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## MONITORING OF ENVIRONMENTAL BURDENS IN SLOVAKIA – PART II



State Geological Institute of Dionýz Štúr Bratislava

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## MONITORING OF ENVIRONMENTAL BURDENS IN SLOVAKIA – PART II

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## Preface

Environmental burdens represent a long-term and serious problem for the quality of the environment of the Slovak Republic. In the past, they arose mainly from improper handling of dangerous substances, which directly or indirectly entered the individual components of the environment and contaminated (or still contaminate) them for a long time. The environmental burdens involve a wide range of areas contaminated by industrial, military, mining, transport and agricultural activities, but also by improper waste management. The environmental burdens can pose a potential threat to human beings and the environment (especially groundwater, rock environment or air pollution).

Since 2012, the State Geological Institute of Dionýz Štúr has been carrying out projects related to the monitoring of contaminated sites, perceived as environmental burdens, currently in more than 300 sites. The aim of the projects is to design and implement the monitoring programme for environmental burdens in Slovakia, to identify leakage of pollutants into the environment (especially into groundwater and surface water) and their extent and to assess the trends in concentrations of pollutants. The monitoring activities carried out are in line with the EU Water Framework Directive and its Daughter Directive on Groundwater Protection. Monitoring of environmental burdens fulfills the programme objectives of the Government of the Slovak Republic, which are defined in the document “State programme of remediation of environmental burdens for the years 2010 – 2015” and the updated document for the years 2016 – 2021. The list of monitored environmental burdens (at SGIDŠ) can be found in Annex at the end of this journal (pages 97 – 105).

Due to the topic extent the articles are submitted in two issues of the journal **in the year 2019** – four articles in the issue 1/2019 and four articles in the issue 2/2019.

Strong groundwater and/or surface water contamination has been monitored by SGIDŠ over a long period of time at 56 sites that represent a wide range of economic activities that have been carried out in the past. **The first paper** focuses on the results of monitoring of groundwater and surface water quality in selected heavily contaminated sites representing waste management facilities, industrial areas and mineral extraction localities. The analytical results are compared with the Directive of the Ministry of Environment of the Slovak Republic No. 1/2015-7 on elaboration of the risk analysis of contaminated area and with the Government Regulation No. 269/2010 laying down requirements for achieving good water status.

Use of additional geological methods and procedures (microchemical analysis) for monitoring of environmental burdens is subject of **the second article**. The specimens for detailed petrographic and mineralogical research were prepared from representative samples taken during field research. Using CAMECA SX 100 electron microanalyser, Back-scattered Electron Images (BEI) were captured, making it possible to study sample details. Chemical elements present in the sample were identified using the Electron Probe Micro-Analyser (EPMA) method. The application of microanalysis to solve the problem of environmental burdens enables microchemical study of different materials (industrial waste sludge, waste material from metalurgy, plant tissue material, sands, fly ash, soils and stream sediments). The aim of this paper is to provide an overview of the applying microanalysis of solid materials on examples, which were solved within the tasks focused on monitoring of environmental burdens realized by the SGIDŠ.

Monitoring of environmental burdens realized by SGIDŠ requires effective and rapid cooperation of a number of staff involved in the monitoring activities. At the same time, a large amount of data of different kinds is used. In view of the above, an information system for monitoring of environmental burdens was created in 2012, which is basically divided into two parts: 1) text and data part used to store information of various text and graphic formats; 2) database and GIS part in a well-defined structured online form. Information system of monitoring of environmental burdens is discussed in **the third paper**.

Evaluation and comparison of results of soil permeability determination by hydrodynamic tests, laboratory tests and empirical methods within the project of environmental burden monitoring are described in **the fourth article**. No significant correlations were found between the values obtained by pumping tests and laboratory methods. Comparison of the coefficients of hydraulic conductivity determined in laboratory instruments compared to empirical methods shows good correlations, which confirms the dependence of permeability on the grain-size distribution of the soil.



## Acknowledgement

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## LIST OF ACRONYMS

|        |                                                                                                   |
|--------|---------------------------------------------------------------------------------------------------|
| AMD    | Acid Mine Water                                                                                   |
| BEI    | Back-scattered Electron Images                                                                    |
| BTEX   | Benzene; Toluene; Ethylbenzene; and o-, m-, and p-Xylenes                                         |
| CHZJD  | Chemical Plants of Juraj Dimitrov                                                                 |
| COD    | Chemical Oxygen Demand                                                                            |
| CSS    | Cascading Style Sheet                                                                             |
| DCE    | DiChloroEthane                                                                                    |
| EB     | Environmental Burden                                                                              |
| EBM    | Environmental Burdens Monitoring                                                                  |
| EC     | Electric Conductivity                                                                             |
| EC     | European Commission                                                                               |
| EDS    | Energy-Dispersive Spectroscopy                                                                    |
| EDXA   | Energy Dispersive X-ray Analysis                                                                  |
| ENO    | Nováky Power Plant                                                                                |
| EPMA   | Electron Probe Micro-Analyser                                                                     |
| EU     | European Union                                                                                    |
| Fm.    | Formation                                                                                         |
| FNS CU | Faculty of Natural Sciences Comenius University                                                   |
| FTP    | File Transfer Protocol                                                                            |
| GAL    | Geoanalytical Laboratories (of SGIDŠ)                                                             |
| GDS    | Geotechnical Digital System                                                                       |
| GIS    | GeoInformation System                                                                             |
| GPL    | General Public License                                                                            |
| GPS    | Global Positioning System                                                                         |
| HTML   | Hypertext Markup Language                                                                         |
| HTTPS  | Hypertext Transfer Protocol Secure                                                                |
| ID     | Indication Criteria                                                                               |
| IS EZ  | Information System of Environmental Burdens ( <i>Informačný Systém Environmentálnych Záťaží</i> ) |
| IS EBM | Information System for Environmental Burdens Monitoring                                           |
| IT     | Intervention Criteria                                                                             |
| KNC    | Lot of the category “C” in the cadastre register (of the Slovak Republic)                         |
| KNE/UO | Lot of the category “E” in the cadastre register (of the Slovak Republic)                         |
| MoE SR | Ministry of Environment                                                                           |
| MTBE   | Methyl Tert-Butyl Ether                                                                           |
| NES    | Nonpolar Extractable Substances                                                                   |
| ODBC   | Open Database Connectivity                                                                        |
| OP     | Operational Programme                                                                             |
| PAH    | Polycyclic Aromatic Hydrocarbons                                                                  |
| PCE    | PerChloroEthylene                                                                                 |
| PCB    | PolyChlorinated Biphenyls                                                                         |
| PHP    | Hypertext Preprocessor                                                                            |
| SEA    | Slovak Environmental Agency                                                                       |

|        |                                                                                                                         |
|--------|-------------------------------------------------------------------------------------------------------------------------|
| SGIDŠ  | State Geological Institute of Dionýz Štúr                                                                               |
| S-JTSK | Krovak East North ( <i>System of Uniform Trigonometric Cadastral Network</i> )                                          |
| STN    | Slovak Technical Standard (Norm)                                                                                        |
| TCE    | TriChloroEthene                                                                                                         |
| TOC    | Total Organic Carbon                                                                                                    |
| TTCE   | TeTraChloroEthane                                                                                                       |
| VC     | VinylChloride                                                                                                           |
| VPN    | Virtual Private Network                                                                                                 |
| WDS    | Wavelength-Dispersive Spectroscopy                                                                                      |
| WFD    | Water Framework Directive                                                                                               |
| WKB    | Well-Known Binary                                                                                                       |
| ZBGIS  | Basic data base for the Geographic Information System ( <i>Základná Báza údajov pre Geografický Informačný Systém</i> ) |

# 1. Influence of Monitored Environmental Burdens on Groundwater and Surface Water Quality – Case Studies

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**Abstract:** Since 2012, the State Geological Institute of Dionýz Štúr has been carrying out tasks related to the monitoring of 309 environmental burdens. Following the article 4 by Kordík et al. (2019), this paper focuses on the results of groundwater and surface water quality monitoring in selected heavily polluted sites representing mainly industrial activities, waste management facilities and raw mineral extraction sites. Pollution from landfills is associated typically with the occurrence of high levels (above IT criteria) of boron, Cl,  $\text{NH}_4^+$  and conductivity. The highest content of TOC ( $1,460 \text{ mg.l}^{-1}$ ) as an indicator of organic pollution was found at the site Komárno – area after the Soviet Army. Extremely high levels of  $\text{COD}_{\text{Mn}}$  (above  $50 \text{ mg.l}^{-1}$ ) were found among the sites of interest at the site Bojná – landfill – part A. Among the organic substances, chlorinated hydrocarbons (concentrations of cis 1,2-dichloroethene, dichloromethane, tetrachloroethene, trichloroethene and chloroethene above the IT criteria) appear to be problematic specifically within the industrial EB (Zlaté Moravce – Calex, Bratislava – Vrakúňa – CHZ-JD landfill, Bratislava – Chemika, Bratislava – Gumon, Čierna nad Tisou – transshipment station, Komárno – area after Soviet Army). Some trace inorganic elements (As, Sb, Cd, Cu, Ni, Zn), also due to the inclusion of mining sites in monitoring, exceeded IT criteria in groundwaters frequently.

**Key words:** monitoring, environmental burdens, quality, groundwater, surface water, case studies

## 1.1 Introduction

State Geological Institute of Dionýz Štúr is concerned with monitoring of 309 environmental burdens. The aim of

the monitoring realized since 2012 is to monitor the release of pollutants into the environment (into groundwater and surface water, particularly) and to assess trends in the development of contamination. Strong groundwater or surface water contamination has been monitored over a long period of time at 56 sites that represent a wide range of economic activities that had been carried out in the past. Results of groundwater and surface water quality monitoring in selected heavily polluted sites representing industrial activities, waste management facilities and mineral extraction sites are discussed in this paper. An overview of the evaluated sites, type of activity and pollution are presented in Tab. 1.1. The map of selected monitored environmental burdens with strong groundwater and/or surface water pollution is shown in Fig. 1.1. These results are linked to several tasks of the Ministry of Environment of the Slovak Republic focused on monitoring and exploration of environmental burdens:

- Kordík & Slaninka et al. (2015): sites Bratislava – Chemika and Gumon, Piešťany – Chirana and Tesla – contamination plume below the housing estate, Sered' – landfill dump and former Nickel plant area, Zlaté Moravce – Calex, Bojná – landfill A.
- Urban et al. (2015a,b): locality Bratislava – Vrakúňa – landfill CHZJD, Bánovce nad Bebravou – railway station.

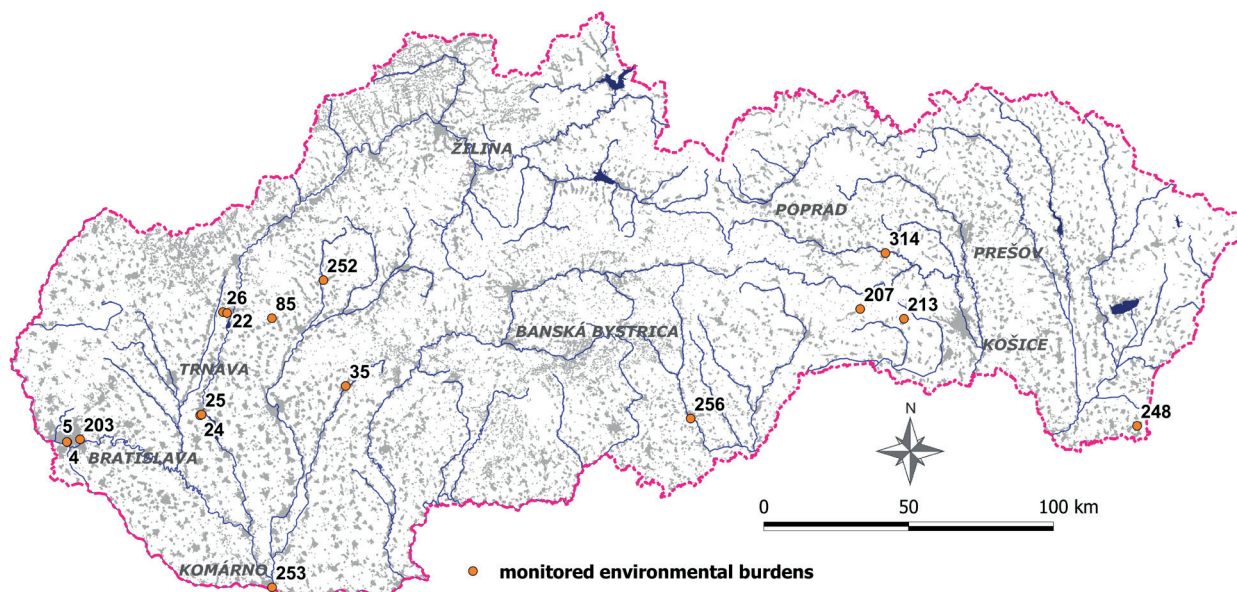


Fig. 1.1 Map of selected monitored environmental burdens with strong groundwater and/or surface water pollution

Table 1.1 Overview of evaluated sites, type of activity and type of pollution

| ID  | Environmental burden                                            | Type of pollution                                                                                                                                                                                                                                                                                                                     | Type of activity                  |
|-----|-----------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|
| 4   | Bratislava – Chemika                                            | NH <sub>4</sub> <sup>+</sup> , COD <sub>Mn</sub> , TOC, conductivity, PAH, dichloromethane, tetrachloroethene                                                                                                                                                                                                                         | Chemical industry                 |
| 5   | Bratislava – Gumon                                              | NH <sub>4</sub> <sup>+</sup> , COD <sub>Mn</sub> , TOC, C <sub>10</sub> -C <sub>40</sub> , anthracene, chrysene, carbon tetrachloride                                                                                                                                                                                                 | Rubber industry                   |
| 22  | Piešťany – Chirana                                              | NH <sub>4</sub> <sup>+</sup> , cis 1,2-dichloroethene, dichloromethane, trichloroethene, vinyl chloride                                                                                                                                                                                                                               | Chemical industry                 |
| 24  | Sereď – Nickel plant – landfill dump                            | Cd, Ni                                                                                                                                                                                                                                                                                                                                | Metallurgical industry            |
| 25  | Sereď – Nickel plant – former factory area                      | Cd, Co, Ni, Zn, NH <sub>4</sub> <sup>+</sup> , conductivity                                                                                                                                                                                                                                                                           | Metallurgical industry            |
| 26  | Piešťany – Tesla – contamination plume under the housing estate | cis 1,2-dichloroethene, vinyl chloride                                                                                                                                                                                                                                                                                                | Chemical industry                 |
| 35  | Zlaté Moravce – Calex                                           | NH <sub>4</sub> <sup>+</sup> , COD <sub>Mn</sub> , cis 1,2-dichloroethene, trans 1,2-dichloroethene, tetrachloroethene, trichloroethene, vinyl chloride                                                                                                                                                                               | Production of refrigerators       |
| 85  | Bojná – landfill – part A                                       | As, Ba, B, Cl <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , COD <sub>Mn</sub> , TOC, conductivity                                                                                                                                                                                                                                     | Waste management equipment        |
| 203 | Bratislava – Vrakuňa – CHZJD landfill                           | As, F <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , NO <sub>2</sub> <sup>-</sup> , TOC, C <sub>10</sub> -C <sub>40</sub> , conductivity, phenol index, benzene, ethylbenzene, toluene, xylene, PAH, chlorobenzene, dichlorobenzenes, trichlorobenzenes, dichloromethane, tetrachloroethene, carbon tetrachloride, vinyl chloride, PCB | Chemical industry                 |
| 207 | Smolník – pyrite ores                                           | Al <sup>3+</sup> , As, Co, Cu, Ni, Zn, conductivity, pH                                                                                                                                                                                                                                                                               | Pollution from mineral extraction |
| 213 | Poproč – Petrova dolina Valley                                  | Al <sup>3+</sup> , As, Cd, Ni, Sb, Zn, pH                                                                                                                                                                                                                                                                                             | Pollution from mineral extraction |
| 248 | Čierna nad Tisou – transshipment station                        | Cl <sup>-</sup> , C <sub>10</sub> -C <sub>40</sub> , NEL-UV, benzene, ethylbenzene, toluene, xylene, carbon tetrachloride                                                                                                                                                                                                             | Transport                         |
| 252 | Bánovce nad Bebravou – railway station                          | NH <sub>4</sub> <sup>+</sup> , TOC, cis 1,2-dichloroethene, tetrachloroethene, trichloroethene                                                                                                                                                                                                                                        | Transport                         |
| 253 | Komárno – area after the Soviet Army                            | NH <sub>4</sub> <sup>+</sup> , TOC, C <sub>10</sub> -C <sub>40</sub> , benzene, xylene, PAH, tetrachloroethene                                                                                                                                                                                                                        | Military area                     |
| 256 | Rimavská Sobota – area after the Soviet Army                    | cis 1,2-dichloroethene, tetrachloroethene, trichloroethene, vinyl chloride                                                                                                                                                                                                                                                            | Military area                     |
| 314 | Krupá – Kovohuty                                                | Al <sup>3+</sup> , B, As, Cd, Co, Cu, Hg, Ni, Pb, Sb, Zn, Cl <sup>-</sup> , F <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , TOC, C <sub>10</sub> -C <sub>40</sub> , conductivity, pH, SO <sub>4</sub> <sup>2-</sup> , Fe-tot., Mn                                                                                                     | Metallurgical industry            |

Notes: PAH – polycyclic aromatic hydrocarbons, C<sub>10</sub>-C<sub>40</sub> – hydrocarbon index, PCB – polychlorinated biphenyls

- Auxt et al. (2015a,b,c): sites Smolník – pyrite ores mining and processing, Poproč – Petrova dolina Valley, Čierna nad Tisou – transshipment station.
- Tupý et al. (2015): site Rimavská Sobota – area after the Soviet Army.
- Matiová et al. (2015): site Komárno – area after the Soviet Army.
- Pospiechová et al. (2015): site Krupá – Kovohuty.

