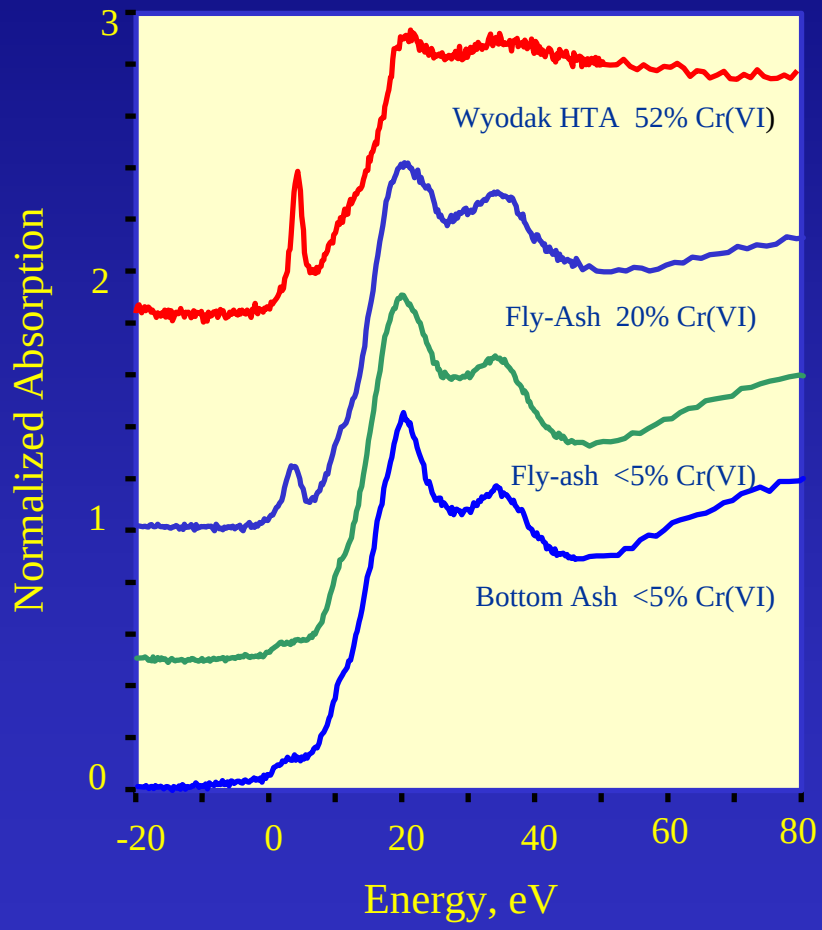
- *Two major forms identified:*
  - *Cr^{3+}/illite*
  - *Org. associated Cr (Amorph. CrOOH)*
- *Chromite- Common only in coals unusually rich in Cr*
- *Oxidation State- Always Cr^{3+}*



Chromium XANES spectra and derivatives for Elkhorn/Hazard coal and separated fractions. Note that a different spectrum is obtained for each fraction indicating that a different form of chromium dominates each fraction.

Cr in Ash: XAFS

- Cr can be found as:
  - Cr/spinel associated with magnetic iron oxides.
  - Cr associated with alumino-silicate glass.
- Oxidation State of Cr
  - Often <5% Cr as Cr(VI) in bottom ash and fly-ash from bituminous coals.
  - Rarely up to 20% Cr as Cr(VI) in fly-ash from lower-rank coals.

