# 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

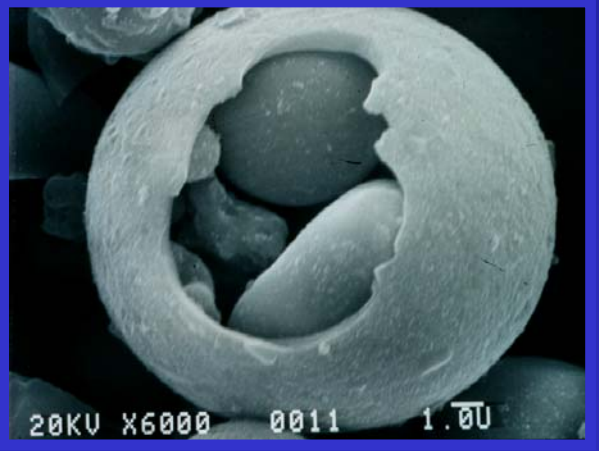
- X-Ray Diffraction (Semi-quant./Direct)
- Scanning Electron Microscopy (Qual.-Semi-quant)
  +Energy Dispersive X-Ray (Indirect)
- Infrared Spectroscopy (Qual.-Semi-quant./Indirect)
- Electron Microprobe Analysis (Qual/Indirect)
- Transmission Electron Microscopy (Qual/Indirect)
- Ion Microprobe (Qual/Indirect)
- 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*

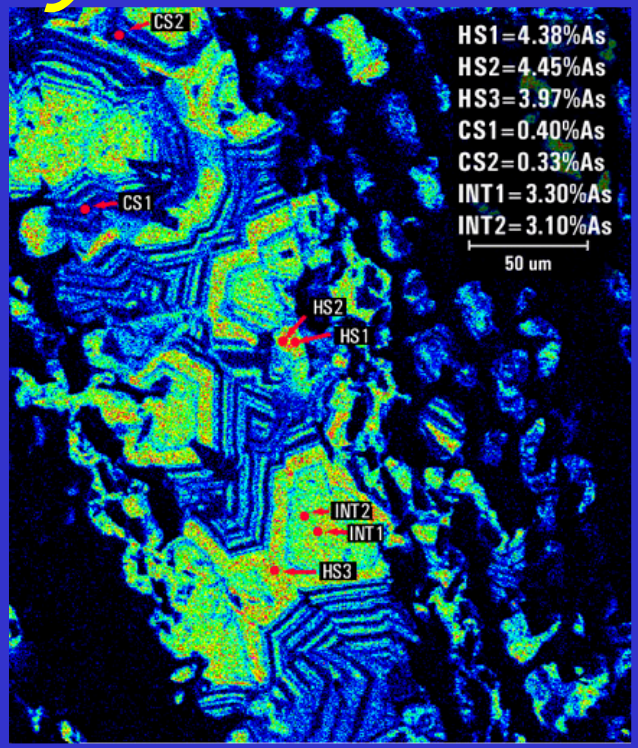
*SEM Image of Fly Ash Particle*



# Electron Microprobe

# *Arsenic in Coal: Microanalysis*

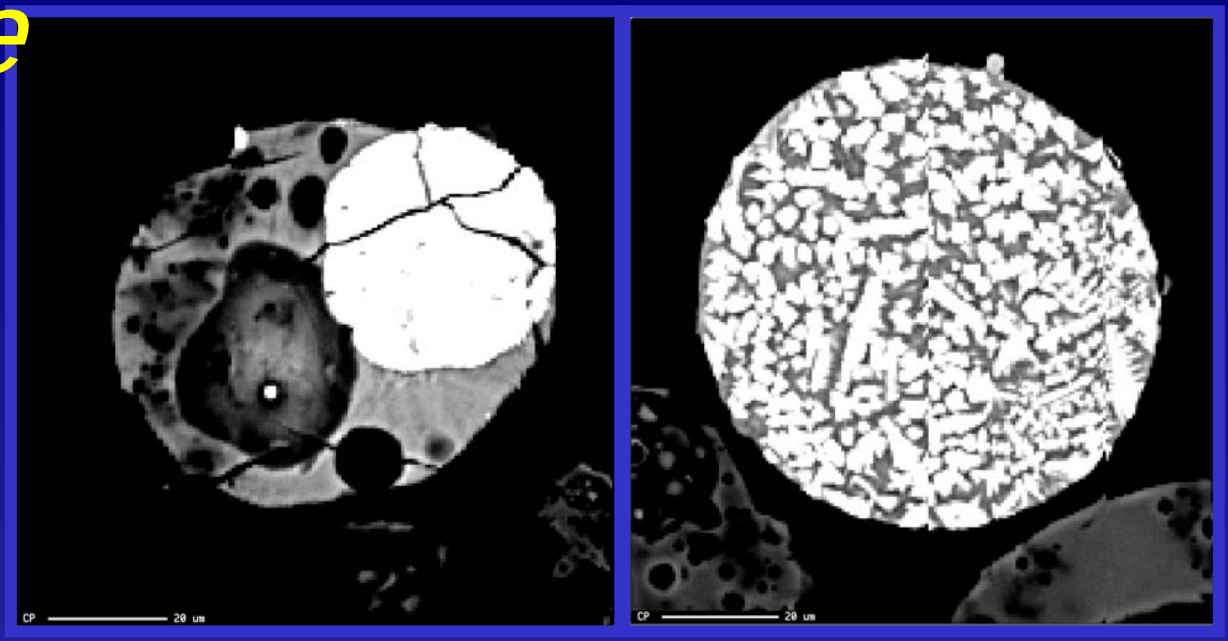
- *Arsenic is a trace to minor element in pyrite; concentrations ≥150 ppm can be determined using the electron microprobe.*
- *Direct confirmation of As residence indicated by other methods, but shows concentrations vary widely within and between grains.*