## 1.2 Methods

Monitoring of groundwaters and surface waters in the areas of environmental burdens is a systematic observation of time changes of concentrations of selected pollutants indicative for a given site. Monitoring of the EBs is carried out in accordance with EU legislation, in particular the Directive 2000/60/EC of the European Parliament and of

the Council of 28 October 2000 establishing a framework for Community action in the field of water policy and the Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration.

Methodological procedures for sampling and analytical processing are summarized in the paper 4 SGM1/2019 by Kordík et al. (2019):

“Influence of monitored environmental burdens on ground water and surface water quality 1 – general results” and presented in more detail at work Kordík & Slaninka et al. (2015).

The analytical results at individual sites are compared with legislation (for groundwater the Directive of the Ministry of Environment of the Slovak Republic No. 1/2015-7 on elaboration of the risk analysis of contaminated area and for surface water the Government Regulation No.



269/2010 laying down requirements for achieving good water status). In accordance with the Directive of the MoE SR No. 1/2015-7 indicating and intervention criteria for contaminants are defined, where:

- Indication criteria (ID) are the concentration limits of a pollutant determined for soil, rock environment and groundwater, the excess of which may endanger human health and the environment; this situation requires monitoring of the polluted area.
- Intervention criteria (IT) is the critical concentration levels of a pollutant determined for soil, rock environment and groundwater, the excess of which in a given landuse scenario assumes a high likelihood of endangering human health and the environment. A detailed geological investigation of the environment with preparation of risk analysis is necessary to carry out in this contaminated area.

### 1.3 Results

#### 1.3.1 Bratislava – former factories Chemika and Gumon (loc. No. 4 and 5)

The Chemika plant, which closed down in 1990, focused mainly on the production of paints, lacquers and distribution, for example, of epoxies and asphalts, and at the same time pumped chlorinated hydrocarbons, mineral acids and other chemicals. As a consequence, chlorinated hydrocarbons (DCE, TCE, PCE) leakages have been observed from the plant. The Gumon plant was in operation until 2005, and it focused on the production of electrical insulating materials, bakelite or artificial asphalt. Mainly polycyclic aromatic hydrocarbons have been spreading from the plant into the environment. After the bombing of the Apollo Refinery (located nearby the Chemika and Gumon factories) in 1944, oil pollution began to spread through the environment – high oil contents in groundwater and soil were found also within the boundaries of both factories.

Neogene and Quaternary formations are involved in the geological setting of the area. The Neogene sediments in the Danube Basin are exposed at the surface only in smaller areas, especially at the contact between the Malé Karpaty Mts. and the Basin. The Neogene strata are found in the area in the facies of colourful clays and sandy clays or sandstones with calcareous concretions. Fluvial and fluvio-limnic sediments dominate the Quaternary of the Danube Basin. The Quaternary fluvial formation consists mainly of medium to coarse-grained gravels, sandy gravels and sands (Pristaš et al., 1996). Holocene sediments of the uppermost strata (loamy and sandy-loamy) form flood-plaincover on the sandy gravels of the Danube. The thickness of the Quaternary sediments is about 10 – 20 m. The most important groundwater aquifers are fluvial gravel-sandy sediments of the Danube River. The groundwater regime is mainly influenced by the hydraulic connection of the Quaternary aquifer to the surface water (Danube River). The Danube at each water level fills the groundwater of the Quaternary sediments by shore and bottom infiltration.

The results of the monitoring show the presence of oil pollution in soil and groundwater. Indication (ID) and intervention (IT) values (according the Directive No. 1/2015–7 of the Ministry of the Environment of the Slovak Republic) have been exceeded for inorganic indicators of  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and EC and organic indicators for TOC,  $\text{COD}_{\text{Mn}}$ , hydrocarbon index, surfactants, PAH, TTCE, chloroethene and benzene (Tab. 1.2). The highest concentrations of inorganic and organic indicators are concentrated in VN4-5, VN5-2 and VN5-7 boreholes, where the oil substances free phase was measured regularly. The survey has confirmed the rule that the thickness of the free phase of oil substances decreases when the groundwater table increases, and vice versa. In the well VR4-1 high concentrations of  $\text{Cl}^-$  dominate, which affect the elevated EC values (460  $\text{mS.m}^{-1}$  to 520  $\text{mS.m}^{-1}$ ). Maps of distribution of surfactants, TOC and hydrocarbon index in groundwaters are presented in Figs. 1.2 to 1.4.

#### 1.3.2 Piešťany – former factories Chirana and Tesla (loc. No. 22 and 26)

In Piešťany, contamination by aliphatic chlorinated hydrocarbons is caused by negligence in handling of hazardous substances and unsuitable storage and handling facilities (former Chirana and Tesla factories). Engineering production, dental equipment and manufacture of medical equipment dominated in the area. For the purpose of degreasing, especially 1,1,2-trichloroethene and 1,1,2,2-tetrachloroethene were intensely used.

The Neogene and Quaternary sediments contribute to the geological settings of the area. The Neogene sediments underlying Quaternary formation consist of varicoloured conglomerates, sandstones and clays and are found in the western foothills of the Považský Inovec Mts. The Quaternary fluvial sediments of the Upper Pleistocene are represented predominantly by sandy gravels of different colour and granularity (Maglay et al., 2011). They reach a maximum thickness of approximately 16 m. The Quaternary alluvial sediments of the Holocene are made up of mainly brown to grey silt, occasionally of dark brown clay with gravel. The maximum thickness of these sediments is 4 m. The main groundwater aquifer, consisting of sands and gravels, has mostly good to very good intergranular permeability. A large part of the groundwater supply is supplemented by infiltration from surface streams in the wider surroundings of the area of interest. To a lesser extent, groundwater supplies are supplemented by groundwater transfer from the rock environment of the surrounding geological units or from precipitation.

From the obtained results it is obvious that most groundwater analyzes have concentrations of at least some aliphatic chlorinated hydrocarbons above the ID or IT criteria of the Directive of the Ministry of the Environment of the Slovak Republic No. 1/2015-7. Particularly dominant are the contents of cis 1,2-dichloroethene, which on average at the site of Piešťany – former factory Chirana reach up to 166  $\mu\text{g.l}^{-1}$  (Tab. 1.3). The maximum value (846  $\mu\text{g.l}^{-1}$ ) was found in the VR22-1 borehole on 11.4.2018. In addition cis 1,2-dichloroethene, the contents

Table 1.2 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – sites Bratislava – Chemika and Bratislava – Gumon

| Bratislava – Chemika                                  | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples > ID | number of samples > IT |
|-------------------------------------------------------|--------------------|------|--------|--------------------|---------|---------|--------|----------|----------|------------------------|------------------------|
| NH <sub>4</sub> <sup>+</sup>                          | mg.l <sup>-1</sup> | 1.82 | 0.64   | 2.87               | <0.05   | 13.6    | 39     | 1.2      | 2.4      | 3                      | 10                     |
| Cl <sup>-</sup>                                       | mg.l <sup>-1</sup> | 171  | 131    | 200                | 24.2    | 1,121   | 39     | 150      | 250      | 10                     | 3                      |
| TOC                                                   | mg.l <sup>-1</sup> | 10.3 | 3.1    | 14.8               | <0.5    | 68.9    | 33     | 2        | 5        | 4                      | 15                     |
| COD <sub>Mn</sub>                                     | mg.l <sup>-1</sup> | 7.38 | 1.59   | 10.9               | <0.5    | 37.3    | 31     | 5        | 10       | 2                      | 8                      |
| surfactants                                           | mg.l <sup>-1</sup> | 0.48 | 0.14   | 1.11               | 0.02    | 6.1     | 35     | 0.25     | 0.5      | 7                      | 6                      |
| hydrocarbon index (C <sub>10</sub> -C <sub>40</sub> ) | mg.l <sup>-1</sup> | 236  | 0.17   | 981                | <0.02   | 4,715   | 38     | 0.25     | 0.5      | 4                      | 11                     |
| 1,1-dichloroethene                                    | µg.l <sup>-1</sup> | 0.44 | 0.2    | 1.59               | <0.1    | 10      | 38     | 10       | 20       | 0                      | 0                      |
| cis 1,2-dichloroethene                                | µg.l <sup>-1</sup> | 4.76 | 1      | 8.57               | <0.1    | 41.1    | 38     | 25       | 50       | 1                      | 0                      |
| tetrachloroethene                                     | µg.l <sup>-1</sup> | 12.4 | 0.7    | 30.7               | <0.2    | 170     | 38     | 10       | 20       | 2                      | 7                      |
| trichloroethene                                       | µg.l <sup>-1</sup> | 2.82 | 0.2    | 5.23               | <0.1    | 22.7    | 38     | 25       | 50       | 0                      | 0                      |
| chloroethene                                          | µg.l <sup>-1</sup> | 2.62 | 0.2    | 8.89               | <0.1    | 50.8    | 38     | 5        | 10       | 2                      | 2                      |
| benzene                                               | µg.l <sup>-1</sup> | 7.87 | <0.2   | 31.4               | <0.2    | 176     | 32     | 15       | 30       | 0                      | 2                      |
| chlorobenzene                                         | µg.l <sup>-1</sup> | 16.8 | 0.2    | 83.0               | <0.1    | 471     | 32     | 15       | 30       | 0                      | 1                      |
| toluene                                               | µg.l <sup>-1</sup> | 1.88 | <0.2   | 8.79               | <0.2    | 50      | 32     | 350      | 700      | 0                      | 0                      |
| xylene                                                | µg.l <sup>-1</sup> | 1.67 | <0.2   | 5.33               | <0.2    | 30      | 32     | 250      | 500      | 0                      | 0                      |
| anthracene                                            | µg.l <sup>-1</sup> | 7.82 | 0.021  | 45.7               | <0.003  | 278     | 37     | 5        | 10       | 1                      | 1                      |
| phenanthrene                                          | µg.l <sup>-1</sup> | 73.2 | 0.163  | 436                | <0.003  | 2,652   | 37     | 5        | 10       | 3                      | 2                      |
| fluoranthene                                          | µg.l <sup>-1</sup> | 4.20 | 0.018  | 23.7               | <0.003  | 144     | 37     | 25       | 50       | 0                      | 1                      |
| fluorene                                              | µg.l <sup>-1</sup> | 10.1 | 0.1    | 57.6               | <0.015  | 351     | 37     |          |          |                        |                        |
| chrysene                                              | µg.l <sup>-1</sup> | 7.79 | 0.01   | 45.5               | <0.003  | 277     | 37     | 0.1      | 0.2      | 1                      | 8                      |
| naphthalene                                           | µg.l <sup>-1</sup> | 2.77 | 0.105  | 12.8               | <0.03   | 82.4    | 42     | 25       | 50       | 0                      | 1                      |
| pyrene                                                | µg.l <sup>-1</sup> | 16.1 | 0.036  | 91.7               | <0.006  | 558     | 37     | 25       | 50       | 1                      | 1                      |
| benzo(a)anthracene                                    | µg.l <sup>-1</sup> | 16.0 | 0.014  | 95.6               | <0.003  | 582     | 37     |          |          |                        |                        |
| Bratislava – Gumon                                    | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples > ID | number of samples > IT |
| NH <sub>4</sub> <sup>+</sup>                          | mg.l <sup>-1</sup> | 1.00 | 0.565  | 2.03               | <0.05   | 11.6    | 42     | 1.2      | 2.4      | 2                      | 3                      |
| Cl <sup>-</sup>                                       | mg.l <sup>-1</sup> | 110  | 85.5   | 167                | 21.6    | 1,030   | 34     | 150      | 250      | 0                      | 1                      |
| TOC                                                   | mg.l <sup>-1</sup> | 5.73 | 5.5    | 3.14               | 0.7     | 14.6    | 38     | 2        | 5        | 10                     | 23                     |
| COD <sub>Mn</sub>                                     | mg.l <sup>-1</sup> | 5.84 | 3.39   | 5.72               | <0.5    | 21.9    | 36     | 5        | 10       | 4                      | 9                      |
| surfactants                                           | mg.l <sup>-1</sup> | 0.64 | 0.605  | 0.44               | <0.05   | 1.99    | 38     | 0.25     | 0.5      | 8                      | 22                     |
| hydrocarbon index (C <sub>10</sub> -C <sub>40</sub> ) | mg.l <sup>-1</sup> | 42.0 | 0.075  | 225                | <0.02   | 1,410   | 40     | 0.25     | 0.5      | 1                      | 10                     |
| 1,1-dichloroethene                                    | µg.l <sup>-1</sup> | 0.52 | <0.2   | 1.03               | <0.2    | 5.8     | 40     | 10       | 20       | 0                      | 0                      |
| cis 1,2-dichloroethene                                | µg.l <sup>-1</sup> | 0.43 | <0.2   | 0.72               | <0.2    | 3.7     | 40     | 25       | 50       | 0                      | 0                      |
| tetrachloroethene                                     | µg.l <sup>-1</sup> | 0.69 | <0.2   | 0.99               | <0.2    | 4.7     | 40     | 10       | 20       | 0                      | 0                      |
| trichloroethene                                       | µg.l <sup>-1</sup> | 0.78 | <0.2   | 3.30               | <0.2    | 21.1    | 40     | 25       | 50       | 0                      | 0                      |
| chloroethene                                          | µg.l <sup>-1</sup> | 1.60 | <0.2   | 7.19               | <0.2    | 45      | 40     | 5        | 10       | 1                      | 1                      |
| benzene                                               | µg.l <sup>-1</sup> | 9.10 | 0.2    | 33.1               | <0.1    | 191     | 40     | 15       | 30       | 2                      | 2                      |
| chlorobenzene                                         | µg.l <sup>-1</sup> | 0.54 | 0.2    | 0.96               | <0.1    | 4.5     | 40     | 15       | 30       | 0                      | 0                      |
| toluene                                               | µg.l <sup>-1</sup> | 19.4 | 0.2    | 103                | <0.1    | 646     | 40     | 350      | 700      | 1                      | 0                      |
| xylene                                                | µg.l <sup>-1</sup> | 2.42 | 0.2    | 7.56               | <0.1    | 39      | 40     | 250      | 500      | 0                      | 0                      |
| anthracene                                            | µg.l <sup>-1</sup> | 0.43 | 0.003  | 2.28               | <0.003  | 13.3    | 34     | 5        | 10       | 0                      | 1                      |
| phenanthrene                                          | µg.l <sup>-1</sup> | 2.52 | 0.027  | 12.1               | <0.003  | 70.6    | 34     | 5        | 10       | 1                      | 1                      |
| fluoranthene                                          | µg.l <sup>-1</sup> | 0.22 | 0.0075 | 1.09               | <0.003  | 6.39    | 34     | 25       | 50       | 0                      | 0                      |
| fluorene                                              | µg.l <sup>-1</sup> | 0.96 | 0.015  | 3.66               | <0.015  | 21.1    | 34     |          |          |                        |                        |
| chrysene                                              | µg.l <sup>-1</sup> | 0.27 | 0.003  | 1.39               | <0.003  | 8.14    | 34     | 0.1      | 0.2      | 0                      | 3                      |
| naphthalene                                           | µg.l <sup>-1</sup> | 0.34 | 0.04   | 1.13               | <0.03   | 6.48    | 34     | 25       | 50       | 0                      | 0                      |
| pyrene                                                | µg.l <sup>-1</sup> | 0.26 | 0.0195 | 1.08               | <0.006  | 6.29    | 34     | 25       | 50       | 0                      | 0                      |
| benzo(a)anthracene                                    | µg.l <sup>-1</sup> | 0.38 | 0.003  | 1.99               | <0.003  | 11.6    | 34     |          |          |                        |                        |