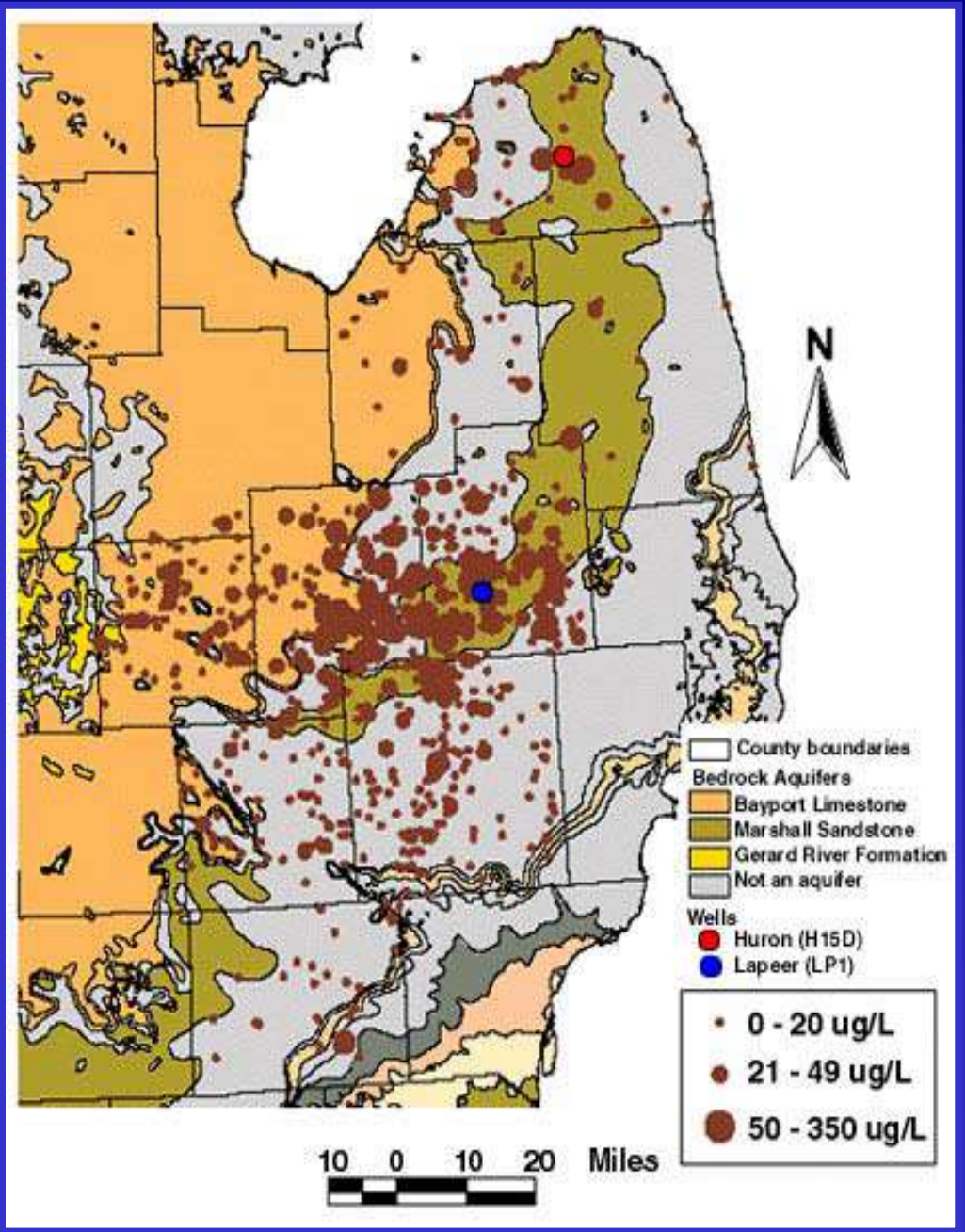


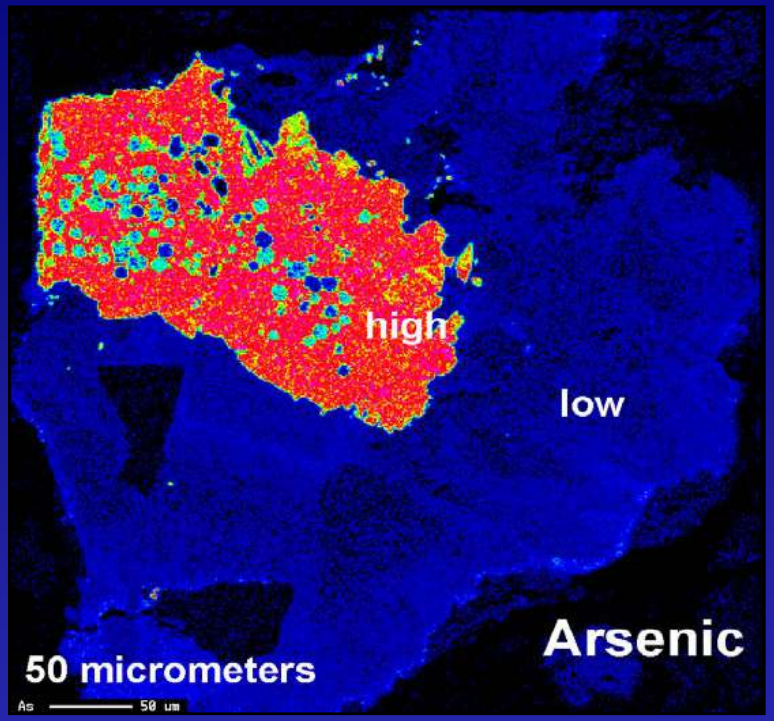
*Distribution of As-levels**

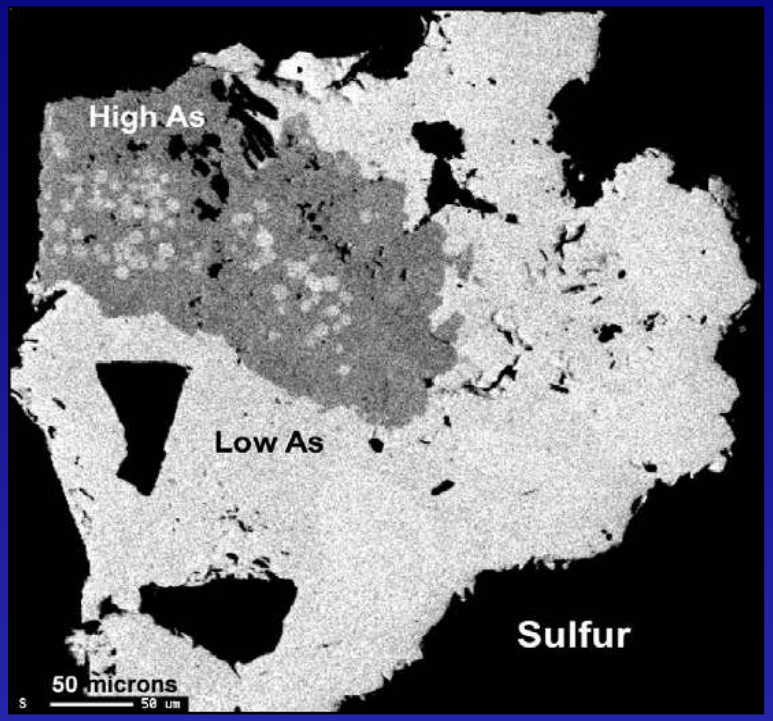
Max. arsenic is 6-8 times EPA standard.

Most problem wells are in the Marshall, but not exclusively so.

**MDCH data*

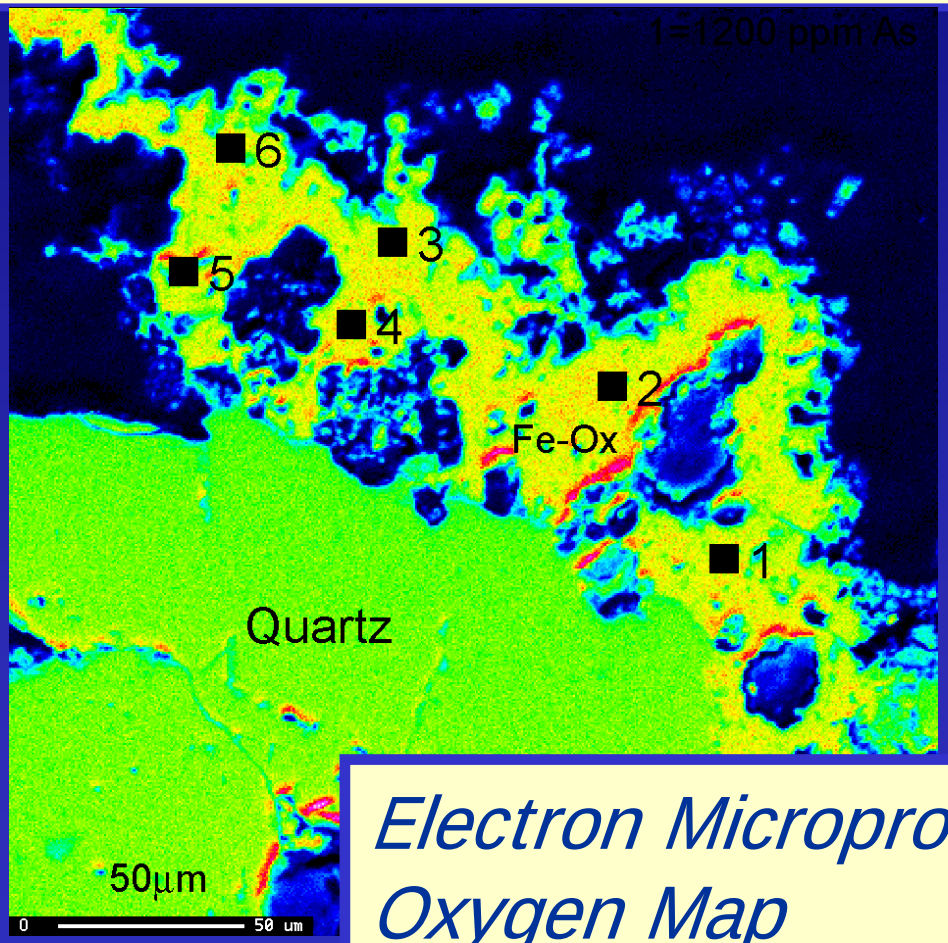






Electron microprobe elemental maps for As and S show high-As (6-7 wt. %) pyrite occurs as the second of 3 pyrite generations.

Arsenic-rich iron oxy-hydroxides (derived from pyrite) in till containing Marshall Sandstone



Electron Microprobe Oxygen Map

Arsenic (ppm)

1 = 1,200

2 = 1,300

3 = 3,300

4 = 1,400

5 = 2,800

6 = 1,000

Max. = 7,300

Conclusions

- *Microanalysis reveals the fine scale distribution of trace metals in coal and other geologic materials.*
- *This information is needed to predict the distribution and behavior of these metals in the environment, and to understand the source of metals that impact human health.*

USGS
science for a changing world

Calculation and Map presentation of Environmental and Health risk assessment in SGR Mts., Slovakia

Rapant, S., Dietzová, Z. & Cicmanová, S.

GOALS

- To evaluate possible adverse effects – **ENVIRONMENTAL RISK** and **HEALTH RISK** from contamination of geological environment of the Slovak Republic, their calculation and map depiction.

- In the pilot area – Spišsko-Gemerské Rudohorie Mts. to elaborate and to verify methodical principles of evaluation of influence of geological environment contamination on the health state of population.