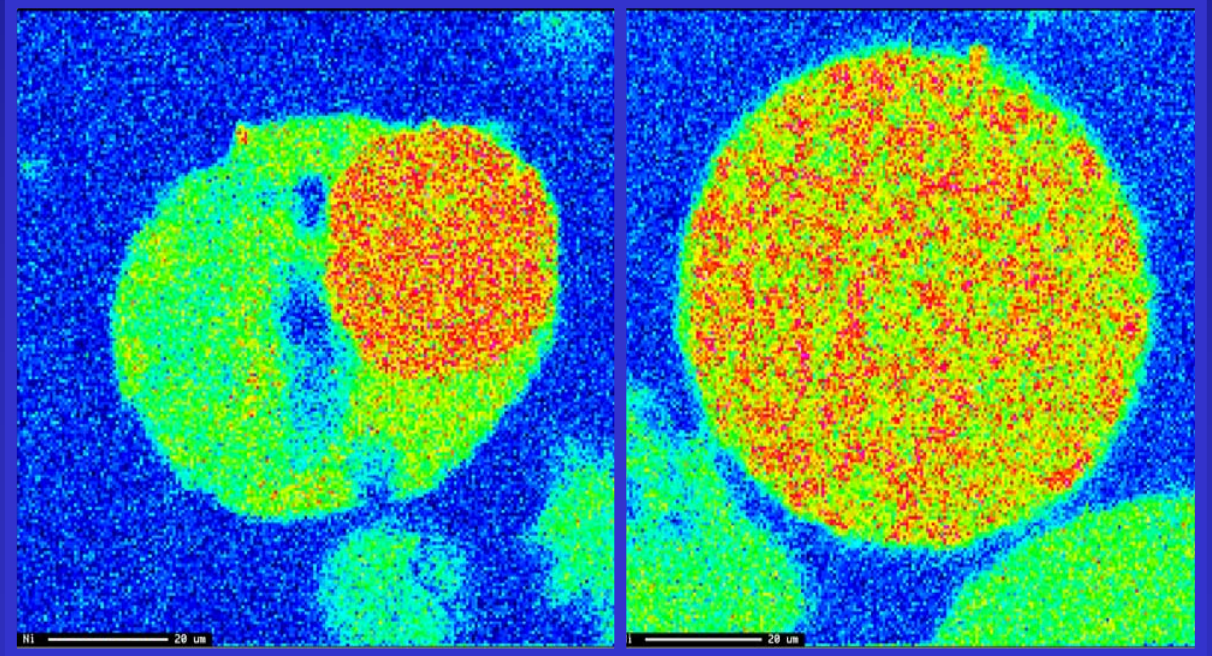

*Arsenic-rich pyrite (to 4.5 wt. % As) with oscillatory zoning, Warrior Basin coal, Alabama.*

# Microprobe Results

*Back-scattered Electron Images*




*Nickel Elemental Maps*



# SHRIMP-RG Ion Microprobe

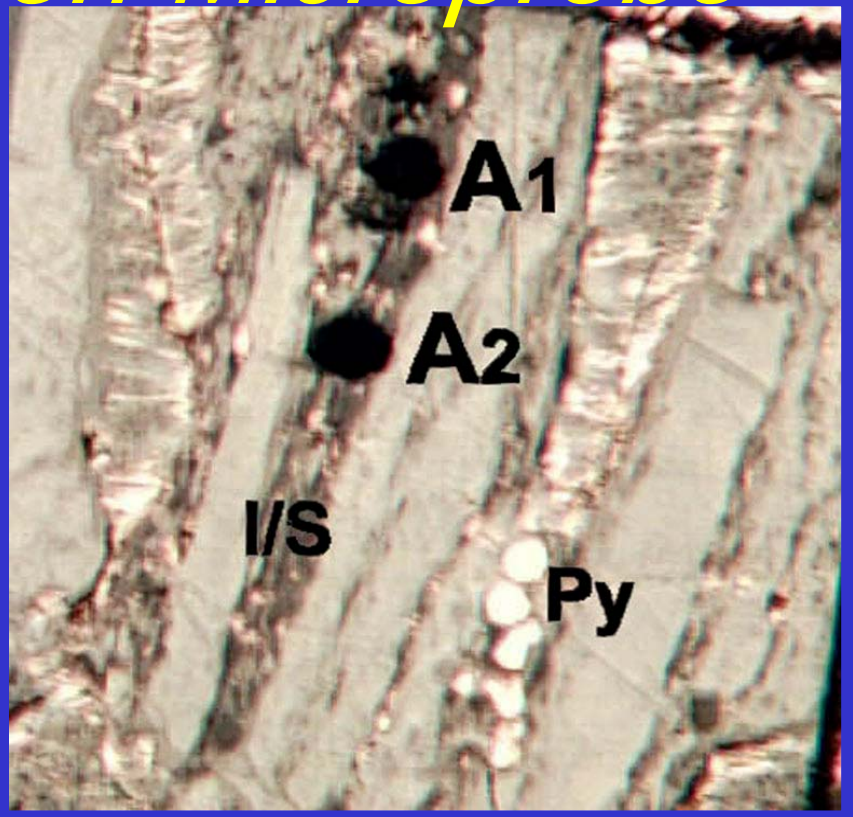

*Sensitive High-Resolution Ion Microprobe Reverse Geometry*

- *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:*

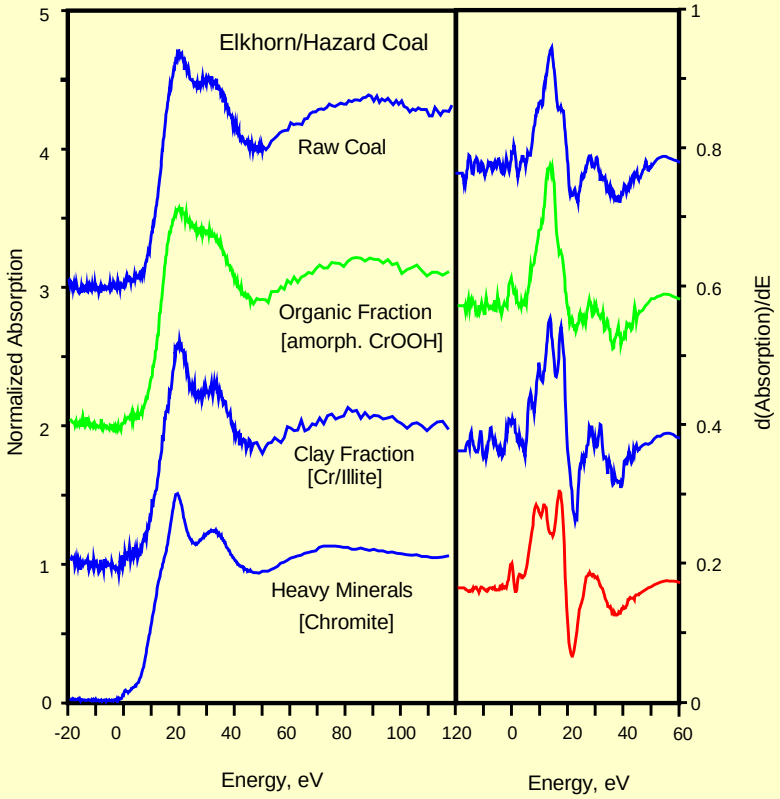
  *Cr = 11 to 176 ppm*
  *Mn = 2 to 149 ppm*
  *V = 23 to 248 ppm*
- *Confirms leaching results and electron microprobe data.*