Fig. 1.2 TOC distribution in groundwaters (median concentrations) – sites Bratislava – Chemika and Bratislava – Gumon (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

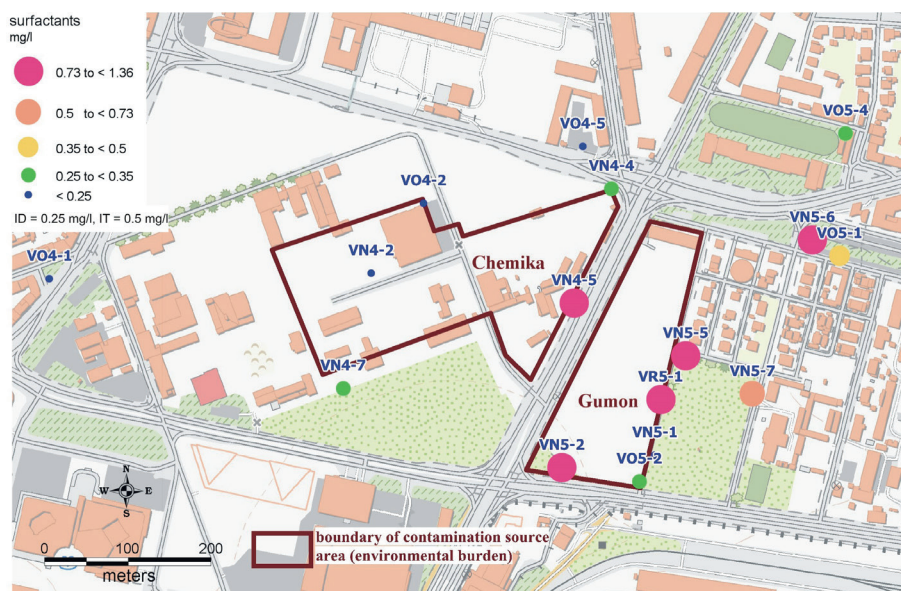
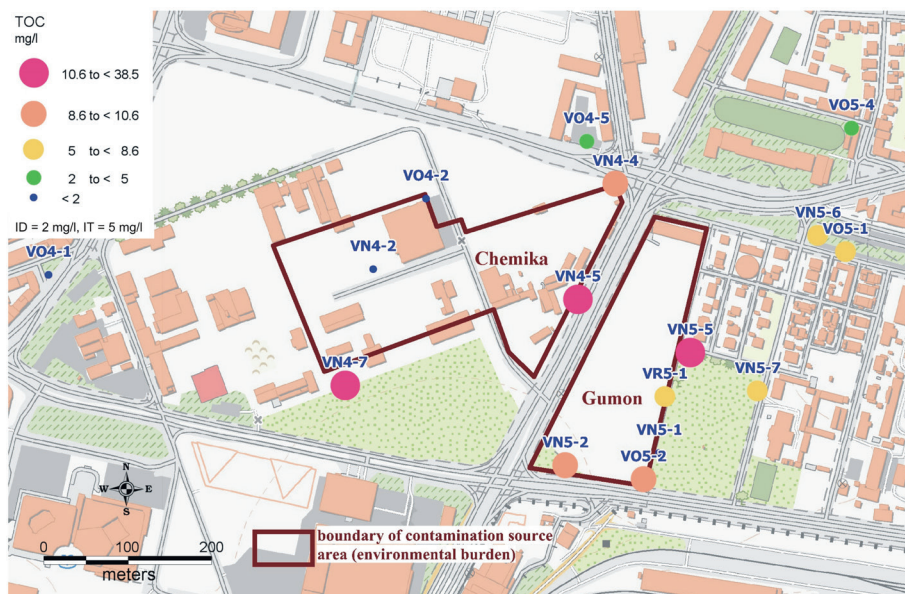
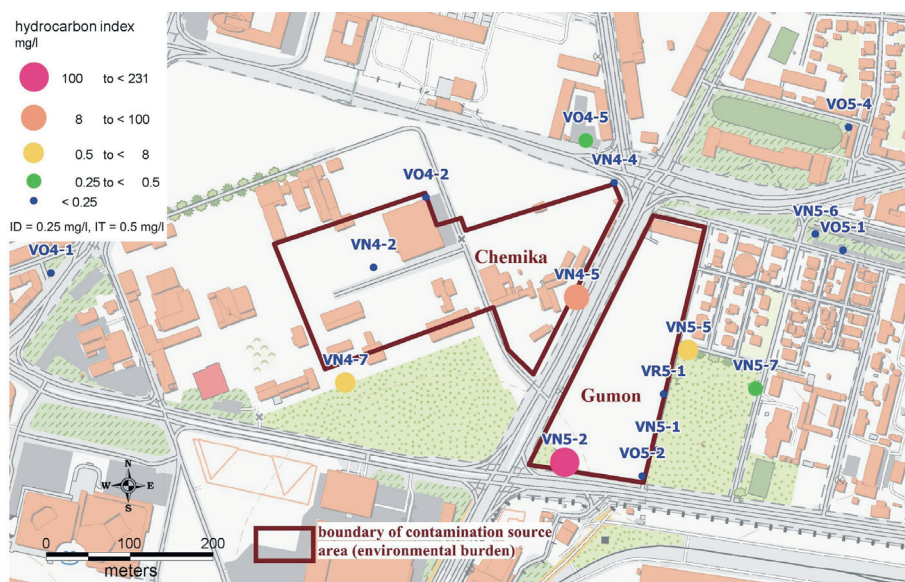


Fig. 1.3 Distribution of surfactants in groundwaters (median concentrations) – sites Bratislava – Chemika and Bratislava – Gumon (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

Fig. 1.4 Distribution of hydrocarbon index in groundwaters (median concentrations) – sites Bratislava – Chemika and Bratislava – Gumon (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



of trichloroethene and in less extent also vinylchloride are also high. The concentrations of trichloroethene in groundwater are on average much lower than those of cis 1,2-dichloroethene (average TCE is 30.2 µg.l<sup>-1</sup> at the site Piešťany – former factory Chirana). The surface area of groundwater pollution is large (reaches several km<sup>2</sup>), the pollutants have been transported to a distance of about 2 km south of the former source and at present the highest detected concentrations of chlorinated hydrocarbons occur in the vicinity of the horticultural settlement Sĺňava and Winter Stadium Piešťany (Figs. 1.5 to 1.7). No significant pollution by chlorinated hydrocarbons was found in surface waters.

### 1.3.3 Sered' – landfill dump and former Nickel plant area (loc. No. 24 and 25)

The Sered' region has long been affected by environmental pollution, mainly due to industrial action in the nickel smelters. Although the plant was the main

polluter of groundwater, soil and air during its operation, the major source of pollution is now deposited material – leach wasted mud.

The area's geological structure is formed by the Neogene and Quaternary sediments. While the Quaternary sediments are characterized by the complex geological structure's variable thickness which generally increases from north to south (Maglay et al., 2011), the Neogene sediments are typical of multi-coloured clay sedimentation (Pristaš et al., 2000). The groundwater mostly originates from the Váh River water which infiltrates the well-drained sandy gravels north of Dolná Streda and Sered'.

Groundwater pollution is monitored in 25 boreholes. Mainly elevated or high contents of SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and Ni in groundwater of several boreholes in the study area were observed (Tab. 1.4). The monitoring revealed that the most polluted groundwater is in the VR24-2 and VR24-4 boreholes which are close to the nickel waste mud dump

Table 1.3 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – sites Piešťany – former factories Chirana and Tesla

| Piešťany – Chirana            | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples<br>ID | number of samples<br>IT |
|-------------------------------|--------------------|------|--------|--------------------|---------|---------|--------|----------|----------|-------------------------|-------------------------|
| Cl <sup>-</sup>               | mg.l <sup>-1</sup> | 48.1 | 51.5   | 20.6               | 8.17    | 125     | 80     | 150      | 250      | 0                       | 0                       |
| SO <sub>4</sub> <sup>2-</sup> | mg.l <sup>-1</sup> | 144  | 154    | 51.3               | 28.6    | 244     | 80     |          |          |                         |                         |
| 1,1-dichloroethene            | µg.l <sup>-1</sup> | 1.02 | 0.2    | 1.67               | <0.1    | 13.1    | 117    | 10       | 20       | 1                       | 0                       |
| cis 1,2-dichloroethene        | µg.l <sup>-1</sup> | 166  | 80.1   | 206                | <0.1    | 846     | 117    | 25       | 50       | 6                       | 65                      |
| trans 1,2-dichloroethene      | µg.l <sup>-1</sup> | 2.13 | 0.8    | 4.17               | <0.1    | 31.2    | 117    | 25       | 50       | 1                       | 0                       |
| dichloromethane               | µg.l <sup>-1</sup> | 3.02 | 0.2    | 12.9               | <0.1    | 82.5    | 59     | 15       | 30       | 0                       | 2                       |
| tetrachloroethene             | µg.l <sup>-1</sup> | 1.51 | 0.2    | 2.37               | <0.1    | 11.4    | 117    | 10       | 20       | 1                       | 0                       |
| 1,1,2-trichloroethene         | µg.l <sup>-1</sup> | 30.2 | 2.7    | 62.6               | <0.1    | 344     | 111    | 25       | 50       | 3                       | 23                      |
| chloroethene                  | µg.l <sup>-1</sup> | 25.1 | 1.3    | 107                | <0.1    | 760     | 112    | 5        | 10       | 5                       | 21                      |
| chloroform                    | µg.l <sup>-1</sup> | 2.39 | 0.2    | 13.8               | <0.1    | 111     | 70     |          |          |                         |                         |
| Piešťany – Tesla              | mg.l <sup>-1</sup> | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples<br>ID | number of samples<br>IT |
| Cl <sup>-</sup>               | mg.l <sup>-1</sup> | 71.2 | 56.0   | 67.5               | 9.89    | 301     | 36     | 150      | 250      | 0                       | 3                       |
| SO <sub>4</sub> <sup>2-</sup> | µg.l <sup>-1</sup> | 168  | 146    | 82.9               | 0.61    | 294     | 36     |          |          |                         |                         |
| 1,1-dichloroethene            | µg.l <sup>-1</sup> | 0.3  | 0.2    | 0.31               | <0.1    | 1.2     | 47     | 10       | 20       | 0                       | 0                       |
| cis 1,2-dichloroethene        | µg.l <sup>-1</sup> | 27.2 | 12.4   | 41.5               | 0.2     | 180     | 47     | 25       | 50       | 7                       | 6                       |
| trans 1,2-dichloroethene      | µg.l <sup>-1</sup> | 0.57 | 0.2    | 0.54               | <0.1    | 2.3     | 47     | 25       | 50       | 0                       | 0                       |
| dichloromethane               | µg.l <sup>-1</sup> | 1.13 | 0.2    | 3.35               | <0.1    | 15.8    | 23     | 15       | 30       | 1                       | 0                       |
| tetrachloroethene             | µg.l <sup>-1</sup> | 0.6  | 0.2    | 0.70               | <0.1    | 3.5     | 47     | 10       | 20       | 0                       | 0                       |
| 1,1,2-trichloroethene         | µg.l <sup>-1</sup> | 6.39 | 2.75   | 10.1               | <0.1    | 44.1    | 44     | 25       | 50       | 3                       | 0                       |
| chloroethene                  | µg.l <sup>-1</sup> | 5.87 | 0.4    | 19.4               | <0.1    | 129     | 46     | 5        | 10       | 5                       | 5                       |
| chloroform                    | µg.l <sup>-1</sup> | 2.04 | 0.2    | 6.85               | <0.1    | 33.1    | 27     |          |          |                         |                         |



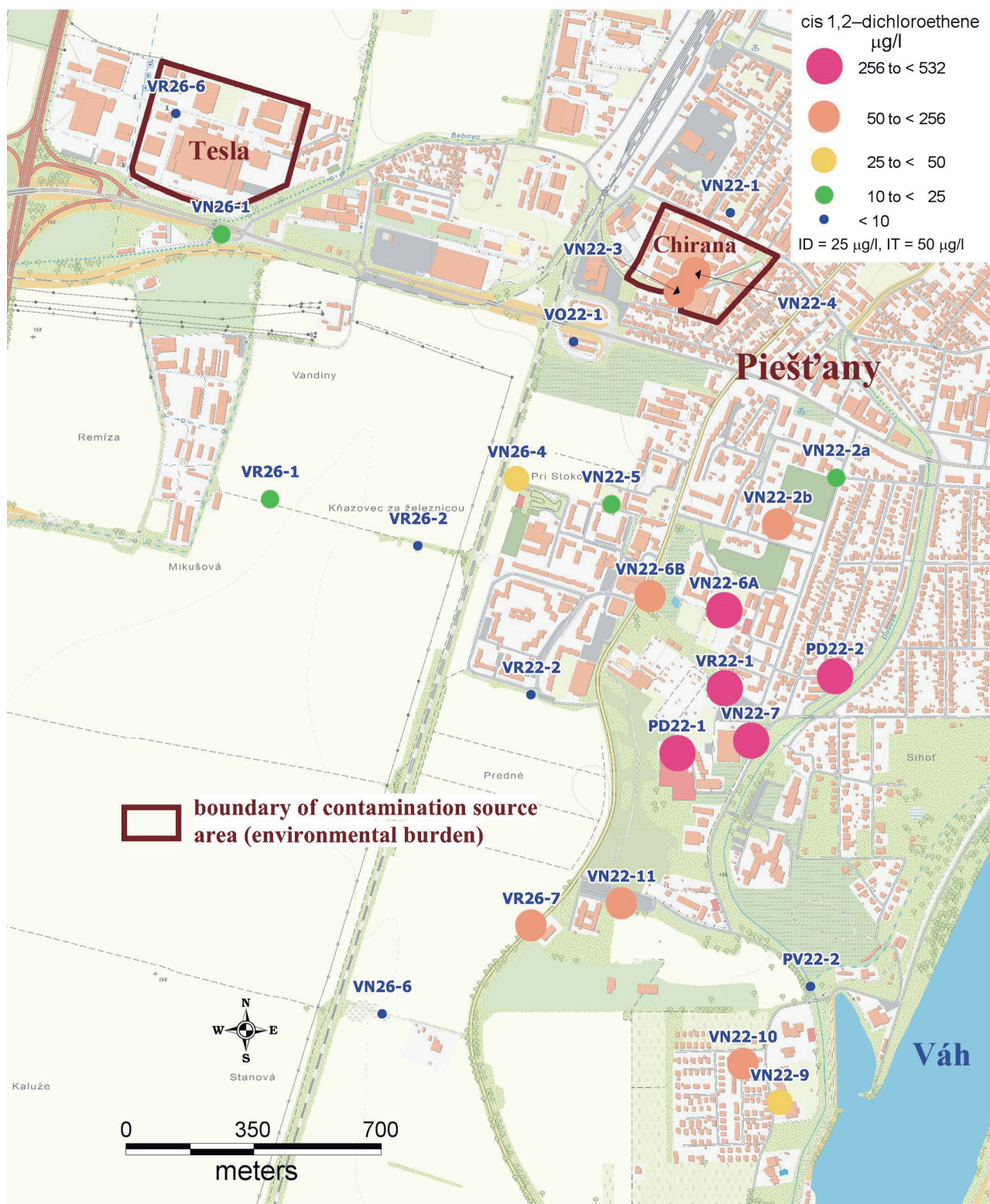


Fig. 1.5 Distribution of cis 1,2-dichloroethene in groundwaters (median concentrations) – sites Piešťany – former factories Chirana and Tesla (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)