INTRODUCTION

HEALTH STATE OF POPULATION

object of many scientific fields, among which also geology has its firm position

HEALTH STATE OF POPULATION (WHO)

- **Life style – 50 %**
- **Genetic factors – 20 %**
- **Level of health care – 10 %**
- **Environment – 20 %**

In regions with markedly polluted environment the influence of environment may be significantly increased

Lack or excess of chemical elements in geochemical environment

↓

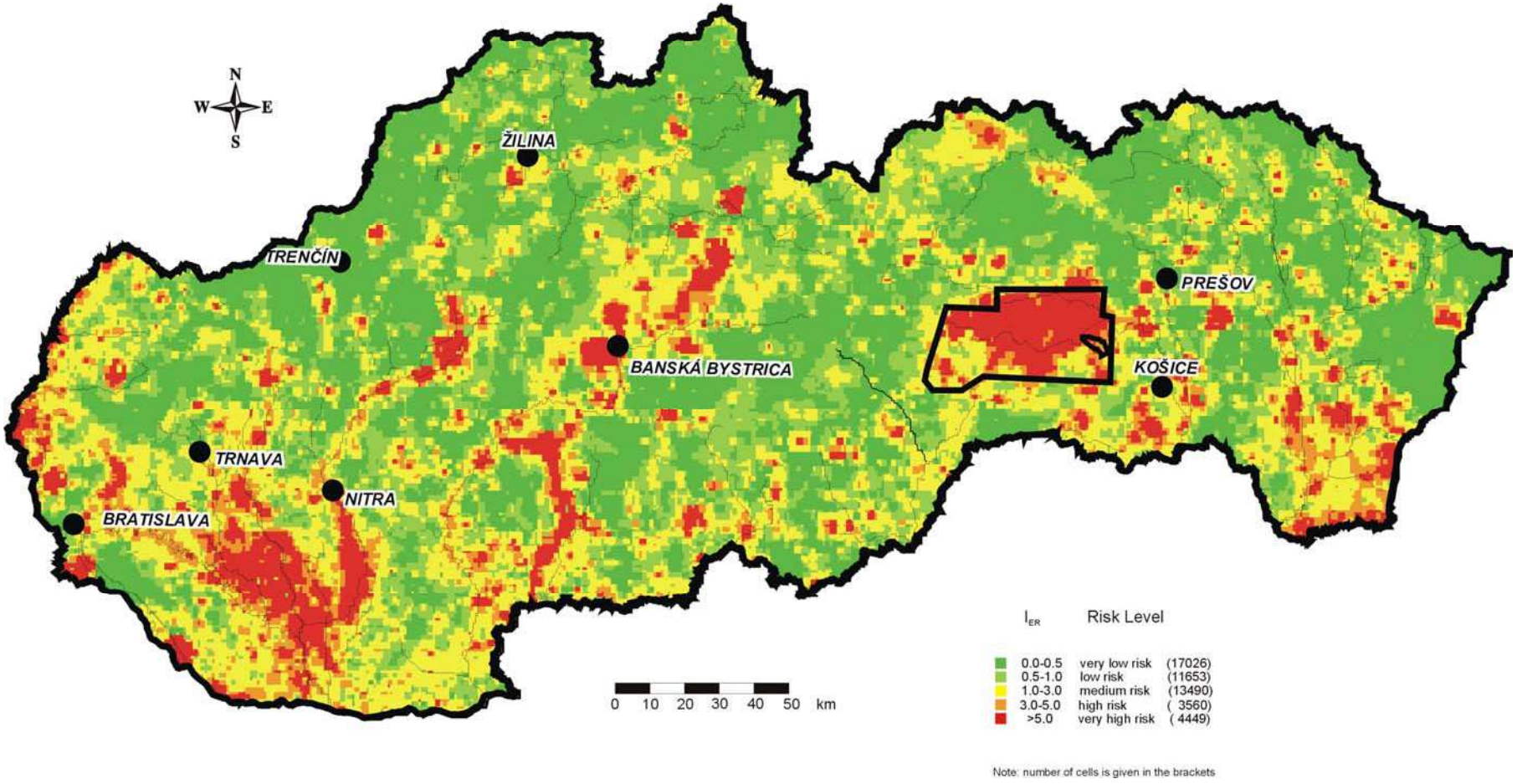
increased occurrence of some diseases

↓

medical-geochemistry research

pilot area

Environmental Risk Assessment Map of the Slovak Republic



Health status of inhabitants monitored and assessed within 2 873 Health - territorial units – municipalities

SGR Mts. – from 18 evaluated Health Indicators

– 10 unfavourable

– 2 favourable

ZLATÁ IDKA vill. – from 18 evaluated indicators

– 15 unfavourable

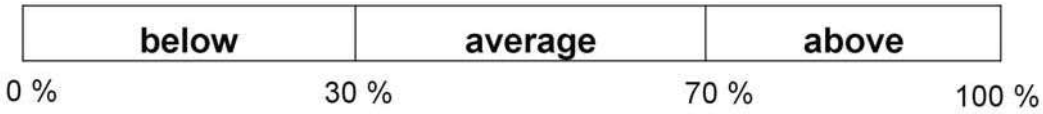
– 1 favourable

in comparison

with Slovakian data

Comparison of selected calculated standardised health indicators between the SGR Mts. and ZLATÁ IDKA village inhabitants and the average Slovak population values (years 1993–1997)

INDICATOR	SLOVAK REPUBLIC of indicator`s values distribution			ZLATÁ IDKA		SGR Mts.	
	below average	average	above average	value	class	value	class
gross mort. per 1000 inhabit.	8,2	9,6	11,2	*14,08*	above	*8,14*	below
men gross mort. per 1000 inhabit.	9	10,6	12,4	*17,19*	above	*8,92*	below
women gross mort. per 1000 inhabit.	7,2	8,7	10,2	*18,16*	above	*7,40*	average
standardised mort. ratio, SMR men	85	99,9	115	*120,48*	above	*119*	above
standardised mort. ratio, SMR women	85	99,9	115	*92,31*	average	*108*	average
percent. of previous deaths inhabit. <65 years	23,2	24,9	28,2	*40,00*	above	*34,5*	above
percent. of previous deaths men <65 years	30,9	32,2	35,8	*50,00*	above	*44,13*	above
percent. of previous deaths women <65 years	14,3	16,4	19	*30,77*	above	*23,27*	above
directly standardised mort.	966	1 076,5	1 186	*1 401,5*	above	*1 603,3*	above
PYLL per 100 000 inhabitants	3 787	4 267	4 747	*7 418,04*	above	*5 784,7*	above
PYLL per 100 000 men	5 400	6 270	7 140	*8 641,75*	above	*9 046*	above
PYLL per 100 000 women	1 892	2 372	2 852	*12 121,75*	above	*9 766*	above
mort. by neoplasms per 100 000 inhabitants	174	199,1	224	*455,3*	above	*205,2*	average
mort. by leukaemia per 100 000 inhabitants	0	3,5	6,2	*0*	below	*8,49*	above
mort. by lungs malig. tumours per 100 000 inhabit.	32,9	44,7	50,2	*113,8*	above	*41,14*	average
mort. by digestive system malig. tumours per 100 000 inhabitants	56,8	71,9	79,8	*56,9*	average	*70,33*	average
mort. by hearth attacks per 100 000 inhabitants	182,3	262,3	277,5	*739,9*	above	*354,6*	above
percent. of spontaneous abortions from all conceptions	5,1	5,9	6,8	*22,22*	above	*6,42*	average



Note: **The below-average value represents 30th percentile of health indicator and the above-average value represents 70th percentile of health indicator for all Slovak inhabitants. The 30th-70th percentile is considered to be the health indicators average. SMR – Standardized Mortality Ratio v %.**

MATERIALS

GEOCHEMICAL DATA & HEALTH INDICATORS

GEOCHEMICAL DATA

- **Data from GEOCHEMICAL ATLAS**
- **New samples and new analyses in SGR Mts.**
  - **Soils** (A horizon, 816 samples)
  - **Stream sediments** (1 844 samples)
  - **Groundwater** (797 samples)
  - **Surface water** (754 samples)
  - **Vegetables** (13 samples)

Total contents, toxicity tests (acute and chronic), **mobility and bioavailability** (5-step extraction), **valence of some metals** (Sb^{3-5}, As^{3-5}, Cr^{t-6}), **mainly toxic metal** (Al, As, Cd, Cu, Cr^{6+}, Hg, Pb, Sb) **organic macro and micro pollutants.**

HEALTH INDICATORS

MEDICAL AND DEMOGRAPHIC DATA

- **Data from national databases**
- **Direct medical research in pilot area**

Health indicators – selected and standardized according to WHO methodology

- **Data from state registers**
- **Data validated by SHI**
- **Data represent average values of 5-years period (1993-1997)**

6 main basic groups of Health indicators are used

- ✓ **Demographic data**
- ✓ **Data of reproductive health**
- ✓ **Total mortality**
- ✓ **Cancer mortality**
- ✓ **Chronic lung diseases**
- ✓ **Cardiovascular diseases**

In each of mentioned groups several separate groups (according to age and sex) and several individual diagnosis are evaluated.