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

# Chromium in Coal: XAFS

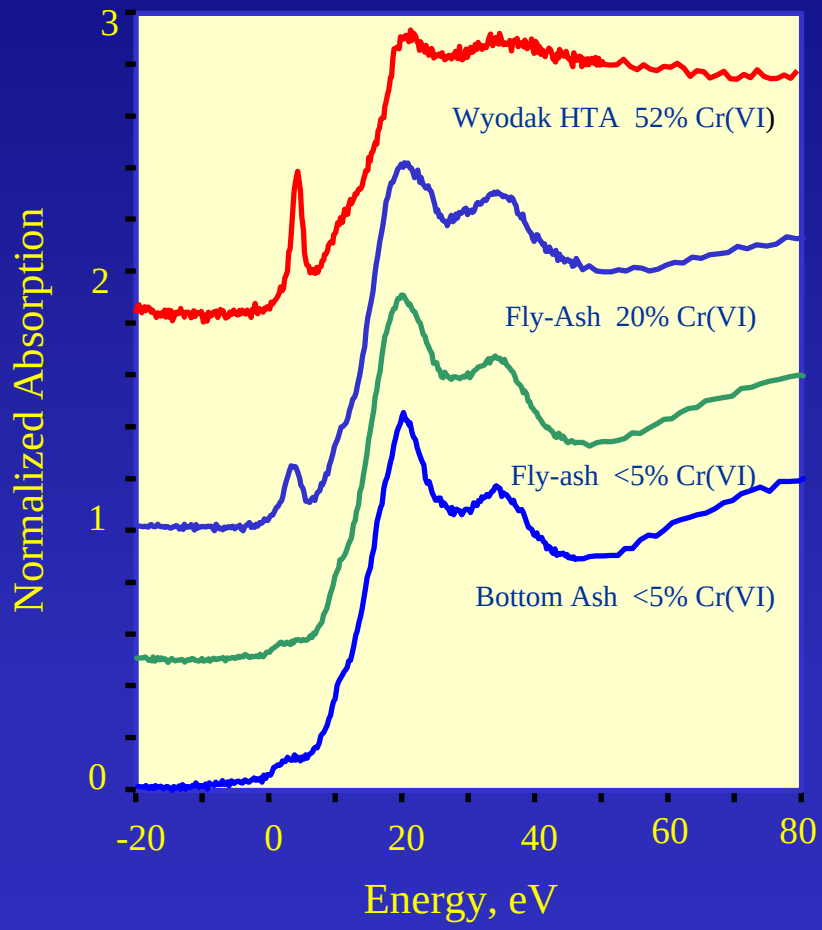
- *Two major forms identified:*
  - *$Cr^{3+}$/illite*
  - *Org. associated Cr (Amorph. CrOOH)*
- *Chromite- Common only in coals unusually rich in Cr*
- *Oxidation State- Always $Cr^{3+}$*




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.