Fig. 1.6 Distribution of trichloroethene in groundwaters (median concentrations) – sites Piešťany – former factories Chirana and Tesla (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



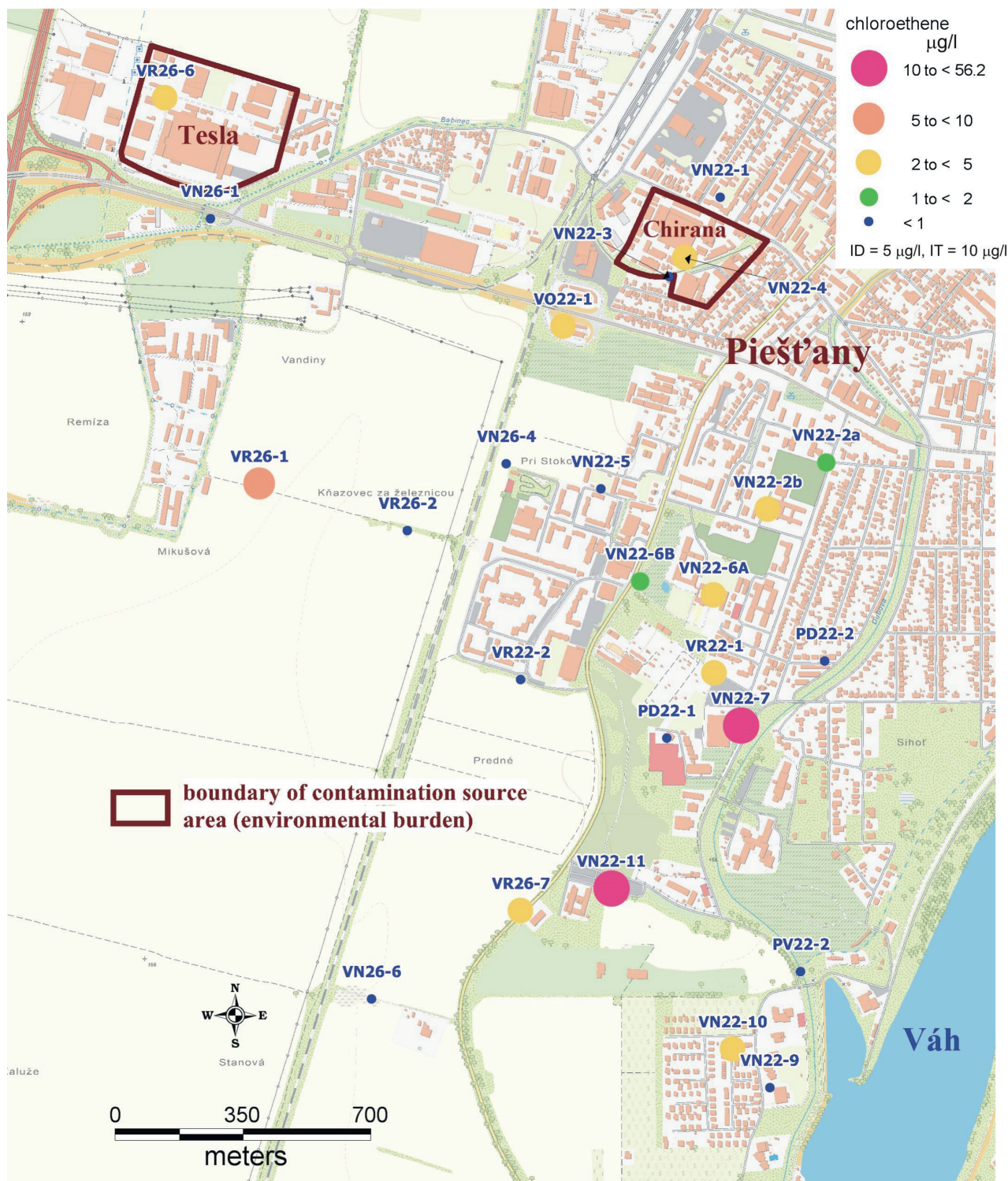


Fig. 1.7 Distribution of chloroethene in groundwaters (median concentrations) – sites Piešťany – former factories Chirana and Tesla (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

where high levels of  $\text{NH}_4^+$  and Ni were found. Borehole VR24-2 also contains  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , Zn and B, and the wells in the downstream groundwater south and southeast of the pollution sources had elevated levels of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ . This originated from both nickel operation and intensive farming. Compared to older studies by Klaučo et al. (1994) we found that groundwater pollution in the original contamination sources from cessation of smelter operations has decreased, but there was gradual propagation of contaminated plume south of the source.

Maps of distribution of  $\text{NH}_4^+$ , Ni and  $\text{NO}_3^-$  in groundwaters are presented in Figs. 1.8 to 1.10.

### 1.3.4 Zlaté Moravce –Calex (loc. No. 35)

Former area of the Calex Zlaté Moravce factory (founded in 1949) has still a significant environmental impact. Mainly refrigerators and other refrigeration equipments were manufactured in the factory. Results of analytical determination of basic inorganic and especially selected organic indicators of chemical composition confirmed high concentrations of hazardous substances such as dichloroethylene (DCE), trichloroethylene (TCE), tetrachloroethylene (PCE) and vinylchloride (VC) in groundwater. The contaminants are found in the wider area of the former Calex industrial park. Based on the results

of several sampling campaigns we found that the contents of DCE, TCE, PCE and VC have fluctuating character in groundwater and with the distance from the main source area of contamination decrease.

The area of interest is mostly built of the Quaternary sediments (sediments of the Žitava River and Hostiansky potok Brook). The uppermost part, up to approx. 2.5 m, is represented by loams and clays below which sandy gravels are located up to a depth of 6 – 7 m. Below them is a Neogene stratified silt (clay), sandy silt or sand (Makuša, 2001).

Mainly elevated or high contents of cis 1,2-dichloroethene, tetrachloroethene, trichloroethene and chloroethene in groundwater of several boreholes in the study area were observed (Tab. 1.5). The most significant pollution of chlorinated hydrocarbons is linked to the contamination sources located in the area of the former Calex factory and to a lesser extent spreads towards residential areas of Zlaté Moravce. The highest trichloroethene concentrations in groundwater (20 – 85  $\text{mg.l}^{-1}$ ) were found near the source of pollution (borehole VO35-9). At a distance of about 160 m from the source of contamination, trichloroethene contents of 0.026  $\text{mg.l}^{-1}$  exceeding the ID limit were found (in household well PD35-1). At a greater distance from the source

Table 1.4 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – sites Sered' – landfill dump and former Nickel plant area

| Landfill dump              | unit                 | mean  | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples $\geq$ ID | number of samples $\geq$ IT |
|----------------------------|----------------------|-------|--------|--------------------|---------|---------|--------|----------|----------|-----------------------------|-----------------------------|
| $\text{NH}_4^+$            | $\text{mg.l}^{-1}$   | 12.9  | 8.98   | 12.1               | 0.02    | 47.3    | 97     | 1.2      | 2.4      | 0                           | 73                          |
| $\text{NO}_3^-$            | $\text{mg.l}^{-1}$   | 61.7  | 68     | 52.5               | <0.5    | 161     | 97     |          |          |                             |                             |
| $\text{Cl}^-$              | $\text{mg.l}^{-1}$   | 80.4  | 69.5   | 49.2               | 32.5    | 282     | 97     | 150      | 250      | 5                           | 3                           |
| $\text{SO}_4^{2-}$         | $\text{mg.l}^{-1}$   | 213   | 161    | 194                | 42.8    | 1,145   | 97     |          |          |                             |                             |
| $\text{Fe}_{\text{total}}$ | $\text{mg.l}^{-1}$   | 0.02  | 0.01   | 0.02               | <0.002  | 0.088   | 90     |          |          |                             |                             |
| Mn                         | $\text{mg.l}^{-1}$   | 0.49  | 0.136  | 0.68               | <0.002  | 3.49    | 90     |          |          |                             |                             |
| B                          | $\text{mg.l}^{-1}$   | 0.27  | 0.173  | 0.29               | <0.02   | 1.496   | 83     | 0.5      | 5        | 14                          | 0                           |
| Ni                         | $\mu\text{g.l}^{-1}$ | 145   | 3      | 542                | <2      | 4,380   | 92     | 100      | 200      | 0                           | 16                          |
| Plant area                 | unit                 | mean  | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples $\geq$ ID | number of samples $\geq$ IT |
| $\text{NH}_4^+$            | $\text{mg.l}^{-1}$   | 5.77  | 4.16   | 6.30               | <0.02   | 21.7    | 96     | 1.2      | 2.4      | 3                           | 52                          |
| $\text{NO}_3^-$            | $\text{mg.l}^{-1}$   | 10.8  | 4.69   | 19.4               | <0.5    | 91.4    | 96     |          |          |                             |                             |
| $\text{Cl}^-$              | $\text{mg.l}^{-1}$   | 33.3  | 30.2   | 20.9               | 3.31    | 91.8    | 96     | 150      | 250      | 0                           | 0                           |
| $\text{SO}_4^{2-}$         | $\text{mg.l}^{-1}$   | 188   | 81.0   | 387                | 7.62    | 3,237   | 96     |          |          |                             |                             |
| $\text{Fe}_{\text{total}}$ | $\text{mg.l}^{-1}$   | 1.49  | 0.016  | 4.47               | <0.002  | 25.4    | 92     |          |          |                             |                             |
| Mn                         | $\text{mg.l}^{-1}$   | 1.71  | 0.624  | 4.02               | <0.003  | 23.9    | 92     |          |          |                             |                             |
| B                          | $\text{mg.l}^{-1}$   | 0.31  | 0.135  | 0.56               | <0.02   | 3.29    | 87     | 0.5      | 5        | 12                          | 0                           |
| Ni                         | $\mu\text{g.l}^{-1}$ | 3,107 | 3      | 12,369             | <2      | 80,523  | 93     | 100      | 200      | 1                           | 20                          |



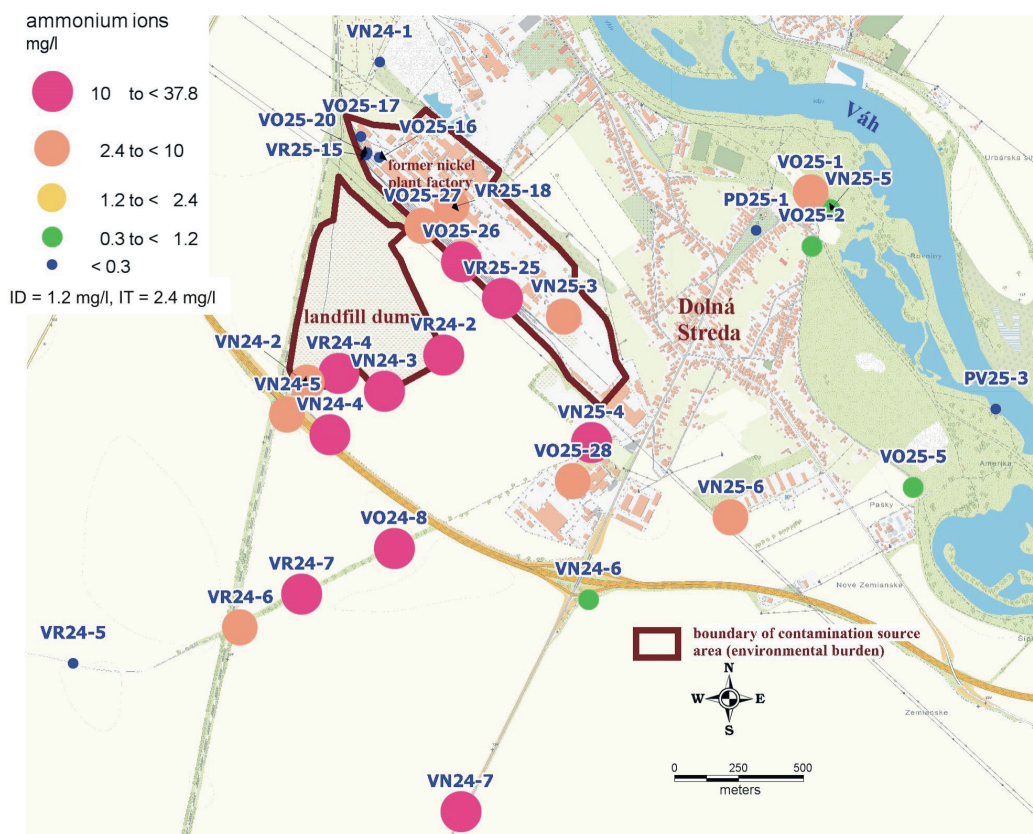


Fig. 1.8 Distribution of  $\text{NH}_4^+$  in groundwaters (median concentrations) – sites Sereď – landfill dump and former Nickel plant area (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