EPIDEMIOLOGICAL – MEDICAL research (ZLATA IDKA vill.)

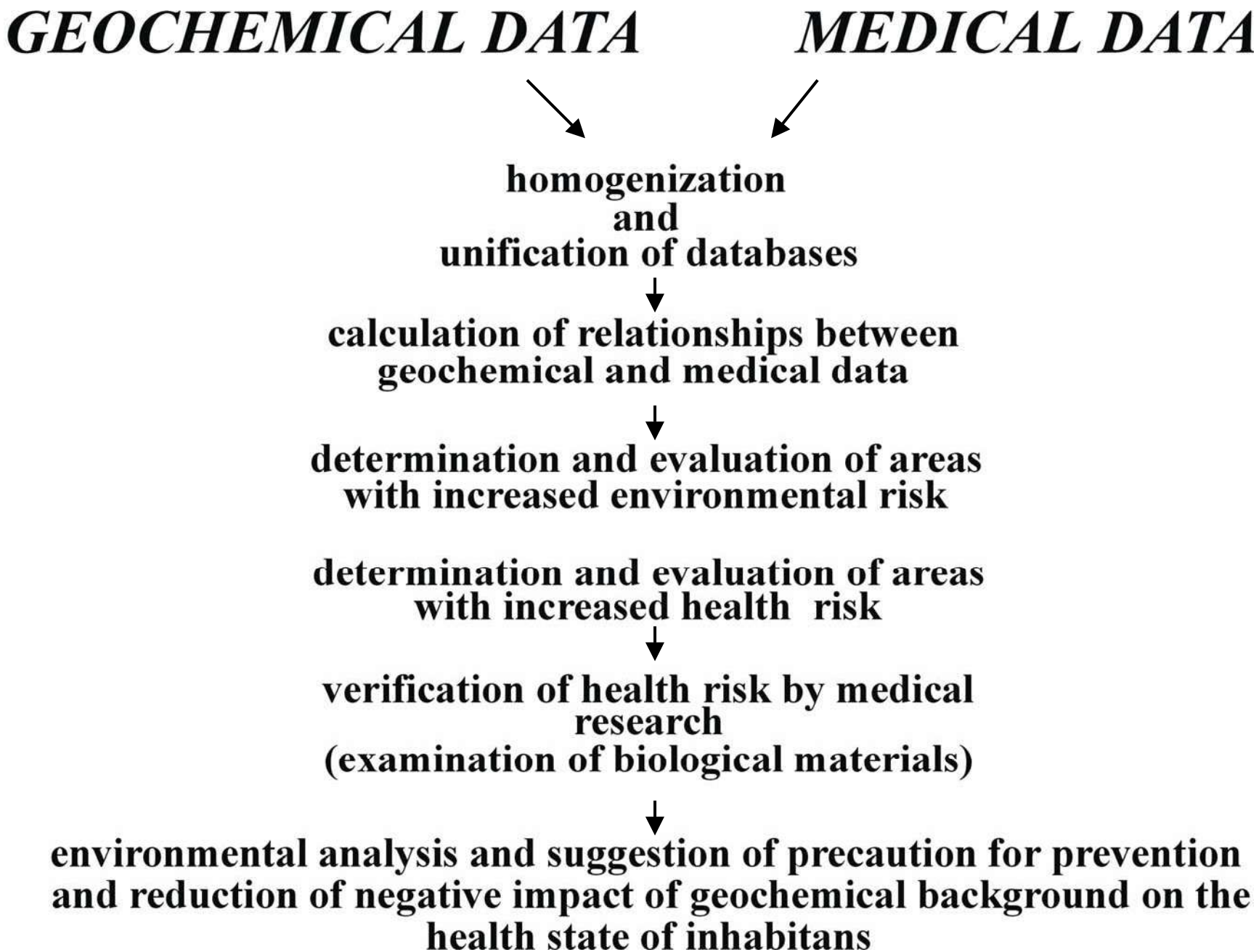
determination of As, Sb in biological materials of people

Hair – 71 respondents

Nails – 73 respondents

Urine – 116 respondents

Blood – 117 respondents


GEOCHEMICAL DATA
MEDICAL DATA
homogenization
and
unification of databases
calculation of relationships between
geochemical and medical data
determination and evaluation of areas
with increased environmental risk
determination and evaluation of areas
with increased health risk
verification of health risk by medical
research
(examination of biological materials)
environmental analysis and suggestion of precaution for prevention
and reduction of negative impact of geochemical background on the
health state of inhabitans

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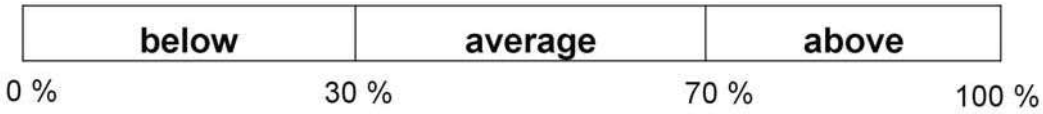

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RESULTS

GEOCHEMISTRY

- Environmental risk calculation and risk assessment maps
- Health risk calculation and risk assessment maps

MEDICAL RESEARCH

- blood, nails, hair, urine

FOOD CHAIN

- locally grown vegetables

RELATIONSHIP – CORRELATION ANALYSIS

Geochemical data – vs. health indicators

Geochemical data – vs. contents of As, Sb in biological materials of people

Environmental risk from contamination of geological environment of the SGR Mts. - municipalities