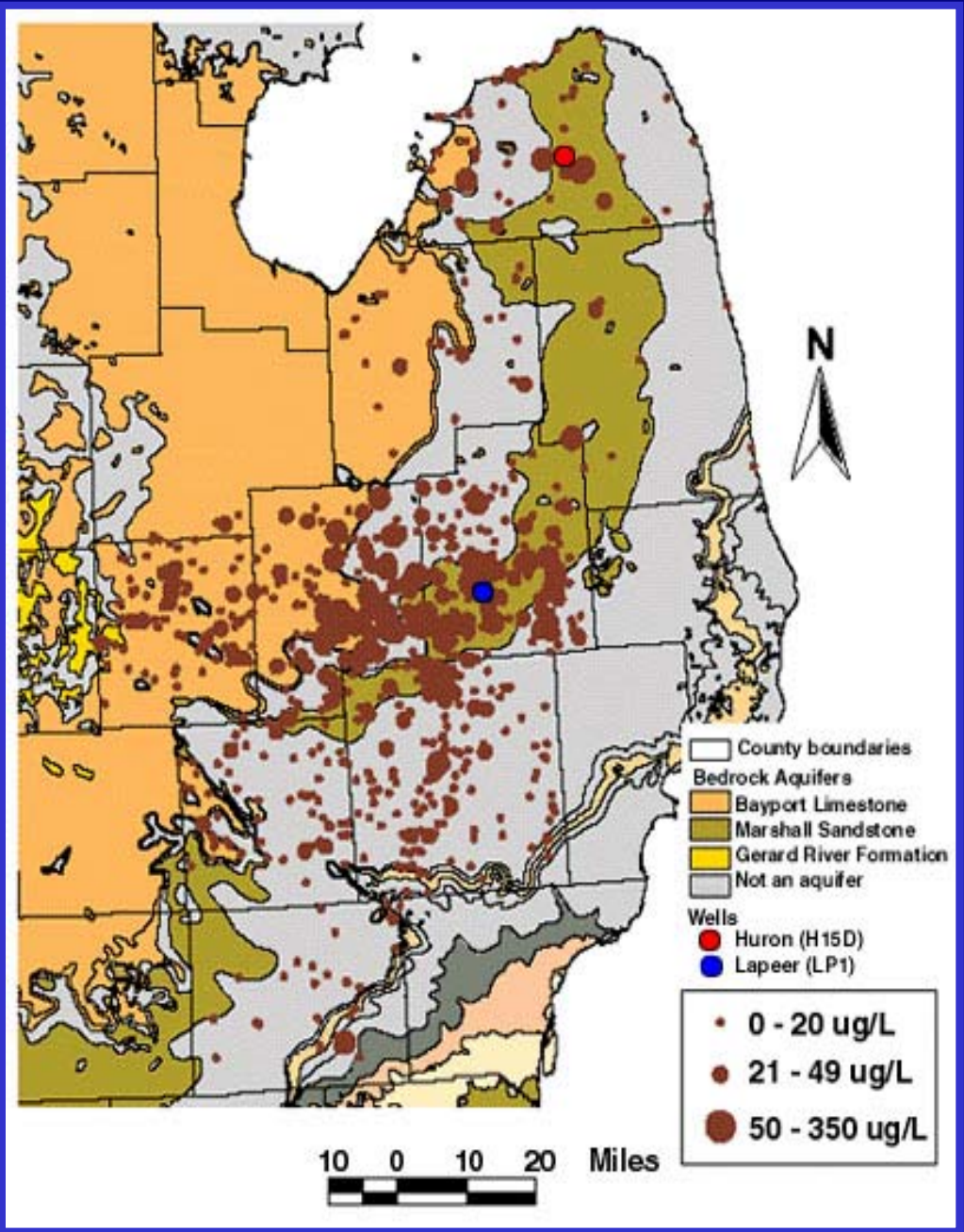


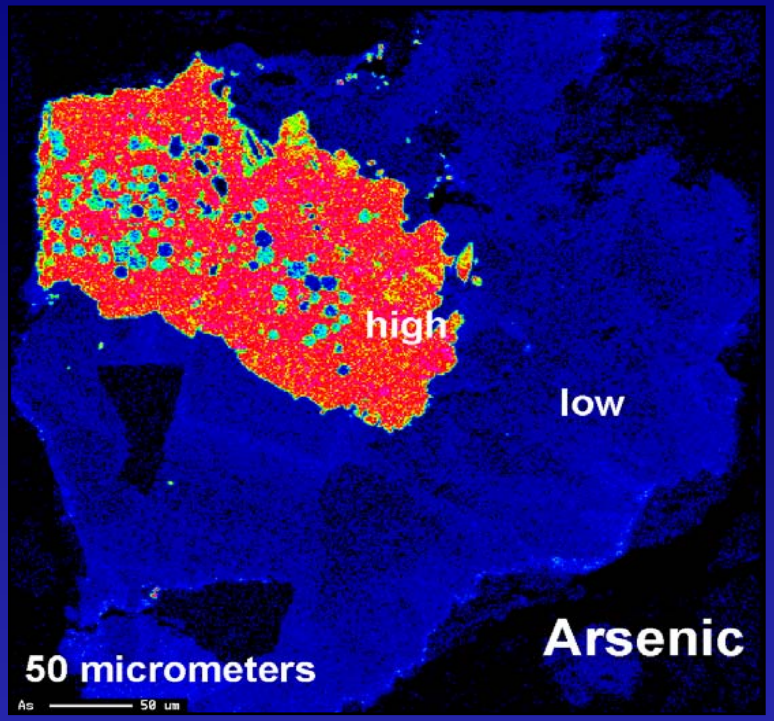
# *Distribution of As-levels**

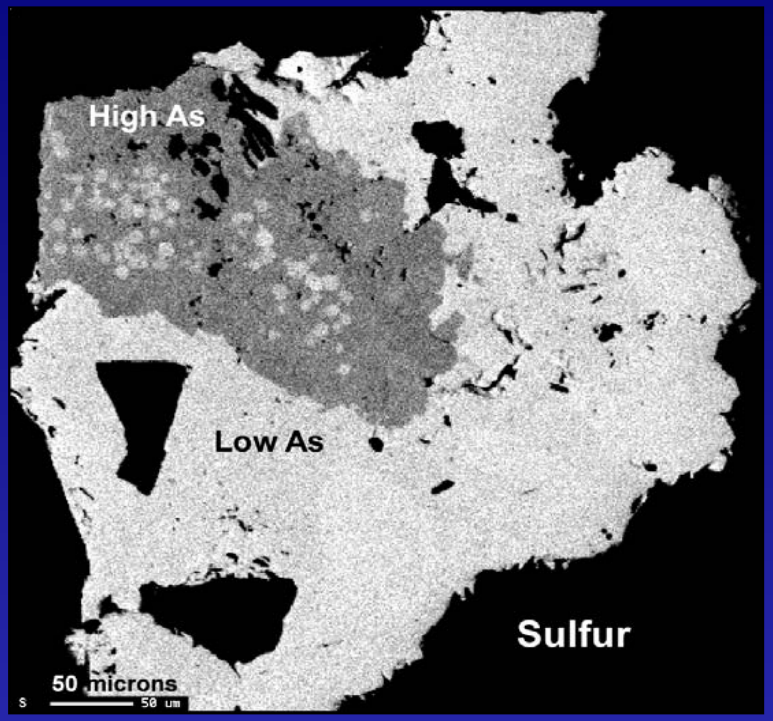
*Max. arsenic is 6-8 times EPA standard.*

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

**MDCH data*

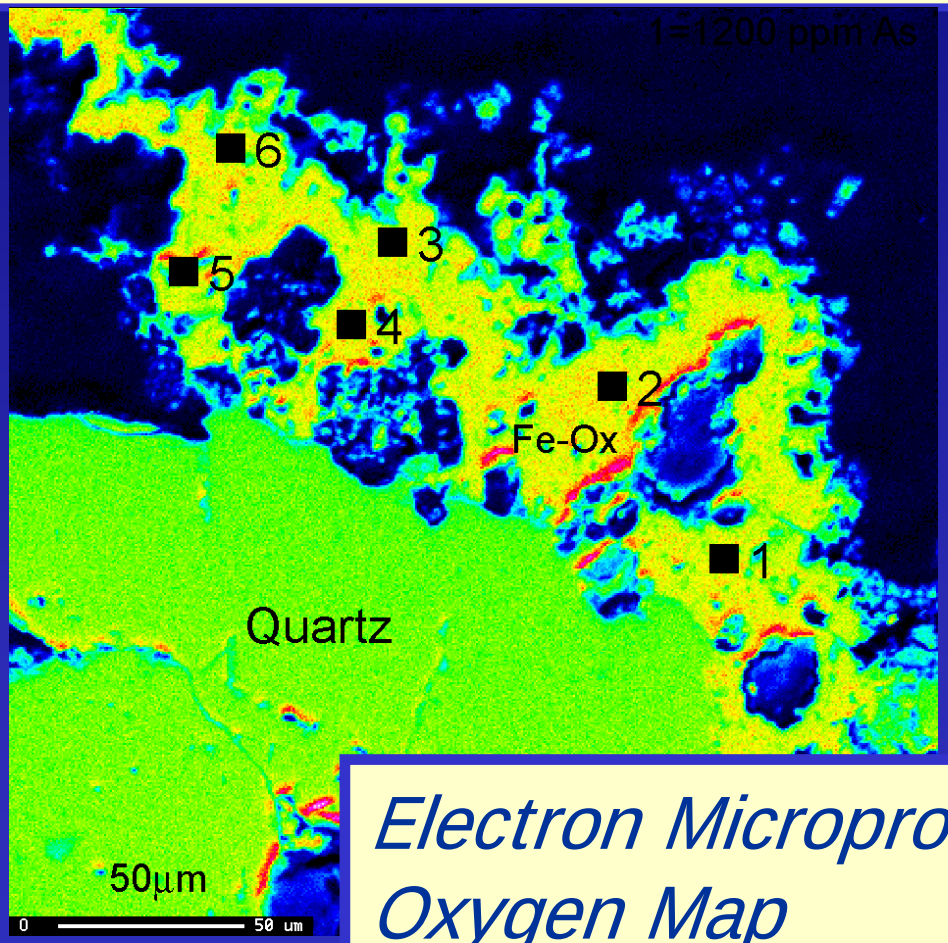





*Electron microprobe elemental maps for As and S show high-As (6-7 wt. %) pyrite occurs as the second of 3 pyrite generations.*