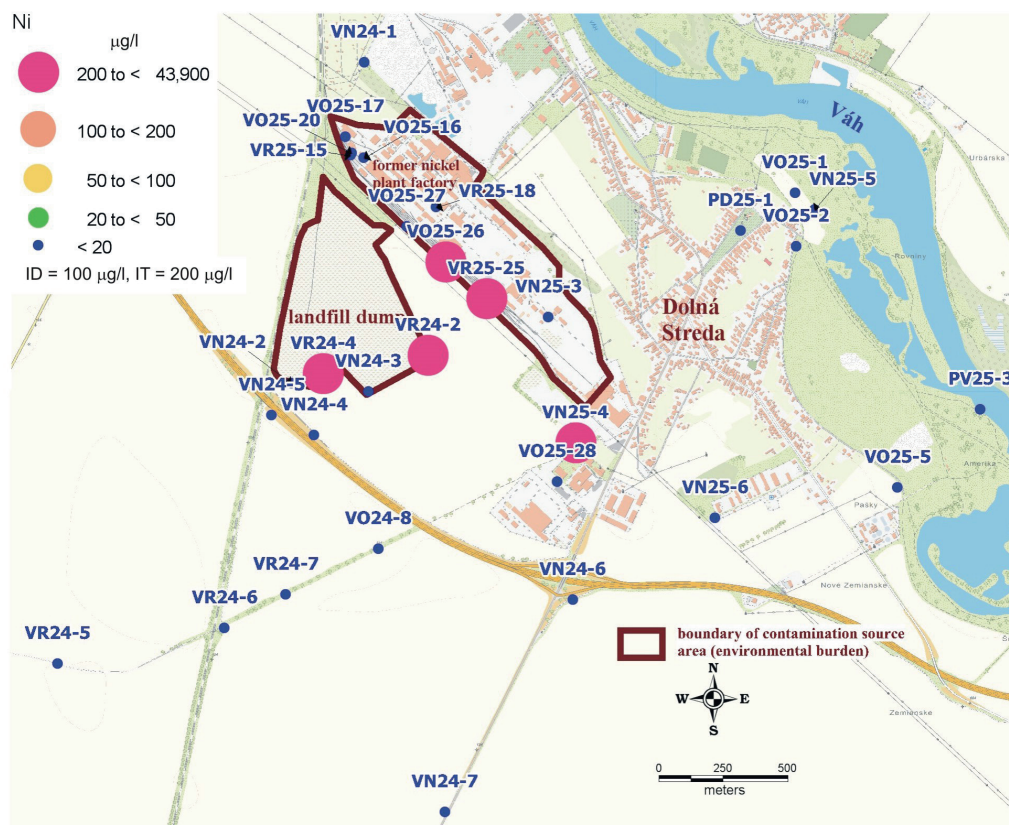
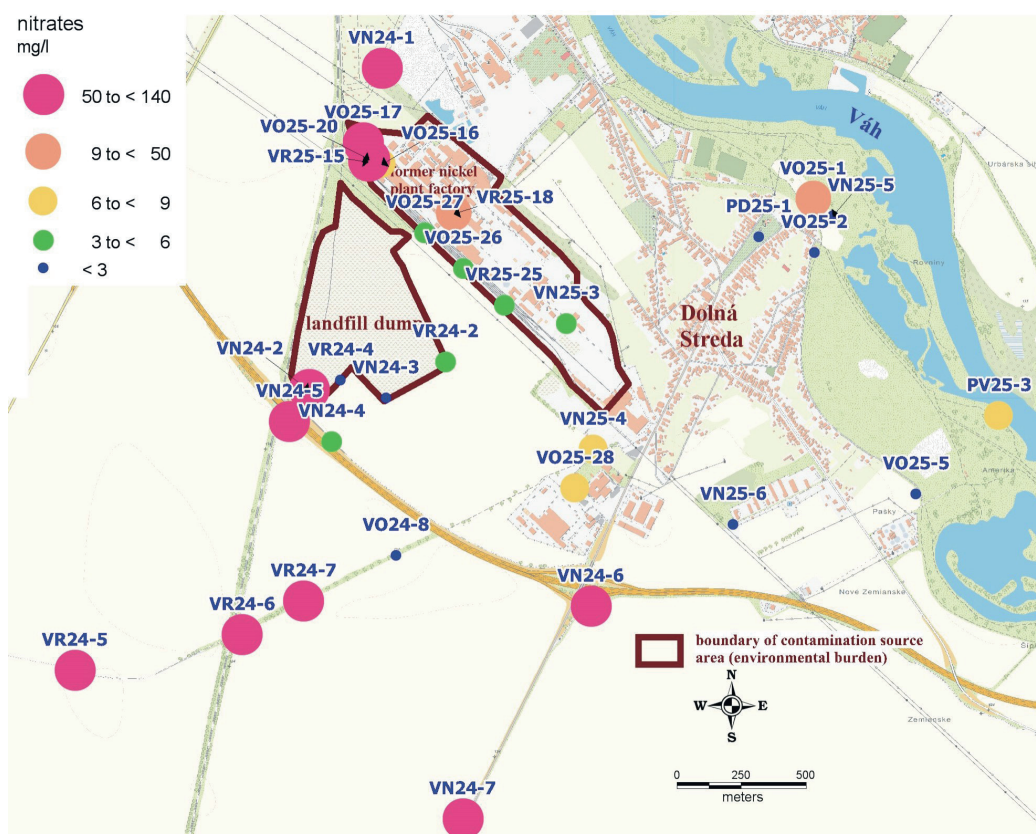


Fig. 1.9 Distribution of Ni in groundwaters (median concentrations) – sites Sereď – landfill dump and former Nickel plant area (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)





**Fig. 1.10** Distribution of  $\text{NO}_3^-$  in groundwaters (median concentrations) – sites Sereď – landfill dump and former Nickel plant area (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

of contamination (approx. 850 m) low levels of chlorinated hydrocarbons in groundwater were found.

Maps of distribution of cis 1,2-dichloroethene, tetrachloroethene and trichloroethene (median concentrations) in groundwaters are presented in Figs. 1.11 to 1.13.

### 1.3.5 Bojná – landfill – part A (loc. No. 85)

The old landfill (part A) has the character of municipal waste with the possibility of leakage of contaminants. The material was transported to the landfill – part A between

1960 and 1992. The waste was spontaneously and uncontrollably put into the erosion pits. The composition of the waste was not registered, mostly it represents domestic waste from the surrounding municipalities. An estimated 350,000 to 400,000 m<sup>3</sup> of solid municipal and industrial waste was deposited in landfill – part A.

The Neogene and Quaternary sediments contribute to the geological settings of the area. The Neogene is represented by clay sediments, in which the positions of loamy sands and gravels often occur. The thickness of the gravel layers reaches up to 4 m and the thickness of the sand

Table 1.5 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Zlaté Moravce – Calex

|                          | unit               | mean  | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples $\geq$ ID | number of samples $\geq$ IT |
|--------------------------|--------------------|-------|--------|--------------------|---------|---------|--------|----------|----------|-----------------------------|-----------------------------|
| TOC                      | mg.l <sup>-1</sup> | 2.02  | 1.7    | 1.23               | 0.3     | 6.6     | 118    | 2        | 5        | 40                          | 4                           |
| COD <sub>Mn</sub>        | mg.l <sup>-1</sup> | 2.59  | 1.12   | 3.15               | <0.5    | 15.3    | 76     | 5        | 10       | 4                           | 5                           |
| 1,1-dichloroethene       | μg.l <sup>-1</sup> | 1.61  | 0.2    | 4.38               | <0.1    | 32.5    | 124    | 10       | 20       | 6                           | 1                           |
| cis 1,2-dichloroethene   | μg.l <sup>-1</sup> | 522   | 0.85   | 3,185              | <0.1    | 34,190  | 124    | 25       | 50       | 2                           | 27                          |
| trans 1,2-dichloroethene | μg.l <sup>-1</sup> | 3.71  | 0.2    | 13.2               | <0.1    | 121     | 124    | 25       | 50       | 3                           | 2                           |
| tetrachloroethene        | μg.l <sup>-1</sup> | 249   | 9.55   | 846                | <0.2    | 6,482   | 124    | 10       | 20       | 7                           | 52                          |
| trichloroethene          | μg.l <sup>-1</sup> | 4,056 | 8.6    | 13,313             | <0.1    | 85,200  | 124    | 25       | 50       | 6                           | 49                          |
| chloroethene             | μg.l <sup>-1</sup> | 84.5  | <0.2   | 517                | <0.2    | 5,186   | 124    | 5        | 10       | 2                           | 19                          |

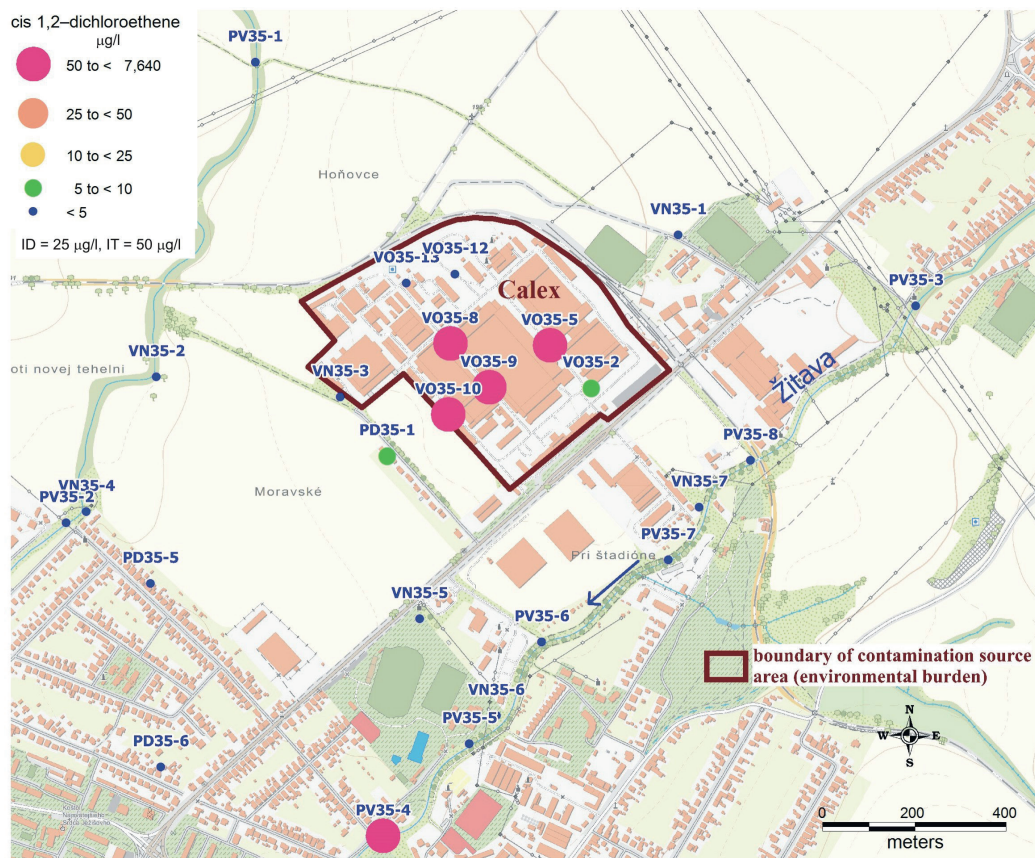


Fig. 1.11 Distribution of cis 1,2-dichloroethene in groundwaters (median concentrations) – site Zlaté Moravce – Calex (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

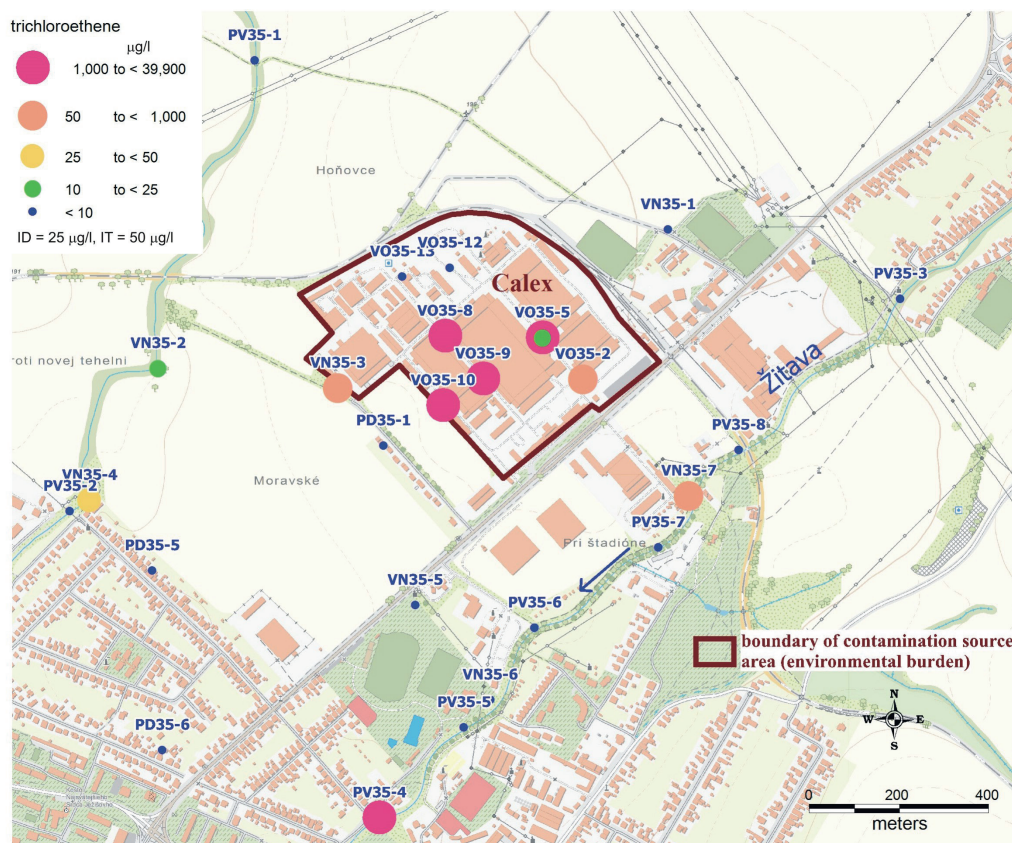


Fig. 1.12 Distribution of trichloroethene in groundwaters (median concentrations) – site Zlaté Moravce – Calex (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



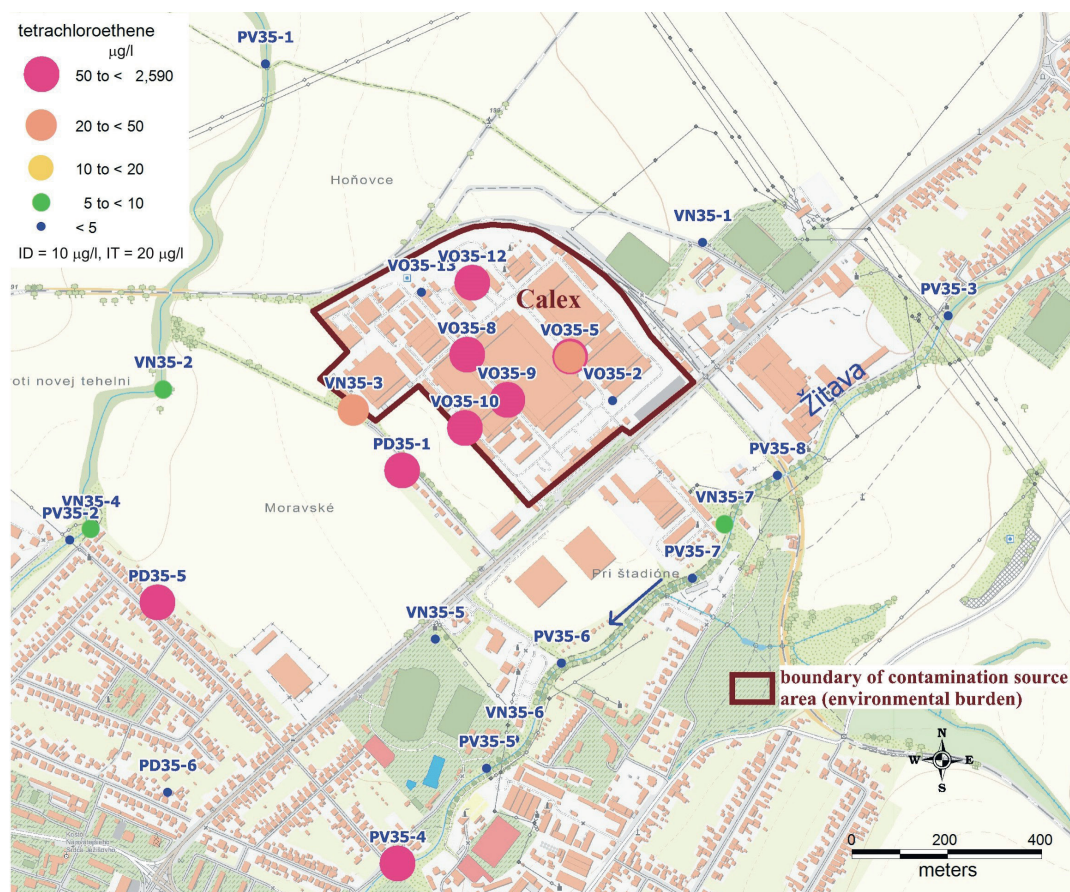


Fig. 1.13 Distribution of tetrachloroethene in groundwaters (median concentrations) – site Zlaté Moravce – Calex (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