	Municipalities	I_{ER}	I_{ERgw}	I_{ERs}	I_{ERss}		Municipalities	I_{ER}	I_{ERgw}	I_{ERs}	I_{ERss}
1	Betliar	36.83	12.55	55.83	84.57	50	Mlynky	13.40	16.07	25.90	28.64
2	Bôrka	7.14	1.33	25.80	5.26	51	Mníšek nad Hníl.	15.72	5.80	22.68	39.26
3	Brdárka	3.31	1.49	5.86	6.39	52	Nálepkovo	30.59	1.84	115.69	19.16
4	Brzotín	16.38	1.56	19.18	43.75	53	Nandraž	0.99	0.96	2.64	0.43
5	Čierna Lehota	0.42	0.23	0.60	1.07	54	Nižná Slaná	23.33	22.72	70.83	17.62
6	Čučma	76.51	38.63	139.08	164.01	55	Ochtiná	2.30	4.45	6.30	2.64
7	Debraď	10.31	2.96	31.28	11.75	56	Olcnava	34.95	0.19	129.57	19.89
8	Dobšiná	15.39	19.56	11.96	70.02	57	Opátka	36.05	1.40	138.56	17.34
9	Drienovec	5.90	1.95	17.70	5.32	58	Pača	6.48	10.47	10.15	9.97
10	Drnava	4.93	14.40	4.24	5.43	59	Pašková	1.18	0.03	2.10	0.22
11	Gelnica	21.67	6.11	43.86	45.97	60	Petrovo	6.85	2.52	19.19	6.65
12	Gemerská Pol.	3.67	1.13	6.01	10.92	61	Plešivec	1.51	1.48	1.79	1.13
13	Gemerské Tepl.	2.34	2.85	9.12	0.39	62	Poproč	315.88	90.45	391.39	1016.72
14	Gemerský Sad	2.84	0.92	8.67	0.31	63	Poráč	165.62	1.13	545.87	150.64
15	Gočaltovo	1.45	0.28	3.90	0.44	64	Prakovce	14.88	3.70	27.01	35.61
16	Gočovo	13.87	18.91	32.64	11.33	65	Prihradzany	0.32	0.53	0.09	0.17
17	Hačava	4.10	0.70	14.96	1.59	66	Rakovnica	2.05	1.24	5.68	3.00
18	Háj	3.27	1.15	10.57	1.29	67	Rejdová	5.48	0.39	28.51	1.52
19	Hanková	1.76	2.90	3.75	2.51	68	Rochovce	1.94	3.78	4.23	1.81
20	Helcmanovce	19.24	7.26	28.69	46.28	69	Roštár	3.77	0.26	14.12	1.45
21	Henckovce	6.57	1.55	19.72	7.49	70	Rozložná	7.41	0.45	30.01	0.53
22	Henclová	10.18	9.50	18.21	22.65	71	Rožňava	51.48	35.49	85.75	105.18
23	Hnilčík	29.37	4.61	85.87	46.78	72	Rožňavské Bystré	2.07	0.29	5.92	2.57
24	Hnilec	9.21	1.28	13.54	30.13	73	Rudná	13.73	1.07	25.71	34.98
25	Honce	1.47	0.12	3.15	1.76	74	Rudňany	638.16	2.33	2221.69	334.88
26	Chrasť nad Horn.	100.03	0.71	306.87	90.50	75	Rudník	211.17	31.98	538.46	366.83
27	Chyžné	1.08	0.99	2.20	1.66	76	Slavoška	3.85	1.62	4.87	9.40
28	Jaklovce	12.30	4.06	27.13	19.08	77	Slavošovce	0.99	0.59	1.87	0.97
29	Jasov	20.03	23.23	67.79	42.94	78	Slovinky	27.19	2.29	31.05	91.62
30	Jelšava	5.69	1.85	26.65	1.35	79	Smolnícka Huta	657.55	2927.25	34.21	187.79
31	Jovice	9.25	8.87	8.19	6.60	80	Smolník	187.78	900.60	24.97	179.24
32	Kameňany	0.43	0.77	0.22	0.23	81	Spišská Nová Ves	15.36	23.04	18.07	24.41
33	Kluknava	21.45	2.37	63.44	30.69	82	Spišské Vlachy	9.07	1.61	27.32	9.69
34	Kobeliarovo	10.73	8.42	23.74	12.79	83	Stará Voda	22.42	0.99	64.41	29.40
35	Kocelovce	4.21	1.87	11.00	4.80	84	Šivetice	0.83	2.45	0.71	0.10
36	Kojšov	15.17	25.48	47.77	9.78	85	Štítnik	4.55	0.57	2.71	0.92
37	Kováčová	4.43	11.55	4.07	4.23	86	Štítnik juh	1.53	0.18	3.10	0.26
38	Krásnohor. Podhr.	16.06	14.32	12.67	50.93	87	Štós	154.98	594.35	11.06	5.86
39	Krompachy	34.50	9.77	56.83	88.51	88	Švedlár	30.04	4.77	70.65	94.61
40	Kružná	2.10	2.80	3.27	1.98	89	Teplička	9.68	5.90	23.89	12.80
41	Kunova Teplica	1.03	0.47	1.54	0.63	90	Teplička - juh	33.81	19.03	68.83	53.72
42	Lipovník	2.83	2.03	3.45	6.31	91	Turňa nad Bodvou	7.68	2.85	27.50	0.92
43	Lúčka	3.13	3.94	6.97	3.84	92	Úhorná	3.56	4.52	4.59	8.58
44	Magnezitovce	1.85	5.10	1.70	0.68	93	Veľký Folkmar	5.68	0.97	12.17	11.46
45	Margecany	12.48	1.90	25.68	23.60	94	Vlachovo	10.56	6.23	10.84	47.58
46	Markuška	2.59	3.28	4.48	2.86	95	Vyšná Slaná	7.07	5.24	21.76	14.25
47	Markušovce	269.73	8.97	443.68	835.27	96	Závadka	158.17	13.19	462.37	276.10
48	Matejovce	533.74	1.75	1436.43	246.23	97	Zlatá Idka	180.80	10.96	483.38	268.19
49	Medzev	4.99	15.98	14.13	4.37	98	Zakarovce	24.18	6.95	65.70	29.45

Note:

I_{ERgw}, I_{ERs}, I_{ERss}, I_{ER} –environmental risk index for groundwater, soils, stream sediments and geological compounds as a whole

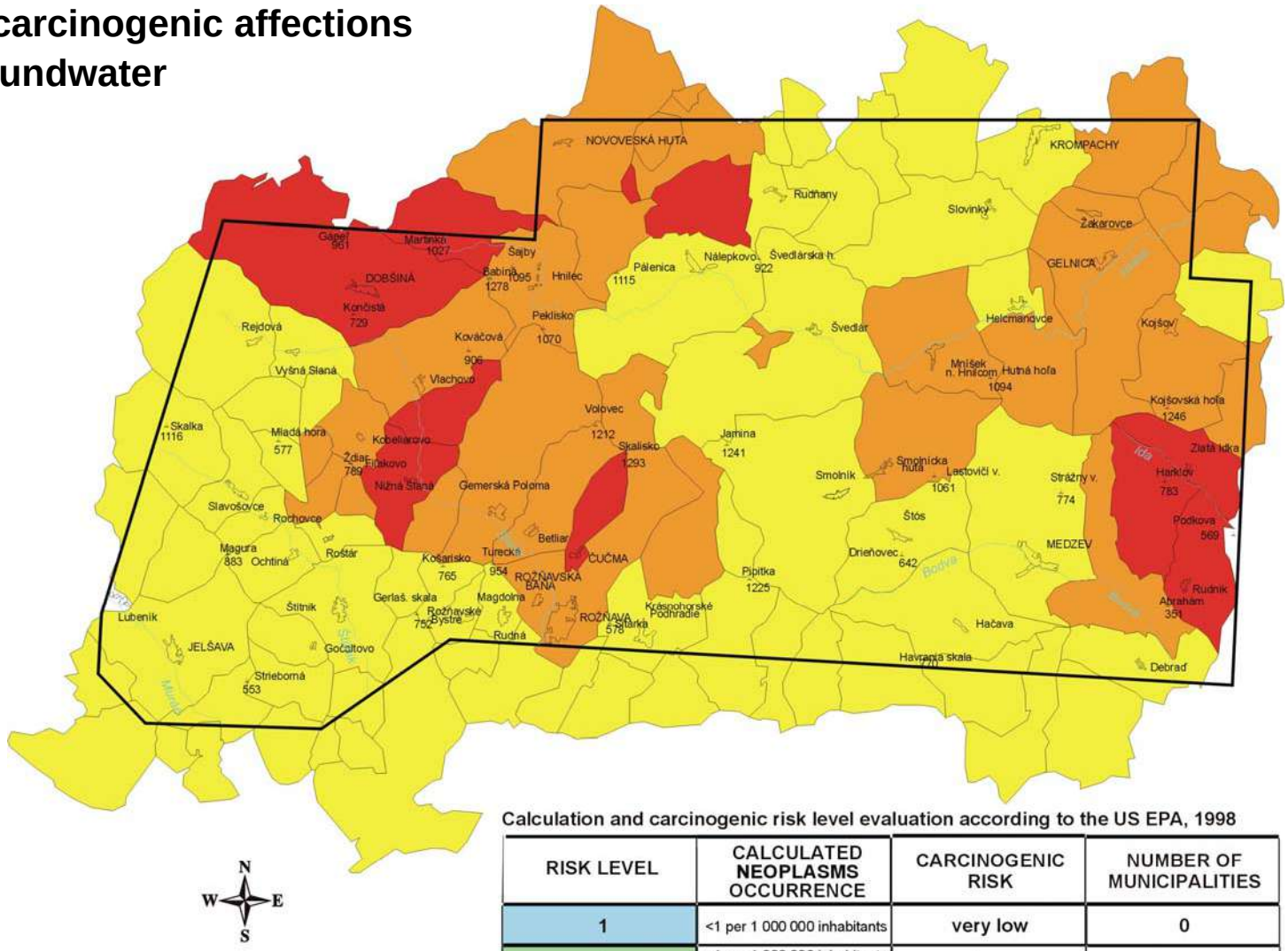
Carcinogenic and chronic health risk calculation from As - groundwater