# *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**

↓

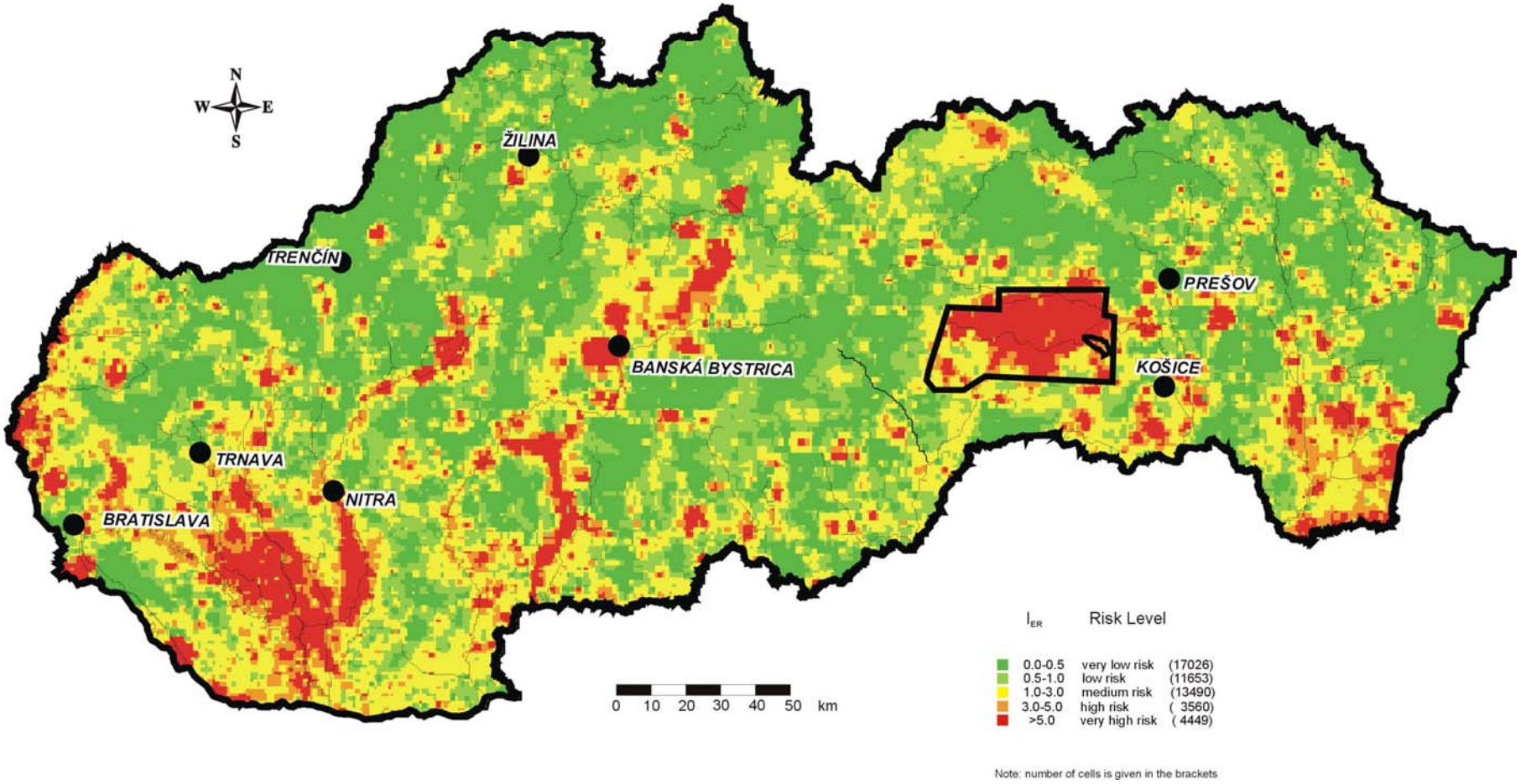
**increased occurrence of some diseases**