Table 1.6 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Bojná – landfill – part A

|                               | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples >ID | number of samples >IT |
|-------------------------------|--------------------|------|--------|--------------------|---------|---------|--------|----------|----------|-----------------------|-----------------------|
| NH <sub>4</sub> <sup>+</sup>  | mg.l <sup>-1</sup> | 19.3 | 0.22   | 87.2               | <0.04   | 779     | 95     | 1.2      | 2.4      | 9                     | 18                    |
| Cl <sup>-</sup>               | mg.l <sup>-1</sup> | 402  | 218    | 515                | 2.28    | 2,168   | 95     | 150      | 250      | 9                     | 42                    |
| SO <sub>4</sub> <sup>2-</sup> | mg.l <sup>-1</sup> | 93.9 | 45.4   | 130                | 2       | 669     | 95     |          |          |                       |                       |
| HCO <sub>3</sub> <sup>-</sup> | mg.l <sup>-1</sup> | 832  | 387    | 978                | 78.1    | 5,161   | 77     |          |          |                       |                       |
| TOC                           | mg.l <sup>-1</sup> | 32.0 | 8.9    | 55.0               | 0.1     | 296     | 90     | 2        | 5        | 8                     | 57                    |
| COD <sub>Mn</sub>             | mg.l <sup>-1</sup> | 17.6 | 6.54   | 30.9               | <0.5    | 150     | 83     | 5        | 10       | 12                    | 31                    |
| Na <sup>+</sup>               | mg.l <sup>-1</sup> | 166  | 66.4   | 231                | 11.5    | 969     | 87     |          |          |                       |                       |
| K <sup>+</sup>                | mg.l <sup>-1</sup> | 24.7 | 2.15   | 91.1               | 0.71    | 602     | 87     |          |          |                       |                       |
| Ca <sup>2+</sup>              | mg.l <sup>-1</sup> | 208  | 110    | 174                | 21.3    | 719     | 87     |          |          |                       |                       |
| Mg <sup>2+</sup>              | mg.l <sup>-1</sup> | 73.4 | 36.7   | 71.5               | 6.82    | 287     | 87     |          |          |                       |                       |
| Fe <sub>total</sub>           | mg.l <sup>-1</sup> | 10.2 | 0.173  | 36.8               | 0.007   | 338     | 94     |          |          |                       |                       |
| Mn                            | mg.l <sup>-1</sup> | 0.93 | 0.134  | 1.90               | <0.001  | 14.5    | 94     |          |          |                       |                       |
| B                             | mg.l <sup>-1</sup> | 0.95 | 0.162  | 1.59               | <<0.01  | 8.09    | 90     | 0.5      | 5        | 27                    | 2                     |
| As                            | µg.l <sup>-1</sup> | 42.4 | 1.4    | 262                | 0.5     | 2,300   | 91     | 50       | 100      | 3                     | 3                     |



fluctuates around 1 – 2 m. The Quaternary is represented by fluvial and deluvial sediments. The fluvial sediments of streams are formed by clayey sands and sandy gravels of different thickness (4 – 10 m) and are often covered by alluvial clays. The deluvial sediments are represented by colluvial clays and debris (Némethyová et al., 1981).

The impact of the landfill on the quality of groundwater has been clearly documented, manifested mainly by high contents of  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{COD}_{\text{Mn}}$ , TOC and B (Tab. 1.6). Following the Directive of the MoE of the Slovak Republic 1/2015-7 on elaboration of the risk analysis of contaminated area, exceedances of ID and/or IT criteria for other physicochemical indicators – pH, conductivity, nitrites, soluble substances, Ba, As, Ni, chloroethene and

benzene were observed in groundwater, especially near landfill (Kordík & Slaninka et al., 2015).

Maps of distribution of  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{COD}_{\text{Mn}}$ , TOC and B (median concentrations) in groundwaters are presented in Figs. 1.14 to 1.18.

The mechanism of environmental contamination in the landfill area is as follows. Rainwater enters the landfill environment where it is enriched with soluble and insoluble substances. Contaminated water, after passing the aeration zone and reaching the groundwater level, contaminates the aquifer in its surroundings. The contamination spreads further into the environment in the direction of groundwater movement in the form of a contamination plume. The contaminated water also rises

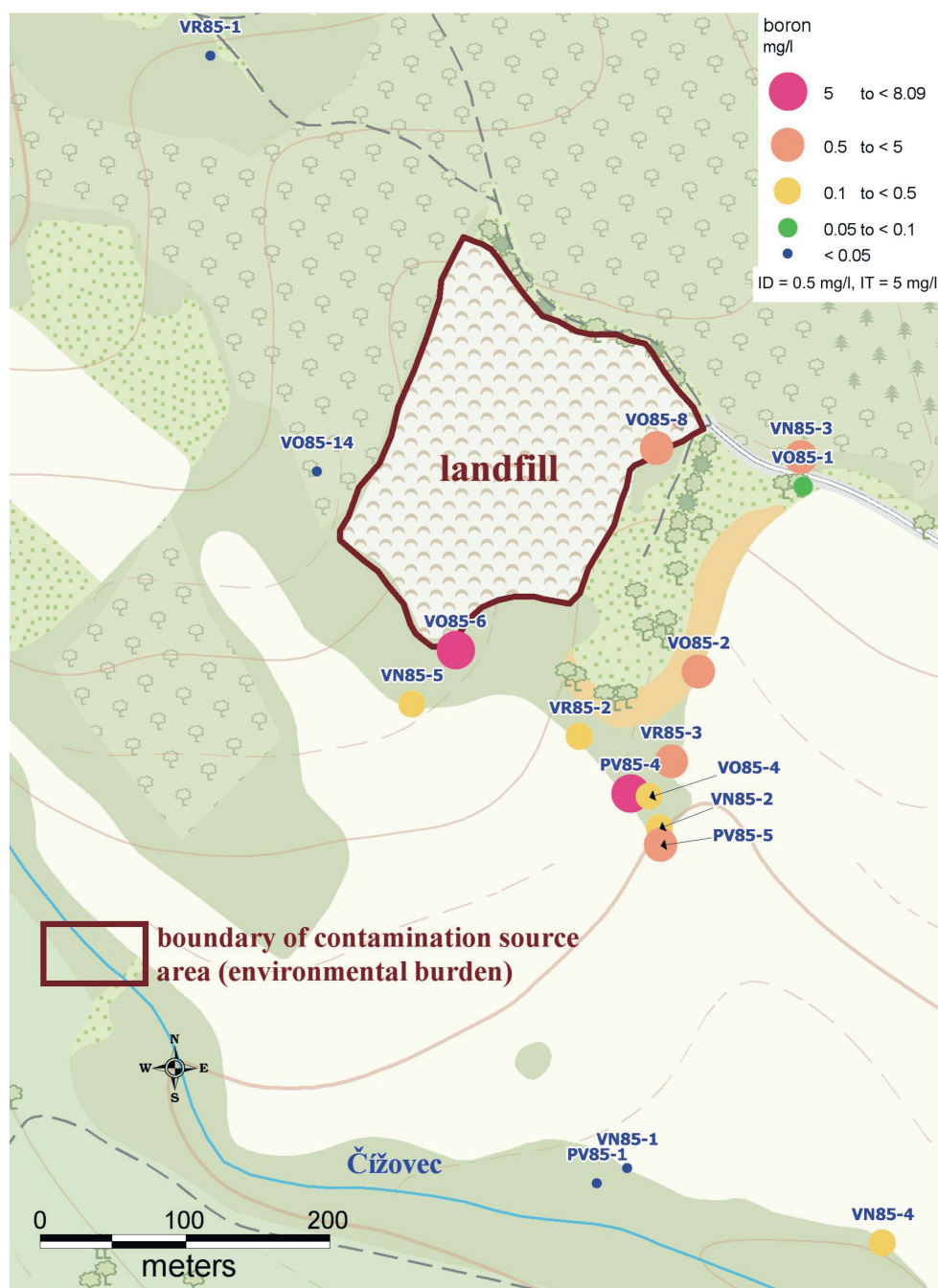


Fig. 1.14 Distribution of boron in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

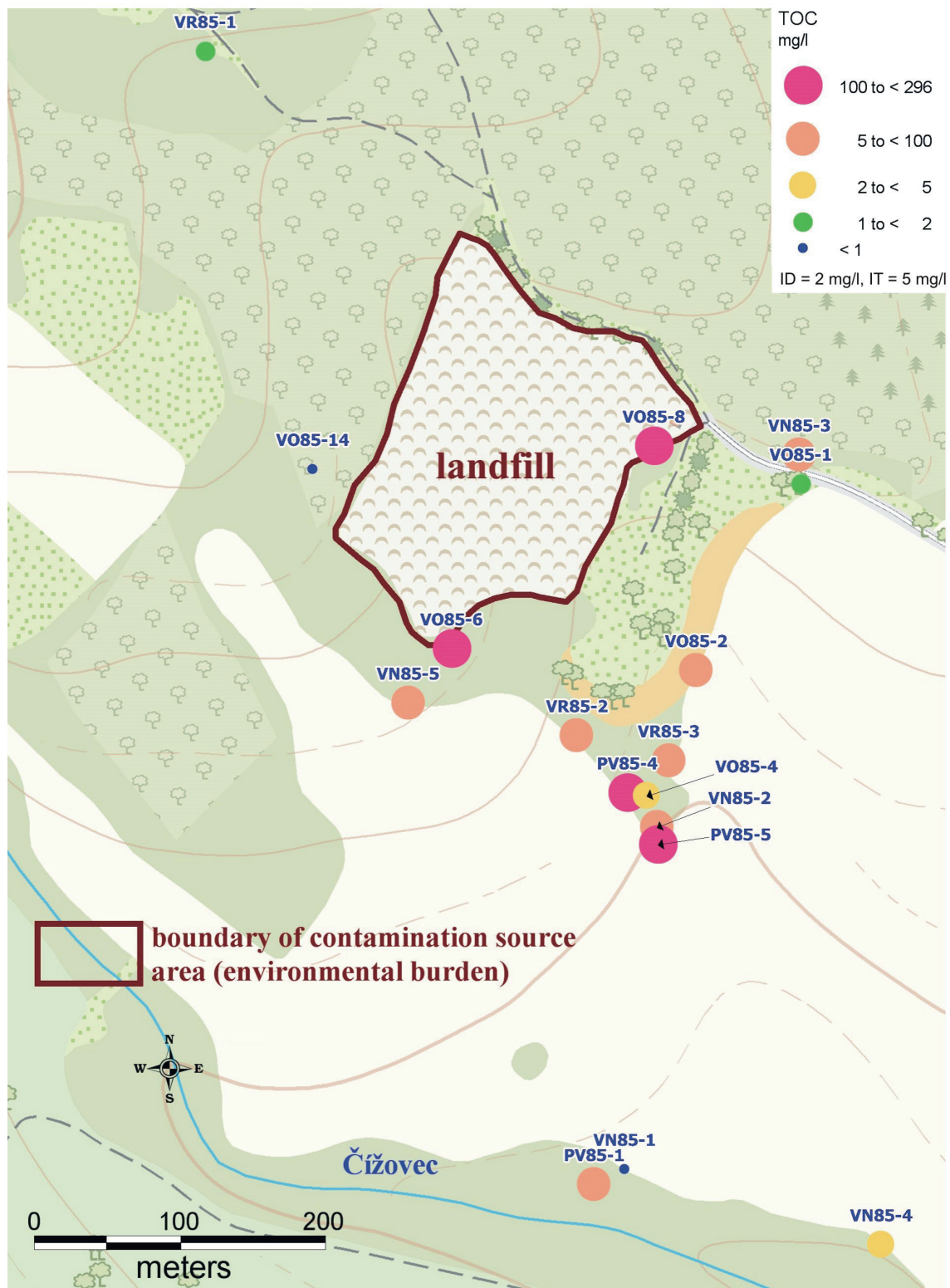


Fig. 1.15 Distribution of TOC in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

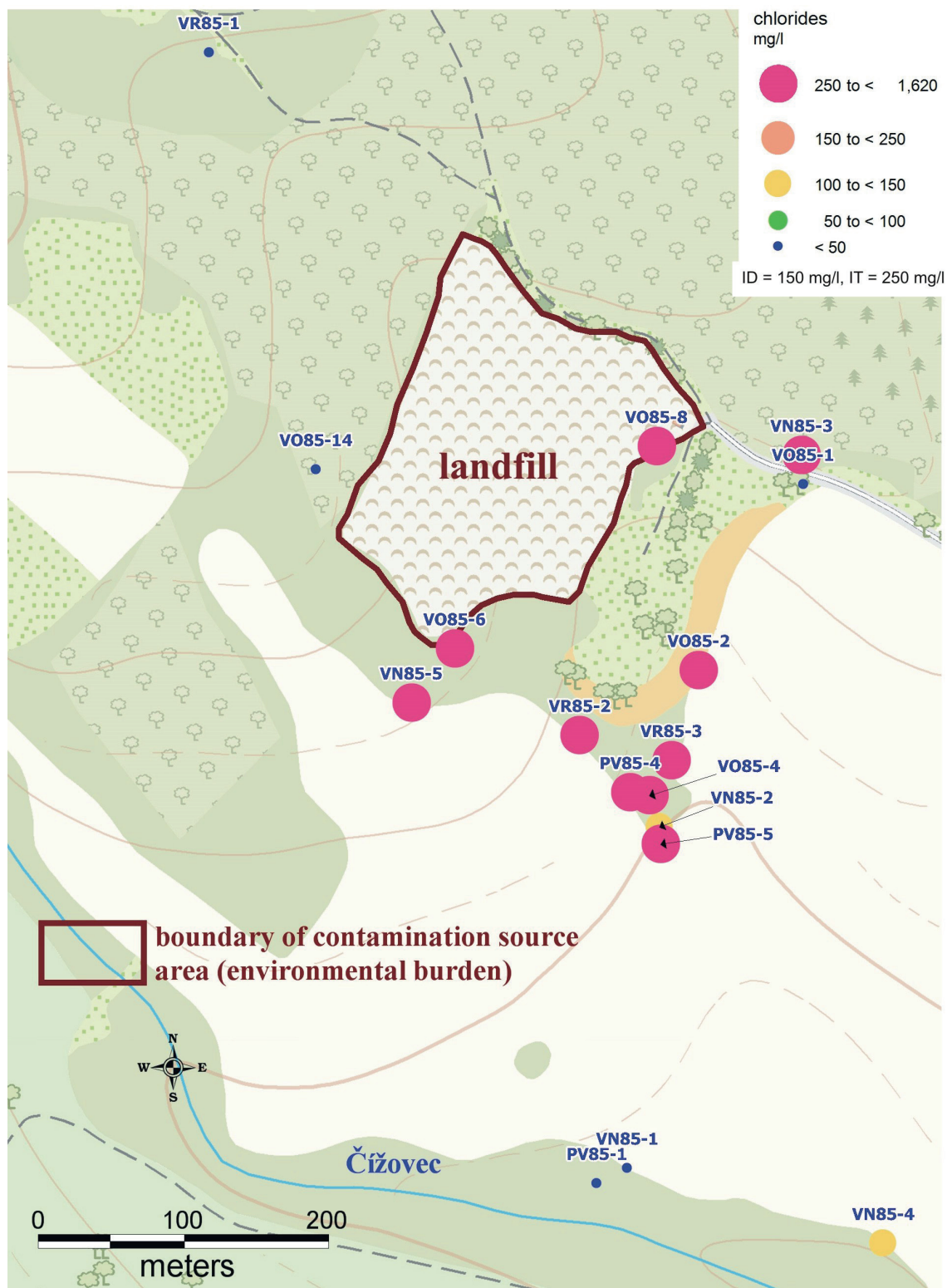


Fig. 1.16 Distribution of chlorides in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