RfD (Reference Dose - Oral Chronic) = 0,3 µg/kg-day (US EPA, 1995)
CSF (Cancer Slope Factor) = 1,5 mg/kg-day (US EPA, 1995)

n	US EPA method, Rissk Assessment										Slovak regulation			
	municipalities	As content	ADD_{ich} (µg/kg-day)	ADD_{ia} (µg/kg-day)	$ELChR_{ch}$	$ELChR_{a}$	$ChRL_{ch}$	$ChRL_{a}$	ELCR	CRL	ADD_{ia} (µg/kg-day)	HQ_{chra} (ADD/RfD)	ELCR	CRL
1	Betliar	0.00948	0.720	0.270	2E+00	9E-01	2	1	3,7E-04	4	0.2709	0.9029	4.1E-04	4
2	Borka	0.00063	0.048	0.018	2E-01	6E-02	1	1	2,5E-05	3	0.0180	0.0600	2.7E-05	3
3	Brdarka	0.00082	0.062	0.023	2E-01	8E-02	1	1	3,2E-05	3	0.0234	0.0781	3.5E-05	3
4	Brzotín	0.00173	0.130	0.049	4E-01	2E-01	1	1	6,8E-05	3	0.0494	0.1648	7.4E-05	3
5	Cierna Lehota	0.00096	0.073	0.027	2E-01	9E-02	1	1	3,8E-05	3	0.0274	0.0914	4.1E-05	3
6	Cucma	0.03484	2.600	1.000	9E+00	3E+00	3	2	1,4E-03	5	0.9954	3.3181	1.5E-03	5
7	Debrad	0.00117	0.089	0.033	3E-01	1E-01	1	1	4,6E-05	3	0.0334	0.1114	5.0E-05	3
8	Dobsina	0.03059	2.300	0.870	8E+00	3E+00	3	2	1,2E-03	5	0.8740	2.9133	1.3E-03	5
9	Drienovec	0.00073	0.055	0.021	2E-01	7E-02	1	1	2,9E-05	3	0.0209	0.0695	3.1E-05	3
10	Drnava	0.00125	0.095	0.036	3E-01	1E-01	1	1	4,9E-05	3	0.0357	0.1190	5.4E-05	3
11	Gelnica	0.00819	0.620	0.230	2E+00	8E-01	2	1	3,2E-04	4	0.2340	0.7800	3.5E-04	4
12	Gemerska Poloma	0.00391	0.300	0.110	1E+00	4E-01	1	1	1,5E-04	4	0.1117	0.3724	1.7E-04	4
↓														
100	Zakarovce	0.01568	1.200	0.450	4E+00	1E+00	2	2	6,1E-04	4	0.4480	1.4933	6.7E-04	4

ADD_{ich} – average daily dose, ingestion, children; ADD – average daily dose, ingestion, adults; $ELChR_{ch}$ – excess lifetime chronic risk affection children; $ELCh_{a}$– excess lifetime chronic risk affection adults; $ChRL_{ch}$ – chronic risk level – children; $ChRL_{a}$ – chronic risk level – adults; ELCR – exess lifetime cancer risk affection (adults); CRL – cancer risk level; HQ_{chra} – hazard quotients, chronic risk, adults

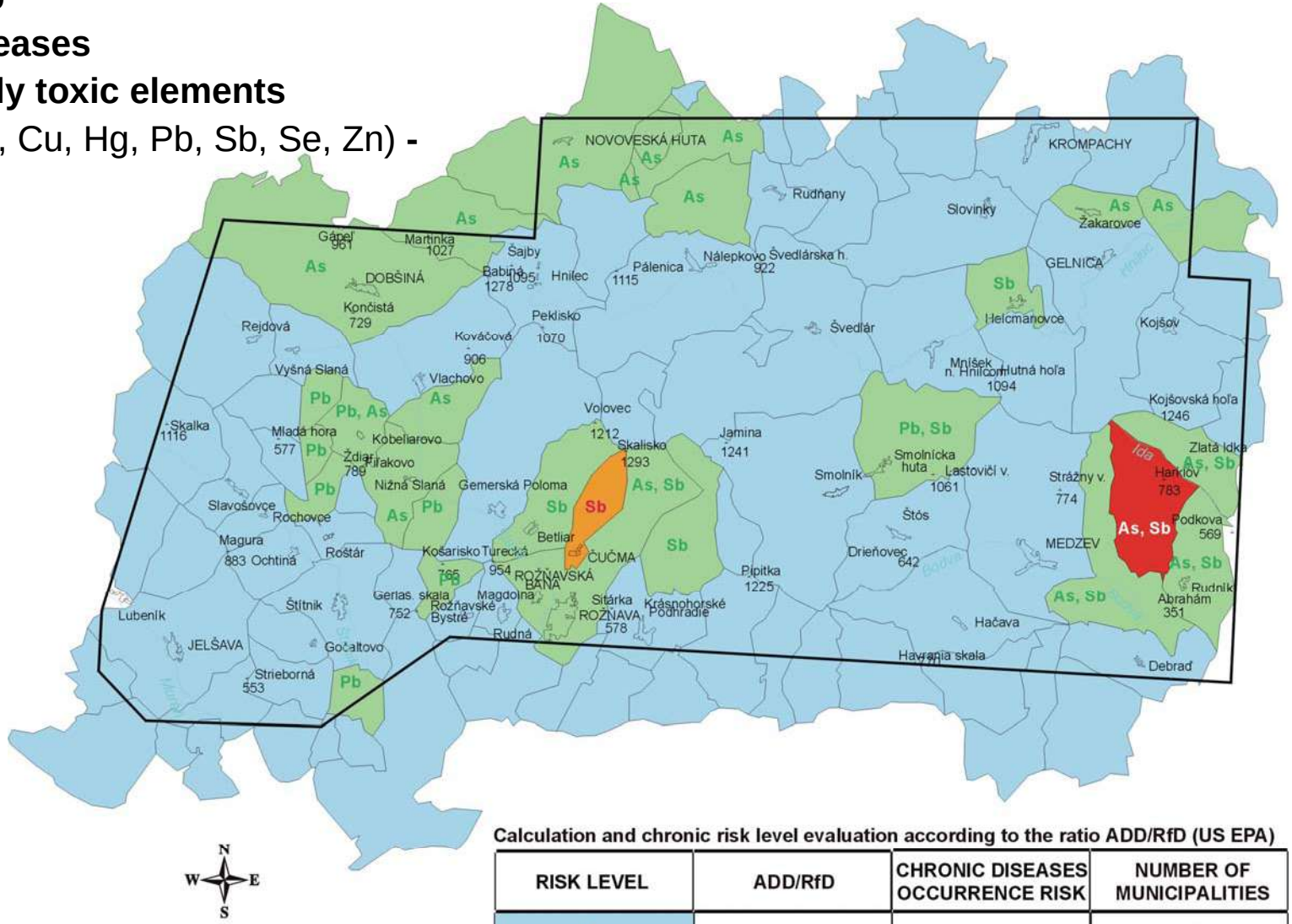
Risk level map of carcinogenic affections from Arsenic - groundwater