↓

**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**

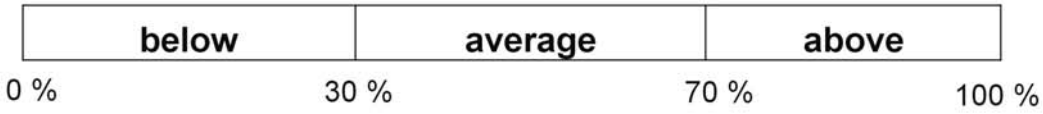
**– 1 favourable**

**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.)

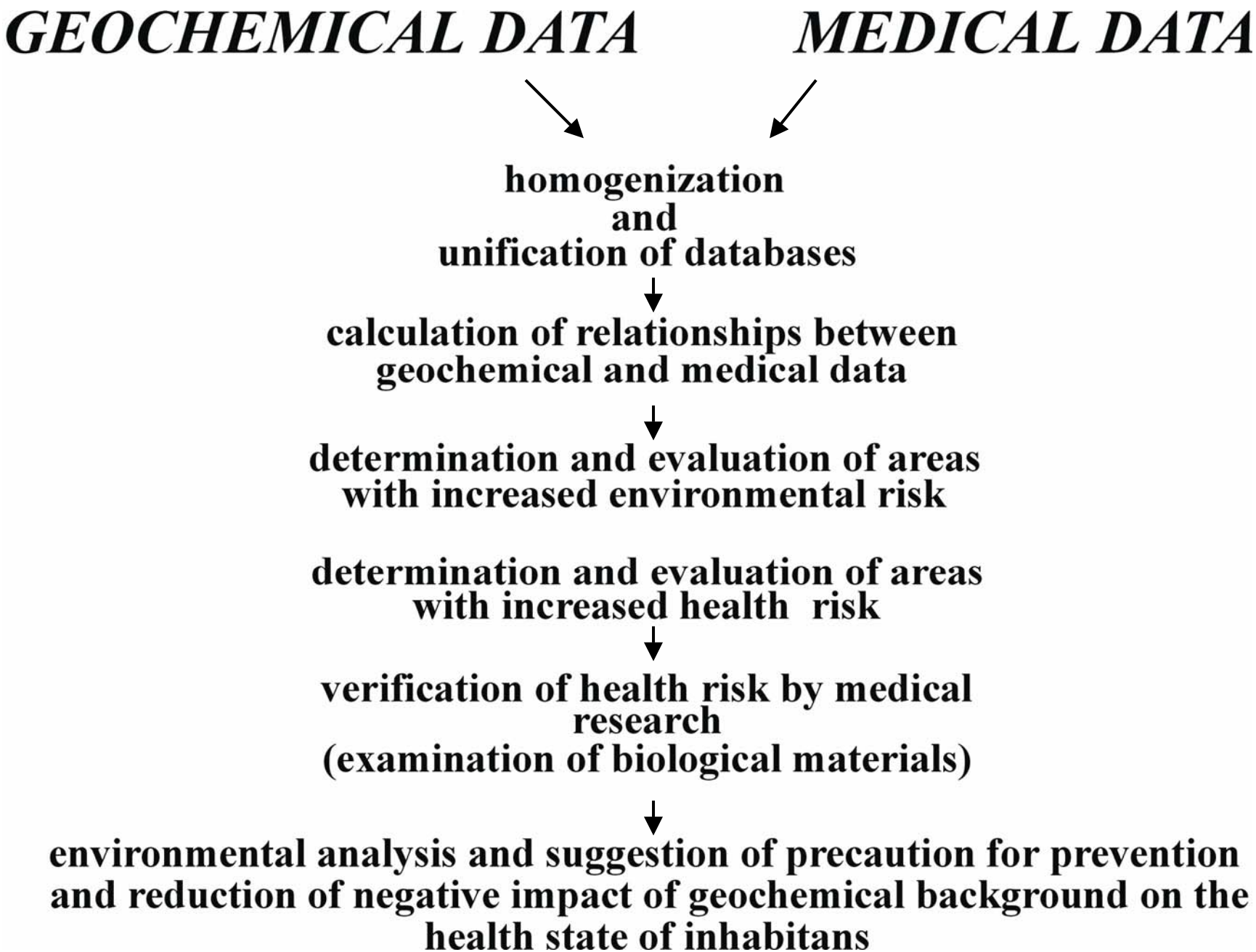
determination of As, Sb in biological materials of people

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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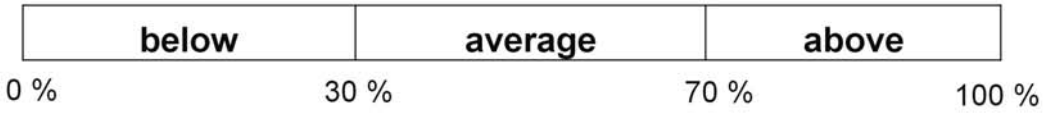


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# RESULTS

## 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 Hnil. | 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 | Teplièka - 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**

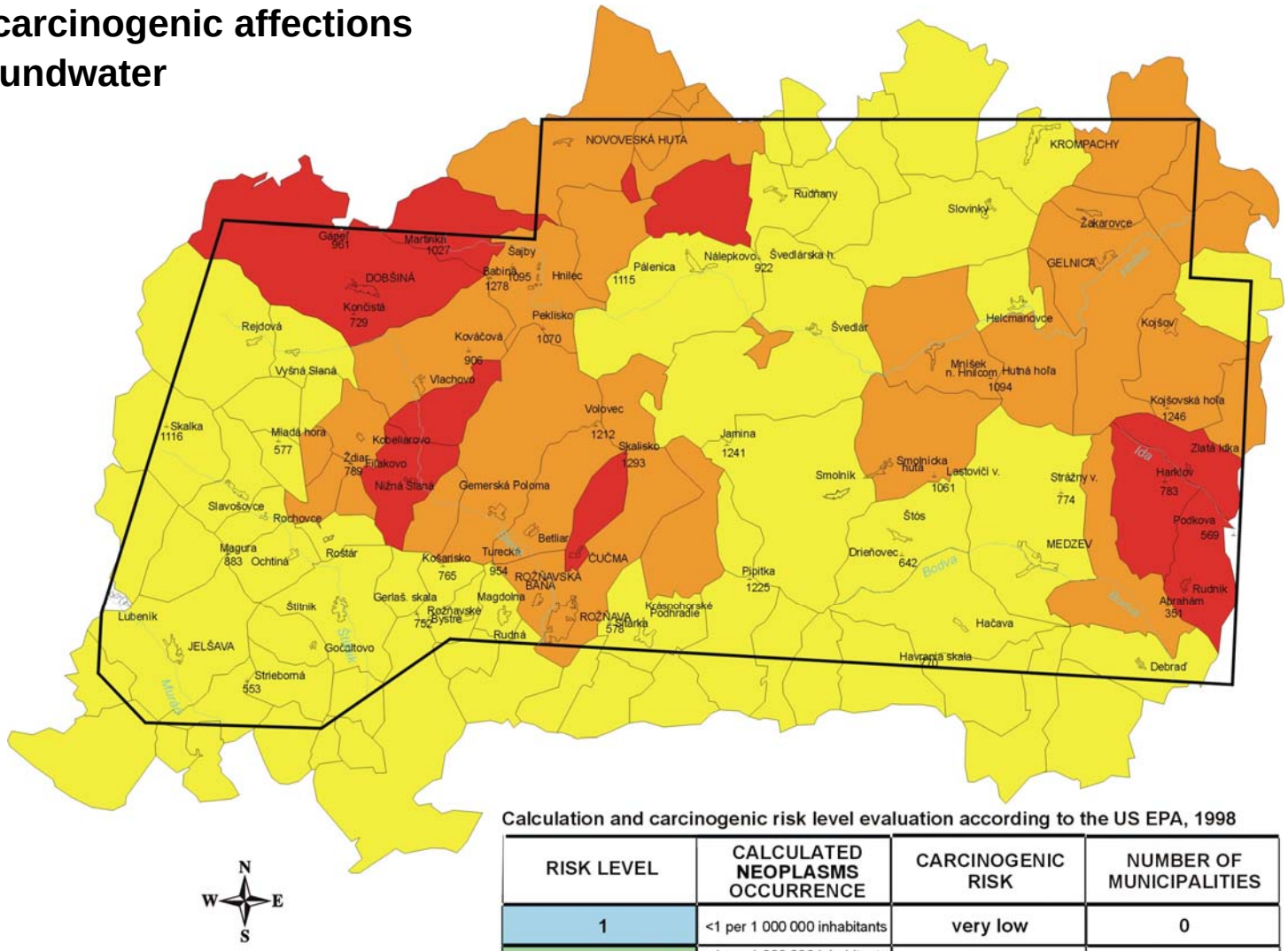
# Carcinogenic and chronic health risk calculation from As - groundwater