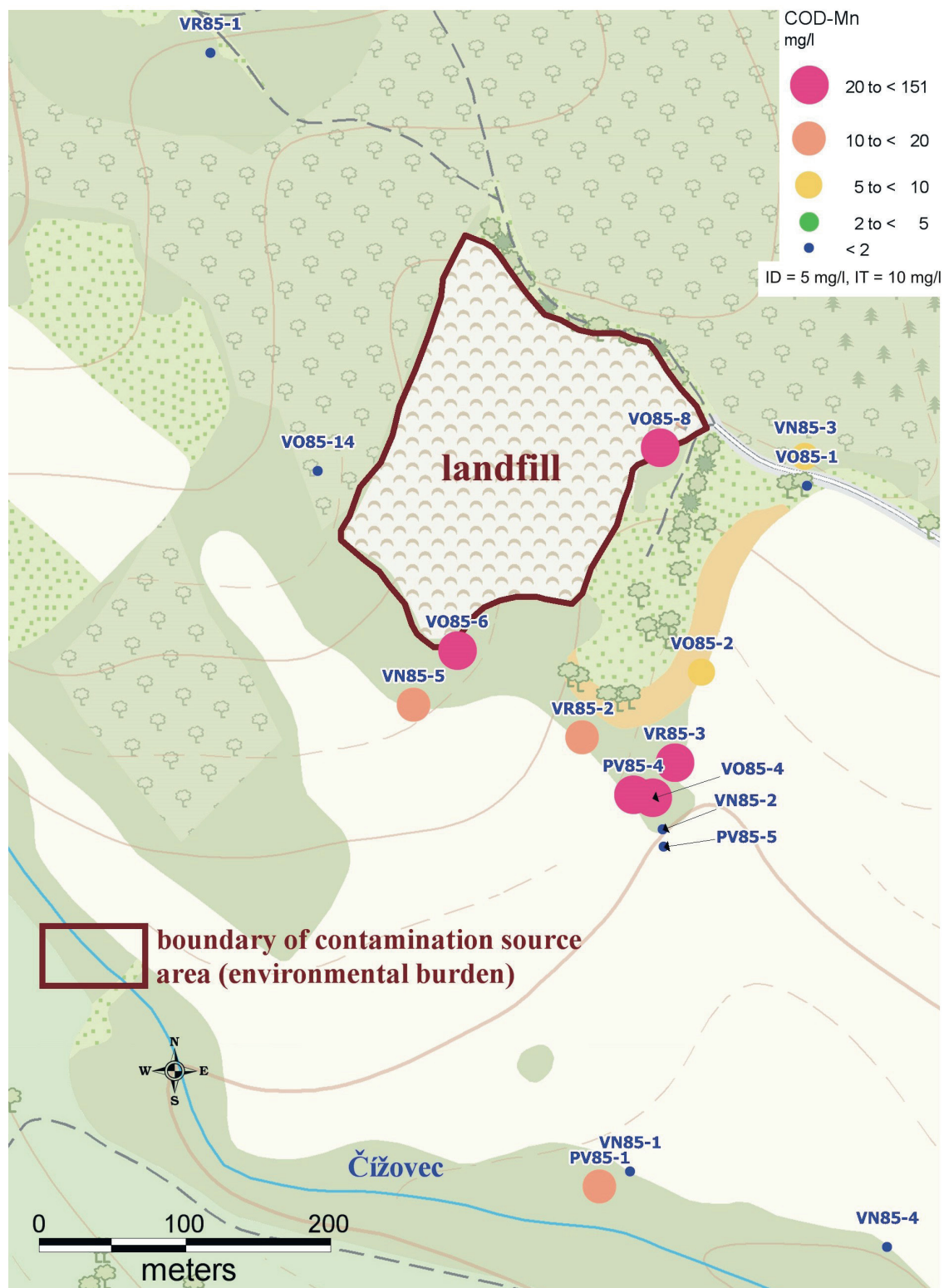


Fig. 1.17 Distribution of  $\text{COD}_{\text{Mn}}$  in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

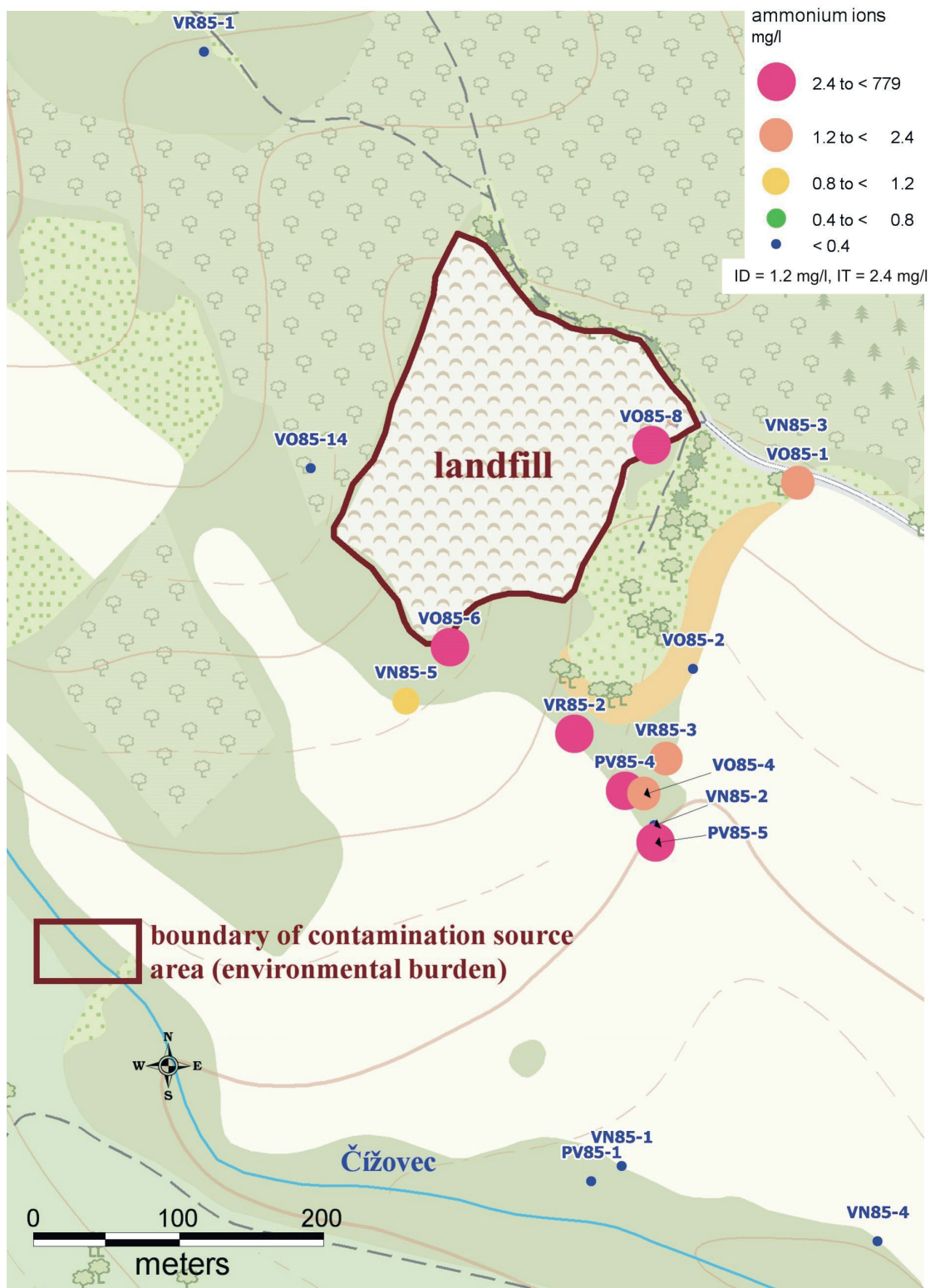


Fig. 1.18 Distribution of  $\text{NH}_4^+$  in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

below the landfill and accumulates in a pond below the landfill, from where it spreads on the surface towards the tributary of the Čížovský potok Brook. The assumption that the groundwater contamination could also spread northeast to the Bojnianka stream has been also confirmed. We do not expect a high risk of pollution from the landfill for surface water (the nameless tributary of the Čížovský potok Brook). The surface water “above and below” the landfill shows essentially constant chemical composition and good quality in terms of both inorganic and organic indicators.

### 1.3.6 Bratislava – Vrakuňa – CHZJD landfill (loc. No. 203)

The landfill was set up in the former cut-off meander of the Little Danube River and was dumped in waste from the production of chemicals, especially pesticides and herbicides. The waste storage began in 1966 and ended in 1979. The thickness of the transported waste ranged from approximately 1.5 to 2.5 m. With an average waste

thickness of 2 m and an area of 4.65 ha, about 90,000 m<sup>3</sup> of waste was deposited here. By the end of landfilling, in 1980 began the remediation of landfill, which consisted of waste covering with inert material. The area of the former landfill gradually began to be used as operational and technological areas; part of the area remains unused to this day. Site is currently being prepared for remediation.

The geological structure is made up of fine-grained Neogene sediments of the Danube Basin, which are covered by fluvial alluviums of the Danube River and adjacent streams. The Neogene sediments do not crop out to the surface. The Neogene sediments are at depths of more than 9 – 14 m and are represented by sandy clay, loamy clay and clayey sand. The Quaternary fluvial sediments overlay the Neogene sediments. Their base is located at a depth of 10 – 15 m. The fluvial sediments consist of gravels, sandy gravels and sands with gravel. Top layers contain loamy clay, loamy sand and coarse fillings of anthropogenic and heterogeneous character (Pristaš et al., 2000).

The groundwater and the rock environment are contaminated with several pollutants in the area. Among the

Table 1.7 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Bratislava – CHZJD landfill

|                                                       | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples >ID | number of samples >IT |
|-------------------------------------------------------|--------------------|------|--------|--------------------|---------|---------|--------|----------|----------|-----------------------|-----------------------|
| NH <sub>4</sub> <sup>+</sup>                          | mg.l <sup>-1</sup> | 1.90 | 0.125  | 4.93               | <0.03   | 25.7    | 54     | 1.2      | 2.4      | 5                     | 8                     |
| TOC                                                   | mg.l <sup>-1</sup> | 19.6 | 2.2    | 40.9               | <0.5    | 219     | 81     | 2        | 5        | 12                    | 29                    |
| As                                                    | mg.l <sup>-1</sup> | 58.5 | 0.5    | 202                | <0.1    | 1,310   | 127    | 50       | 100      | 5                     | 13                    |
| COD <sub>Cr</sub>                                     | mg.l <sup>-1</sup> | 108  | 23     | 212                | 6       | 993     | 43     |          |          |                       |                       |
| surfactants                                           | mg.l <sup>-1</sup> | 1.16 | 0.235  | 2.81               | <0.05   | 13.8    | 54     | 0.25     | 0.5      | 9                     | 16                    |
| phenol index                                          | mg.l <sup>-1</sup> | 0.51 | <0.01  | 1.92               | <0.01   | 11.4    | 77     | 0.015    | 0.06     | 7                     | 18                    |
| hydrocarbon index (C <sub>10</sub> -C <sub>40</sub> ) | mg.l <sup>-1</sup> | 0.07 | 0.02   | 0.16               | <0.02   | 1.33    | 100    | 0.25     | 0.5      | 1                     | 3                     |
| tetrachloroethene                                     | µg.l <sup>-1</sup> | 18.3 | 9.6    | 22.2               | <0.2    | 110     | 138    | 10       | 20       | 27                    | 40                    |
| tetrachloromethane                                    | µg.l <sup>-1</sup> | 1.93 | 0.2    | 10.2               | <0.1    | 91.8    | 84     | 5        | 10       | 5                     | 1                     |
| trichloroethene                                       | µg.l <sup>-1</sup> | 4.38 | 1.4    | 9.27               | <0.2    | 47.6    | 137    | 25       | 50       | 5                     | 0                     |
| chloroethene                                          | µg.l <sup>-1</sup> | 3.14 | 0.5    | 9.45               | <0.2    | 50      | 138    | 5        | 10       | 4                     | 9                     |
| 1,2-dichlorobenzene                                   | µg.l <sup>-1</sup> | 1.15 | 0.2    | 3.70               | <0.1    | 25.1    | 137    | 1.5      | 3        | 2                     | 12                    |
| 1,3-dichlorobenzene                                   | µg.l <sup>-1</sup> | 0.81 | 0.2    | 2.17               | <0.1    | 11.3    | 137    | 1.5      | 3        | 1                     | 9                     |
| 1,4-dichlorobenzene                                   | µg.l <sup>-1</sup> | 3.05 | 0.2    | 10.5               | <0.1    | 70.5    | 137    | 1.5      | 3        | 4                     | 18                    |
| benzene                                               | µg.l <sup>-1</sup> | 86.9 | <0.2   | 350                | <0.2    | 2,440   | 138    | 15       | 30       | 5                     | 14                    |
| ethylbenzene                                          | µg.l <sup>-1</sup> | 34.5 | 0.2    | 150                | <0.1    | 1,140   | 138    | 150      | 300      | 2                     | 5                     |
| chlorobenzene                                         | µg.l <sup>-1</sup> | 250  | 1.3    | 906                | <0.1    | 6,900   | 137    | 15       | 30       | 5                     | 31                    |
| toluene                                               | µg.l <sup>-1</sup> | 48.9 | 0.4    | 191                | <0.2    | 1,700   | 138    | 350      | 700      | 3                     | 3                     |
| xylene                                                | µg.l <sup>-1</sup> | 85.4 | 0.5    | 333                | <0.2    | 2,448   | 138    | 250      | 500      | 2                     | 8                     |
| atrazine                                              | µg.l <sup>-1</sup> | 90.9 | 0.03   | 538                | <0.02   | 4,060   | 121    | 100      | 500      | 2                     | 3                     |
| simazine                                              | µg.l <sup>-1</sup> | 4.73 | <0.02  | 27.5               | <0.02   | 225     | 121    | 100      | 500      | 2                     | 3                     |
| desethylatrazine                                      | µg.l <sup>-1</sup> | 0.26 | <0.02  | 1.36               | <0.02   | 11.1    | 121    | 100      | 500      | 0                     | 0                     |
| propazine                                             | µg.l <sup>-1</sup> | 5.21 | <0.02  | 26.2               | <0.02   | 183     | 121    | 100      | 500      | 3                     | 0                     |
| sebutylazine                                          | µg.l <sup>-1</sup> | 0.03 | <0.02  | 0.04               | <0.02   | 0.25    | 93     | 100      | 500      | 0                     | 0                     |
| prometryne                                            | µg.l <sup>-1</sup> | 118  | 0.12   | 781                | <0.02   | 6,190   | 121    | 100      | 500      | 1                     | 3                     |
| terbutryn                                             | µg.l <sup>-1</sup> | 0.11 | <0.02  | 0.45               | <0.02   | 3.18    | 121    | 100      | 500      | 0                     | 0                     |



organic substances mainly petroleum substances, pesticides (e.g. prometryne, simazine, lindane, chloridazone, and others), chlorinated volatile aliphatic and aromatic hydrocarbons (chlorobenzenes, tetrachloroethene), less PCB, BTEX, PAH, and among inorganic substances, in particular As, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, contaminate the groundwater (Tab. 1.7). Some contaminants (e.g. triazine pesticides, chlorinated hydrocarbons) have been identified at long distances from landfill. The monitoring also showed seasonal changes in the concentrations of some contaminants.

Under the present conditions of the water levels in the Danube River and the current conditions of operation of

significant water resources Kalinkovo, Šamorín and Jelka in the vicinity of the CHZJD landfill, as well as operation of the system of hydraulic protection of groundwater of the Slovnaft Refinery, we do not expect a direct threat to the groundwater quality of the above mentioned water resources. However, the situation could change if there is a change in the current hydraulic conditions in the area of interest (for example, in case of increased water abstraction from mentioned water resources, etc.). As already mentioned, several pollutants significantly threaten the water quality in the area of Vrakuňa, Podunajské Biskupice and penetrate further into the Žitný ostrov area (probably also within a distance of about 5 km from the landfill).