Calculation and carcinogenic risk level evaluation according to the US EPA, 1998

RISK LEVEL	CALCULATED **NEOPLASMS** OCCURRENCE	CARCINOGENIC RISK	NUMBER OF MUNICIPALITIES
1	<1 per 1 000 000 inhabitants	very low	0
2	>1 per 1 000 000 inhabitants <1 per 100 000 inhabitants	low	0
3	>1 per 100 000 inhabitants <1 per 10 000 inhabitants	medium	61
4	>1 per 10 000 inhabitants <1 per 1 000 inhabitants	high	29
5	>1 per 1 000 inhabitants	very high	10

Risk level map
of chronic diseases
from potentially toxic elements
(As, Ba, Cd, Cr, Cu, Hg, Pb, Sb, Se, Zn) **-**
groundwater

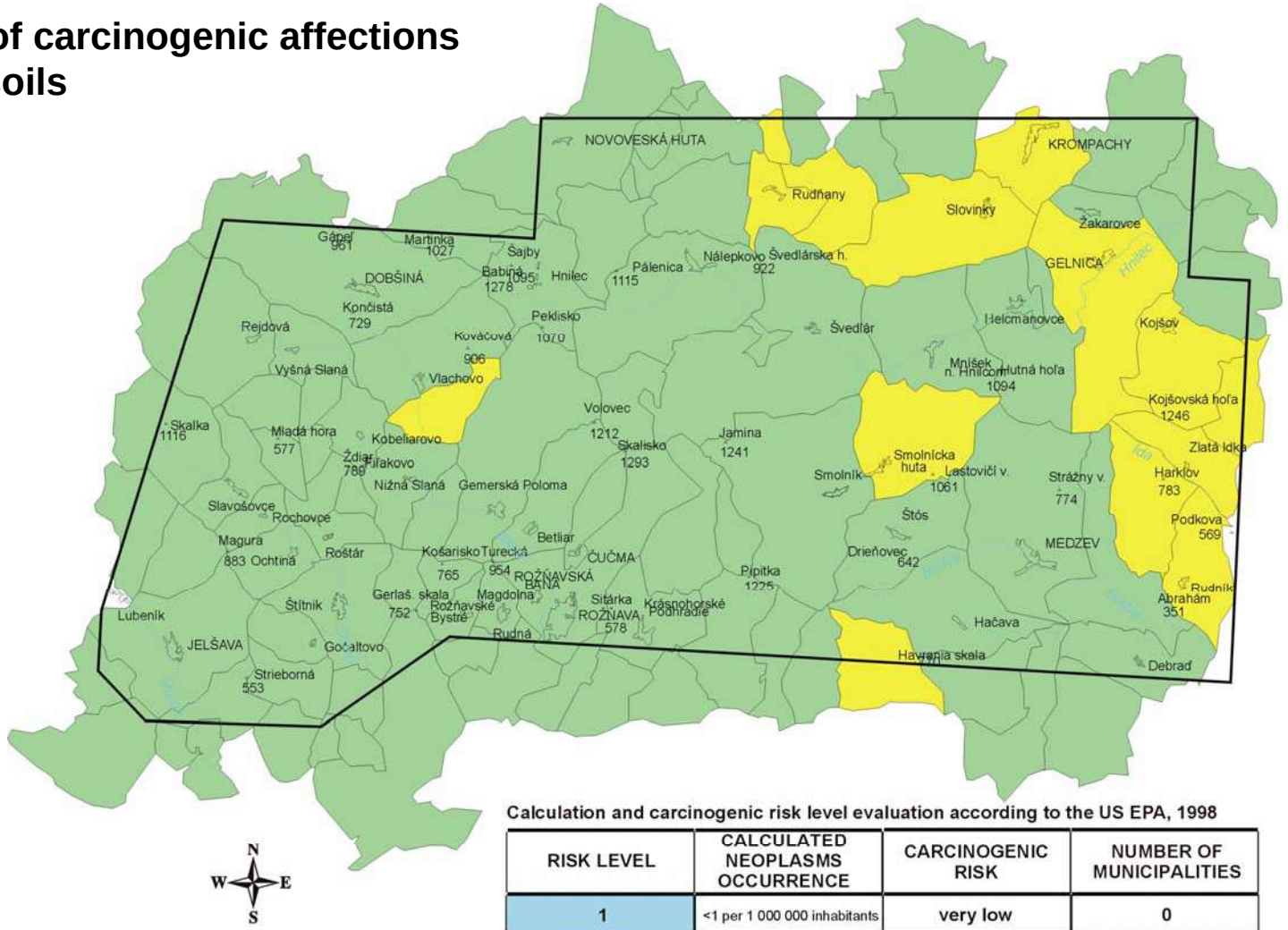


Calculation and chronic risk level evaluation according to the ratio ADD/RfD (US EPA)

RISK LEVEL	ADD/RfD	CHRONIC DISEASES OCCURRENCE RISK	NUMBER OF MUNICIPALITIES
1	≤ 1	no risk	72
2	> 1 ≤ 5	low	26
3	> 5 ≤ 10	medium	1
4	> 10	high	1

Symbols - risk elements

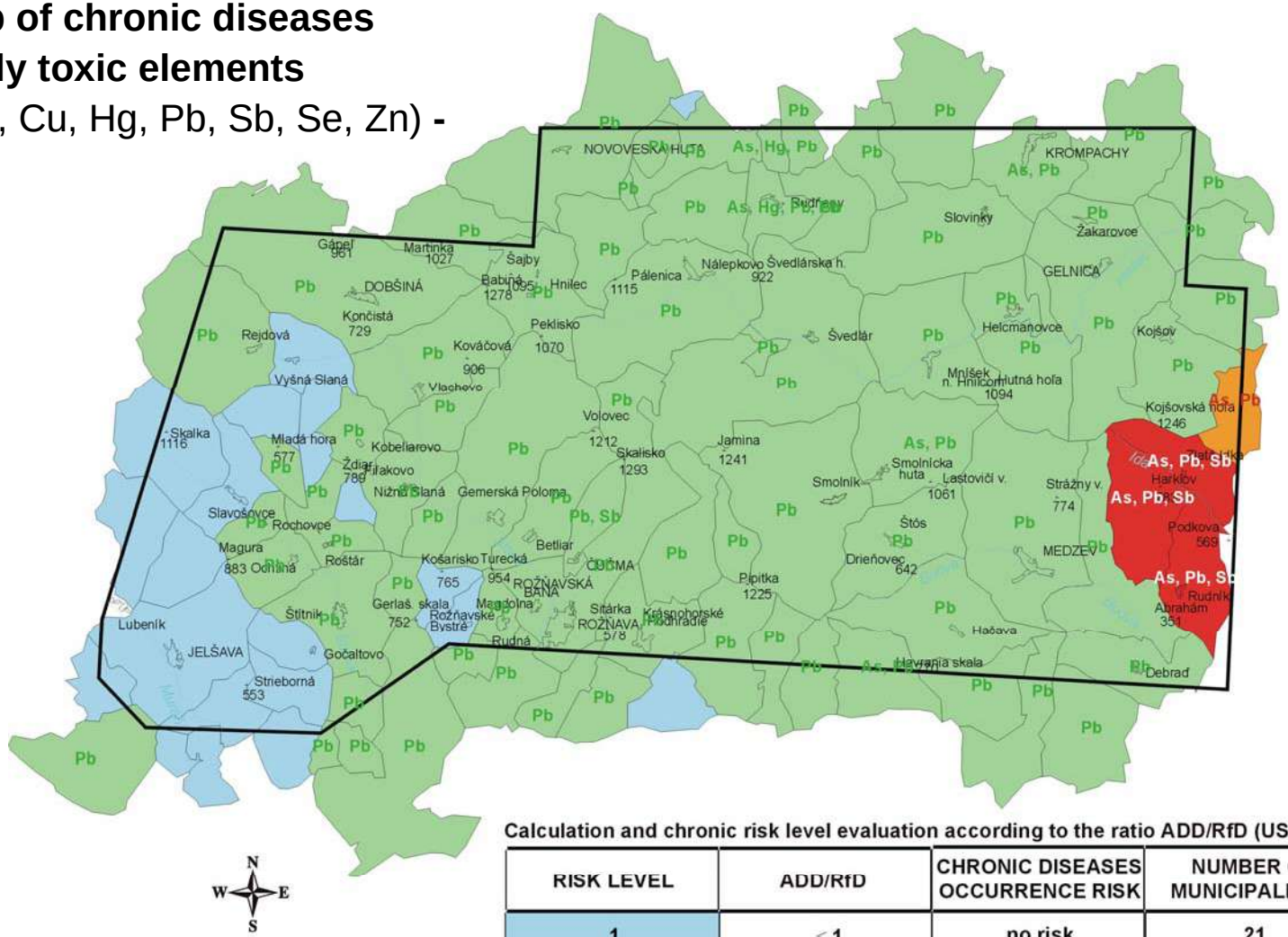
Risk level map of carcinogenic affections from Arsenic - soils