**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**

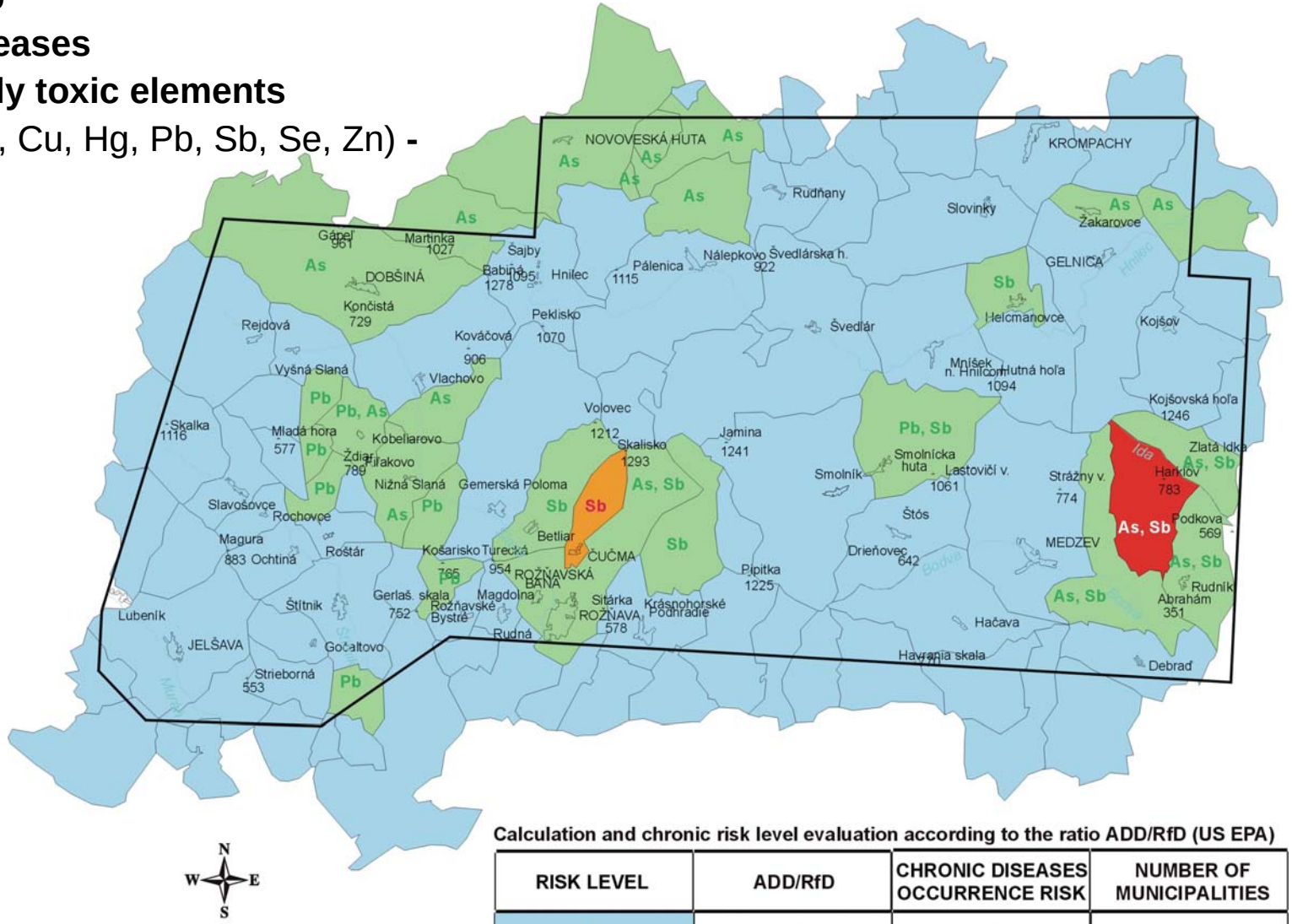
# Risk level map of carcinogenic affections from Arsenic - groundwater




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<br><1 per 100 000 inhabitants | low | 0 |
| 3 | >1 per 100 000 inhabitants<br><1 per 10 000 inhabitants | medium | 61 |
| 4 | >1 per 10 000 inhabitants<br><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**