Calculation and carcinogenic risk level evaluation according to the US EPA, 1998

RISK LEVEL	CALCULATED NEOPLASMS OCCURRENCE	CARCINOGENIC RISK	NUMBER OF MUNICIPALITIES
1	<1 per 1 000 000 inhabitants	very low	0
2	>1 per 1 000 000 inhabitants <1 per 100 000 inhabitants	low	86
3	>1 per 100 000 inhabitants <1 per 10 000 inhabitants	medium	14
4	>1 per 10 000 inhabitants <1 per 1 000 inhabitants	high	0
5	>1 per 1 000 inhabitants	very high	0

Risk level map of chronic diseases from potentially toxic elements (As, Ba, Cd, Cr, Cu, Hg, Pb, Sb, Se, Zn) **- children, soils**



Calculation and chronic risk level evaluation according to the ratio ADD/RfD (US EPA)

RISK LEVEL	ADD/RfD	CHRONIC DISEASES OCCURRENCE RISK	NUMBER OF MUNICIPALITIES
1	≤ 1	no risk	21
2	> 1 ≤ 5	low	75
3	> 5 ≤ 10	medium	1
4	> 10	high	3

Symbols - risk elements

RELATIONSHIP – geochemistry and medical data

Sperman correlation coefficients, confidence levels α and significance of relationship of chemical elements and health indicators, SGR - groundwater

elements	health indicator	n	R	α	significance
As	mortality by neoplasms	100	0,263	0,008	++
As	mortality by lungs malignant tumours	100	0,2395	0,016	+
Cr	mortality by neoplasms	100	0,3385	0,0006	+++
Cr	mortality by lungs malignant tumours	100	0,2757	0,0055	++
Cu	mortality by neoplasms	100	0,3745	0,0001	+++
Cu	mortality by lungs malignant tumours	100	0,3092	0,0017	++
Sb	mortality by neoplasms	100	0,5070	0,0000	+++
Sb	mortality by lungs malignant tumours	100	0,4422	0,0000	+++

α <0,001 – very high dependence +++, α <0,01 – high dependence ++, α <0,005 – proved dependence +

Sperman correlation coefficients, confidence levels α and significance of relationship of chemical elements and health indicators, SGR - soils

elements	health indicator	n	R	α	significance
As	mortality by neoplasms	100	0,2670	0,0072	++
As	mortality by lungs malignant tumours	100	0,2591	0,0092	++
Cr	mortality by neoplasms	100	0,2435	0,0147	+
Cr	mortality by lungs malignant tumours	100	0,1706	0,0897	
Cu	mortality by neoplasms	100	0,2567	0,0099	++
Cu	mortality by lungs malignant tumours	100	0,2103	0,0357	+
Sb	mortality by neoplasms	100	0,3697	0,0002	+++
Sb	mortality by lungs malignant tumours	100	0,3150	0,0014	++

α <0,001 – very high dependence +++, α <0,01 – high dependence ++, α <0,005 – proved dependence +

Sperman correlation coefficients, confidence levels α and significance of relationship of chemical elements and health indicators, SGR – stream sediments

elements	health indicator	n	R	α	significance
As	mortality by neoplasms	100	0,4258	0,0000	+++
As	mortality by lungs malignant tumours	100	0,3947	0,0000	+++
Cr	mortality by neoplasms	100	0,1300	0,1973	
Cr	mortality by lungs malignant tumours	100	0,1516	0,1322	
Cu	mortality by neoplasms	100	0,3364	0,0006	+++
Cu	mortality by lungs malignant tumours	100	0,2898	0,0034	++
Sb	mortality by neoplasms	100	0,3382	0,0006	+++
Sb	mortality by lungs malignant tumours	100	0,2677	0,0071	++

α <0,001 – very high dependence +++, α <0,01 – high dependence ++, α <0,005 – proved dependence +

Correlation between As and Sb in soil and biological materials of people, ZLATÁ IDKA vill.

Linear correlation (n=17)

	As – blood	As – urine	Sb – blood	Sb – urine	As – soil	Sb – soil
As – blood	1					
As – urine	0,11	1				
Sb – blood	0,12	0,46	1			
Sb – urine	0,07	0,57	0,72	1		
As – soil	0,52	0,29	0,35	0,29	1	
Sb – soil	0,43	0,32	0,40	0,33	0,99	1

Spermans order correlation coefficients between soil and biological materials

element	biological mat.	n	R	α	significance
As	blood	27	0,031	0,881	
	urine	36	0,248	0,188	
	nail	24	0,698	0,0001	+++
	hair	25	0,295	0,157	
Sb	blood	17	0,241	0,393	
	urine	22	0,146	0,543	
	nail	25	0,597	0,0010	+++
	hair	23	0,091	0,693	

- **Statistics proves significant correlation between contents of chemical elements in the environment and health indicators. Some relations can be evaluated as STOCHASTICH only and some of them as CAUSAL.**

- **Chemical elements regarding to their relationship to Health indicators could be divided:**

  - ✓ **Causal elements** (e.g.:As, Sb, Hg, Pb, ...) **with confirmed and approved relation to health indicators**

  - ✓ **Indicative elements** (e.g.: Bi, Be, Ga, Li, ...) **with high stochastic dependence thanks to the geochemical relationships with causal elements**

CONCLUSIONS

- In areas with higher toxic element contents in environment there were documented also their higher contents in biological materials of people and in food chain , as well as significant unfavourable health indicators.
- It is relatively simple to prove direct negative impact of geological environment on the human health status in the strong polluted areas. On the other hand, to show the negative impact in the low and medium contaminated areas is more problematic, but it may be more important.
- Approved relation between health and geochemical parameters can have a very important role in early recognition of the health risk. Although this risk might not be prevented completely, but its consequences may be reduced.
- Realised calculations and maps of Environmental and Health risk enable to assess influence of geological environment contamination on other compounds of Environment and Human health. They are objective base for following detail works for treatment of the environment and for the improvement of human health.