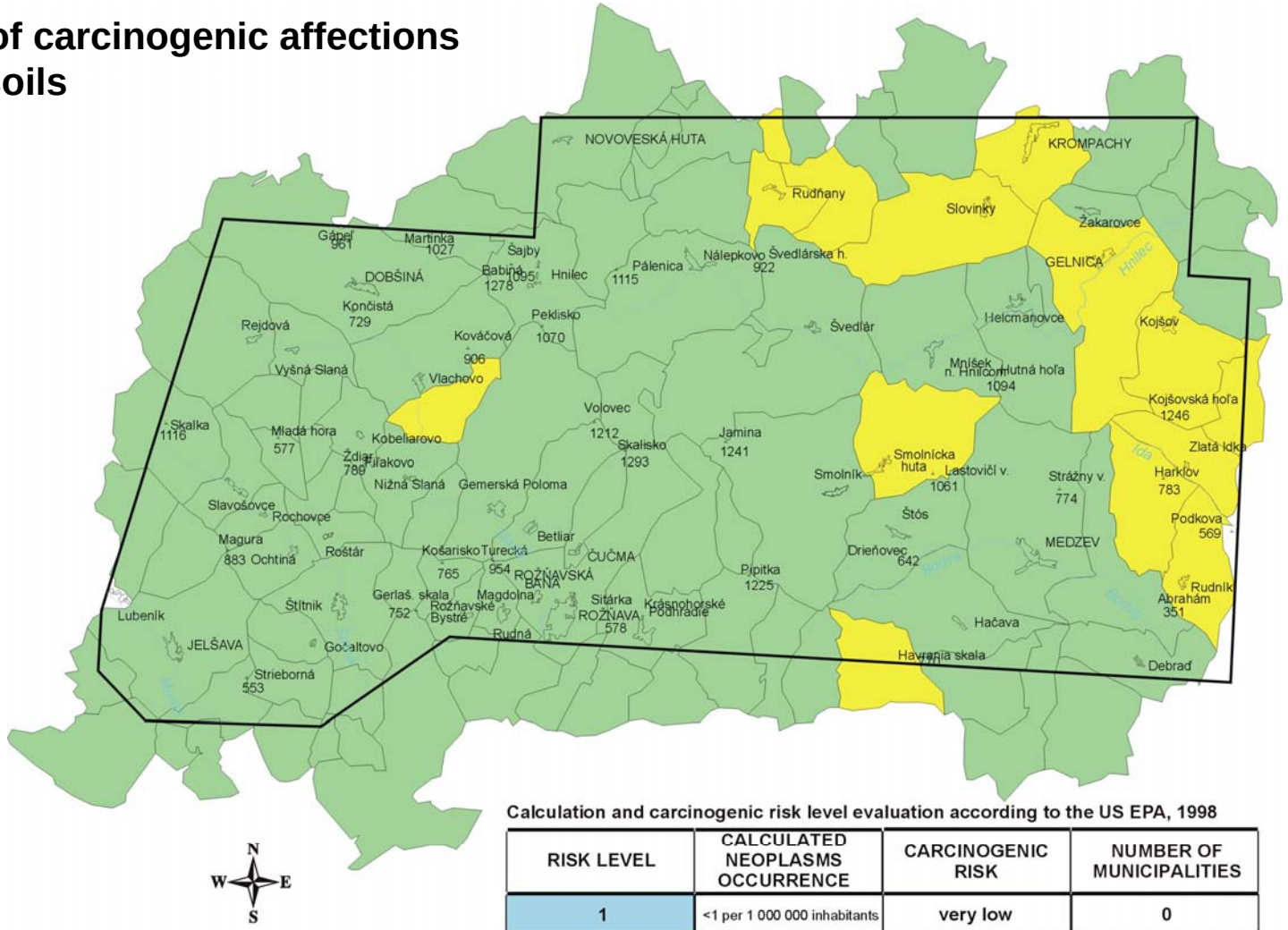


**Calculation and chronic risk level evaluation according to the ratio ADD/RfD (US EPA)**

| 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

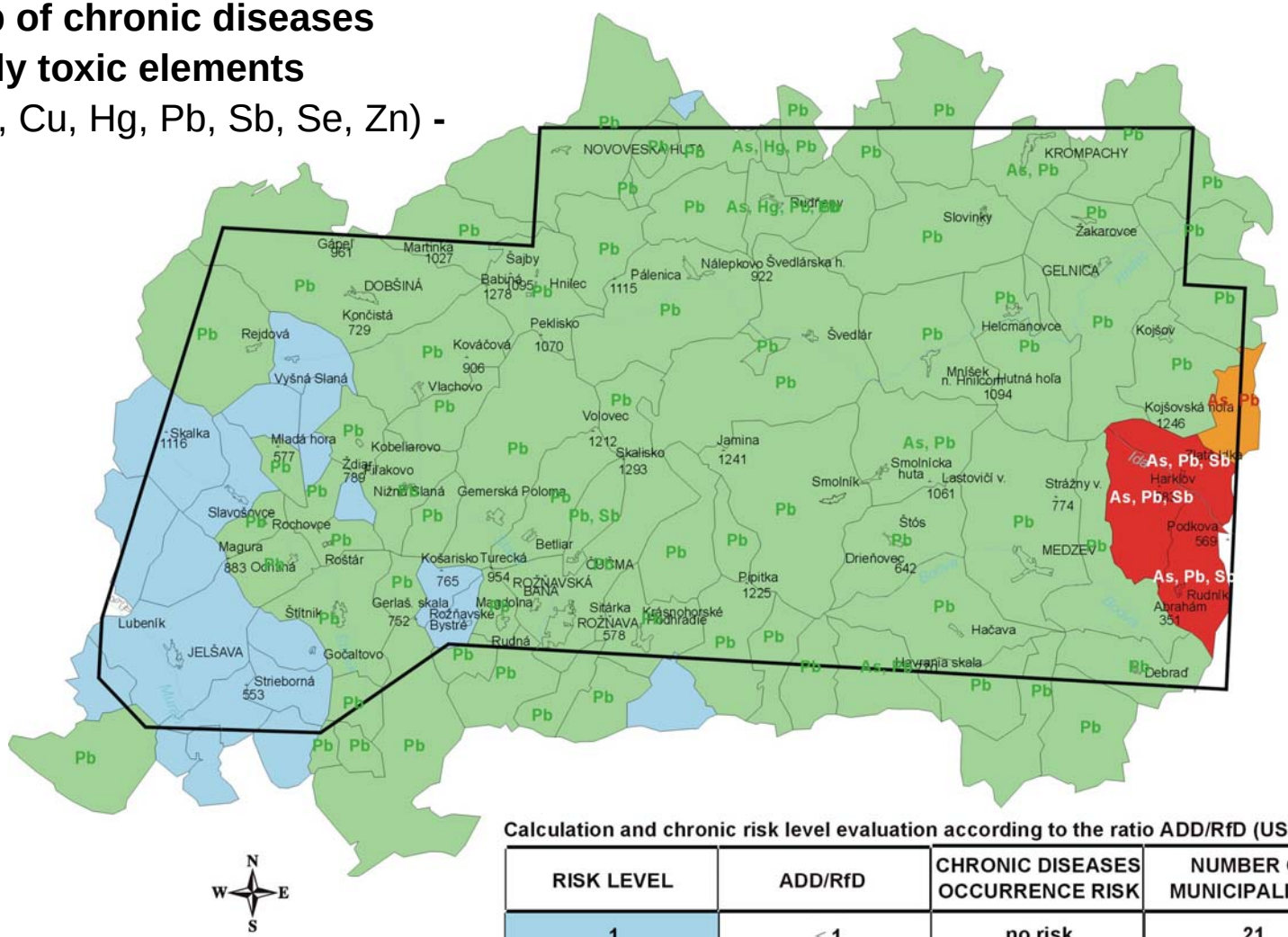
# Risk level map of carcinogenic affections from Arsenic - soils




**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<br><1 per 100 000 inhabitants | low | 86 |
| 3 | >1 per 100 000 inhabitants<br><1 per 10 000 inhabitants | medium | 14 |
| 4 | >1 per 10 000 inhabitants<br><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.