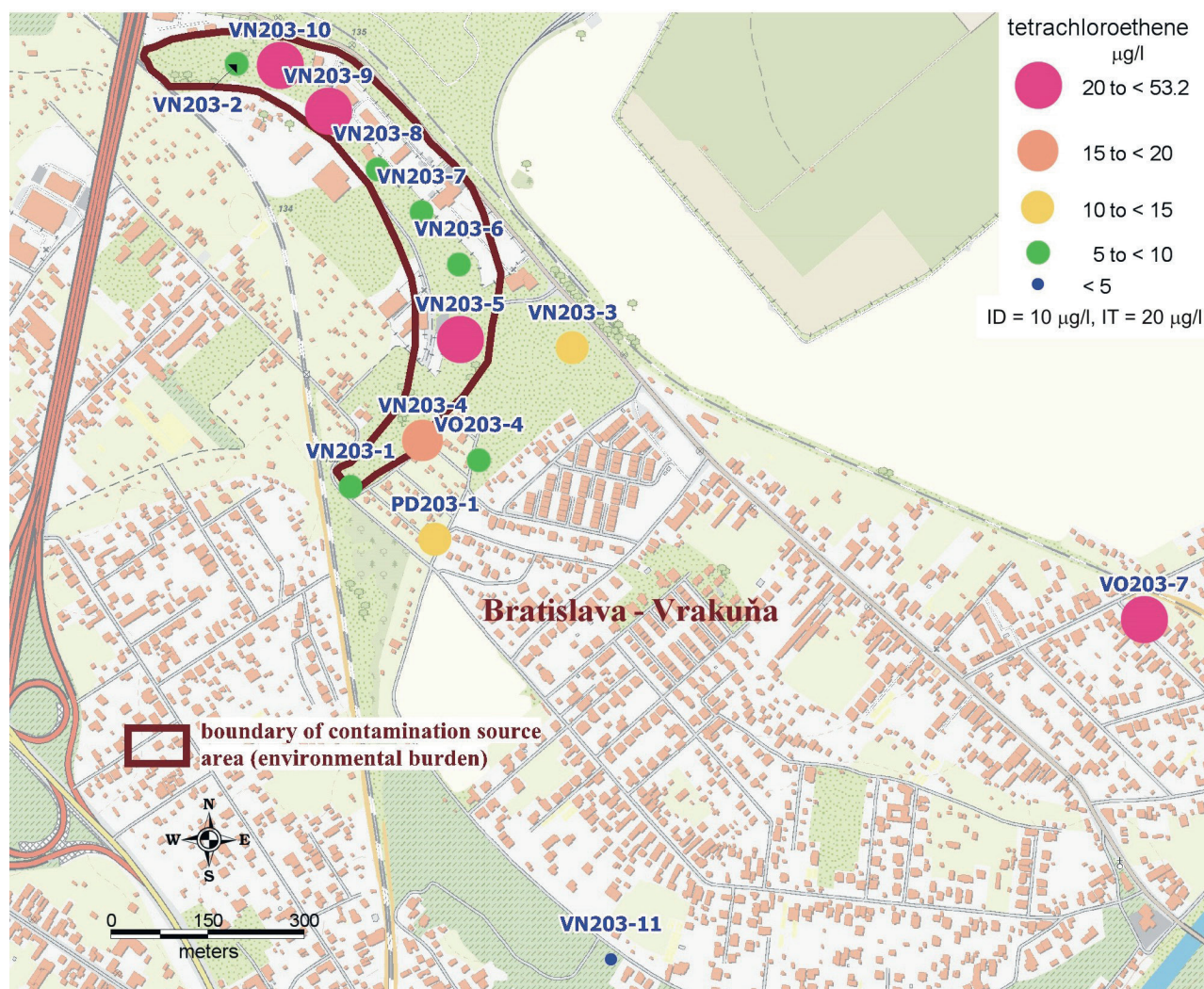


Fig. 1.19 Distribution of tetrachloroethene in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



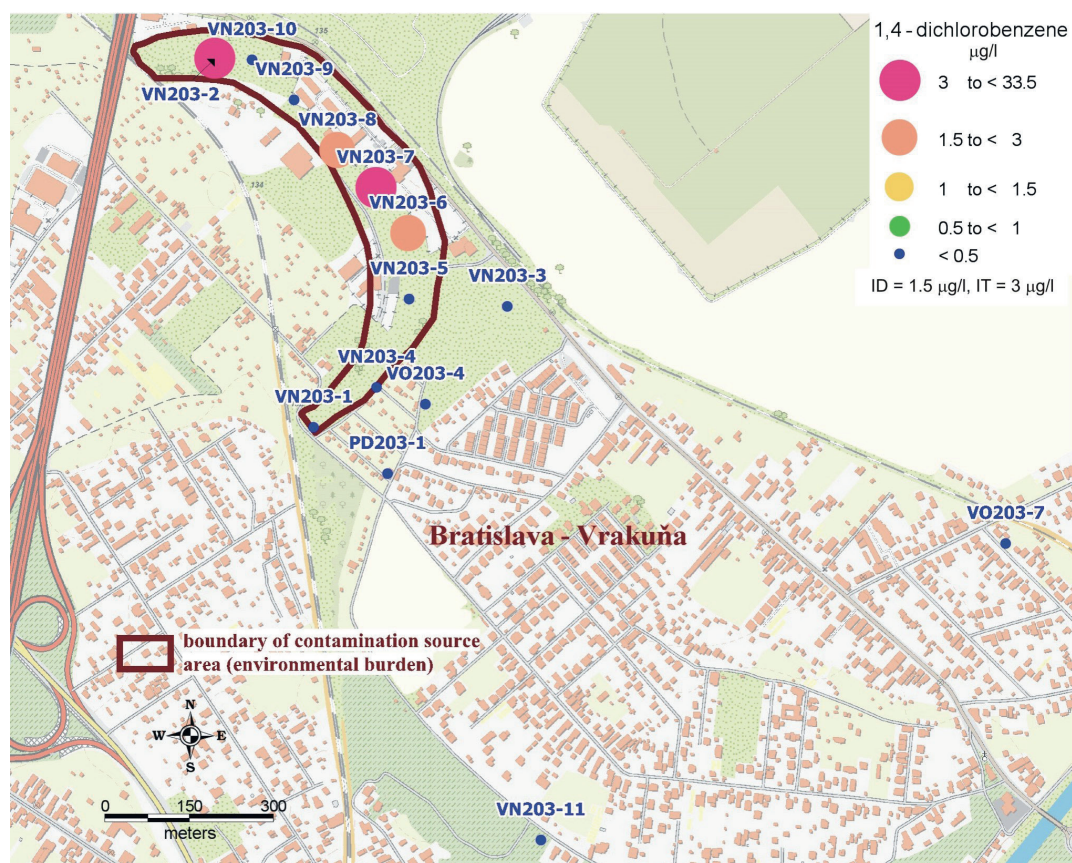


Fig. 1.20 Distribution of 1,4-dichlorobenzene in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

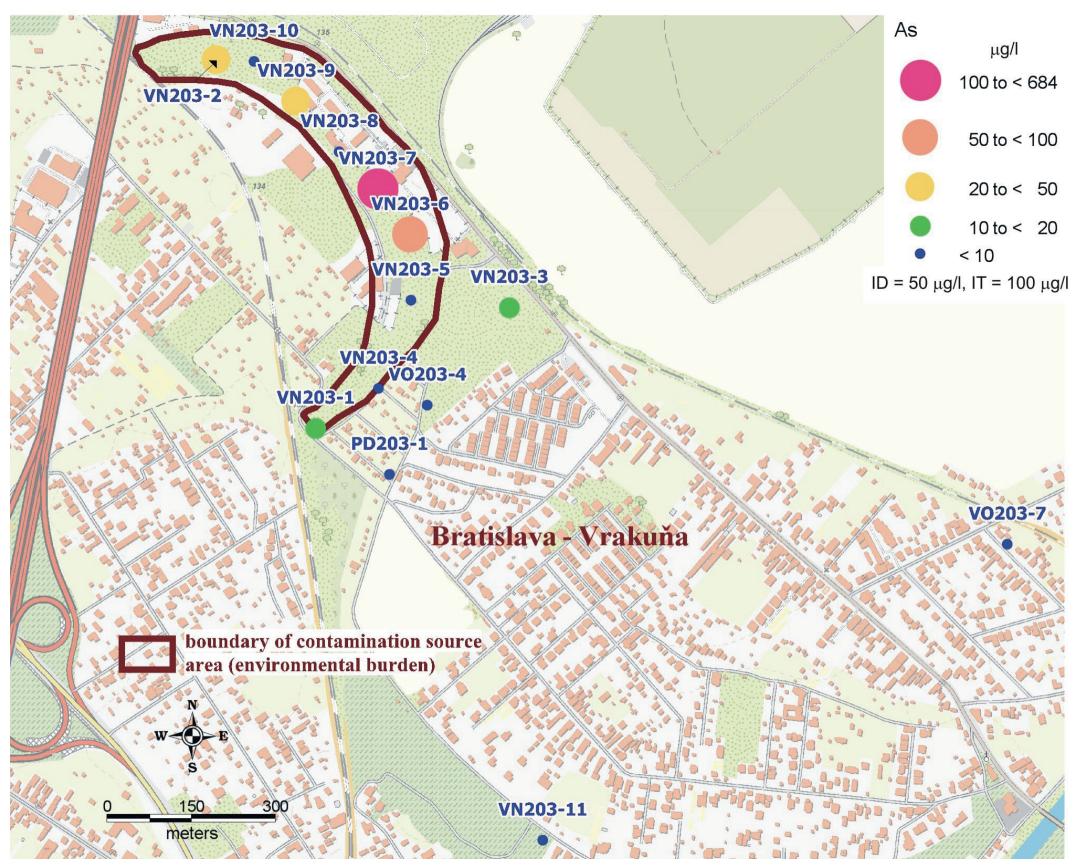


Fig. 1.21 Distribution of As in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



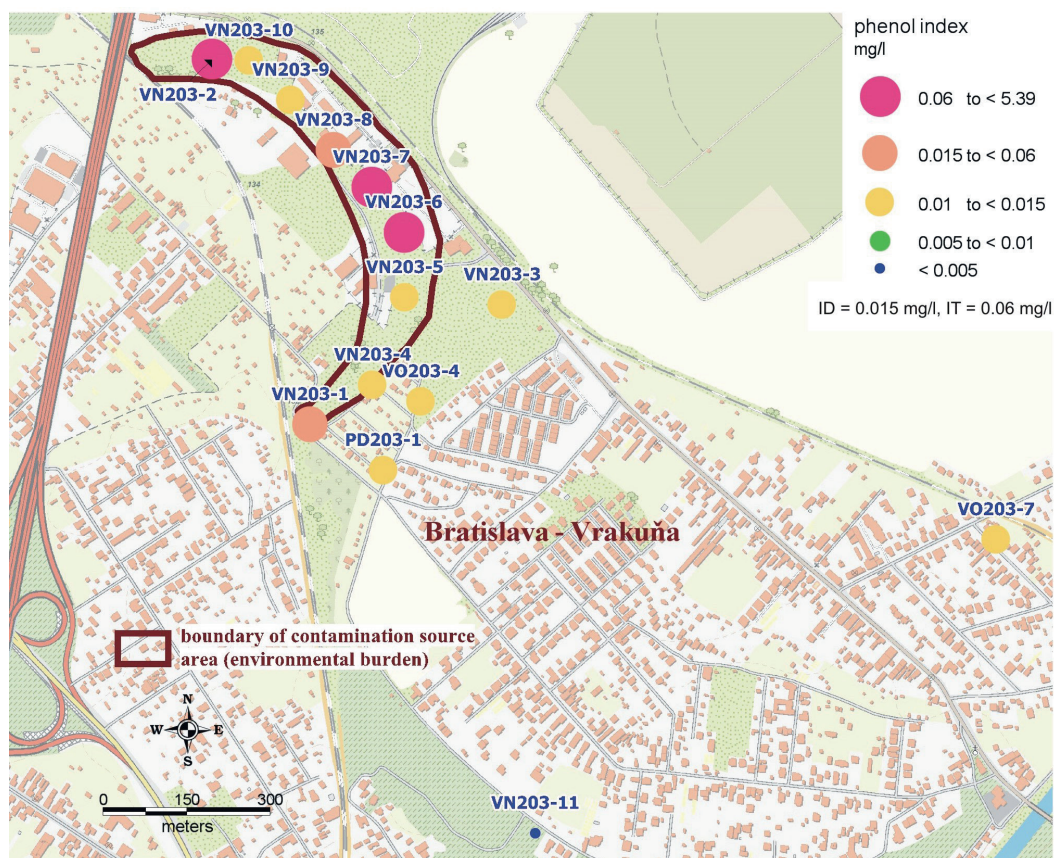


Fig. 1.22 Distribution of phenol index in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

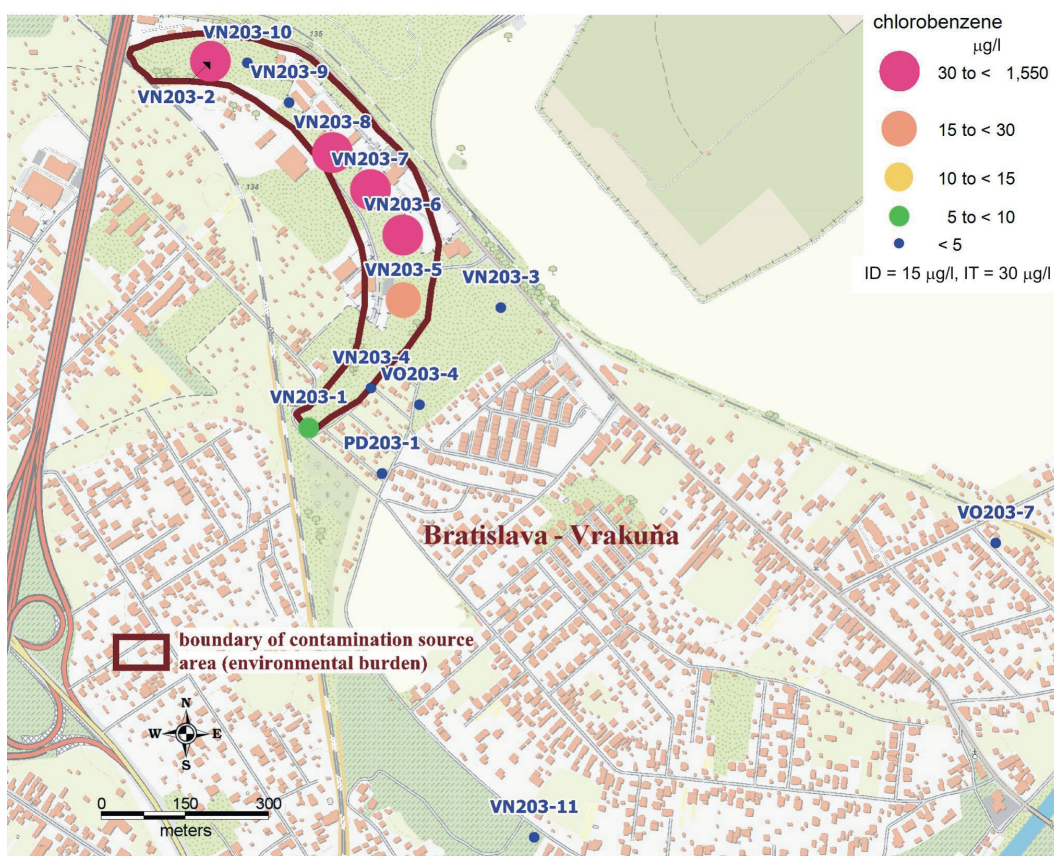


Fig. 1.23 Distribution of chlorobenzene in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



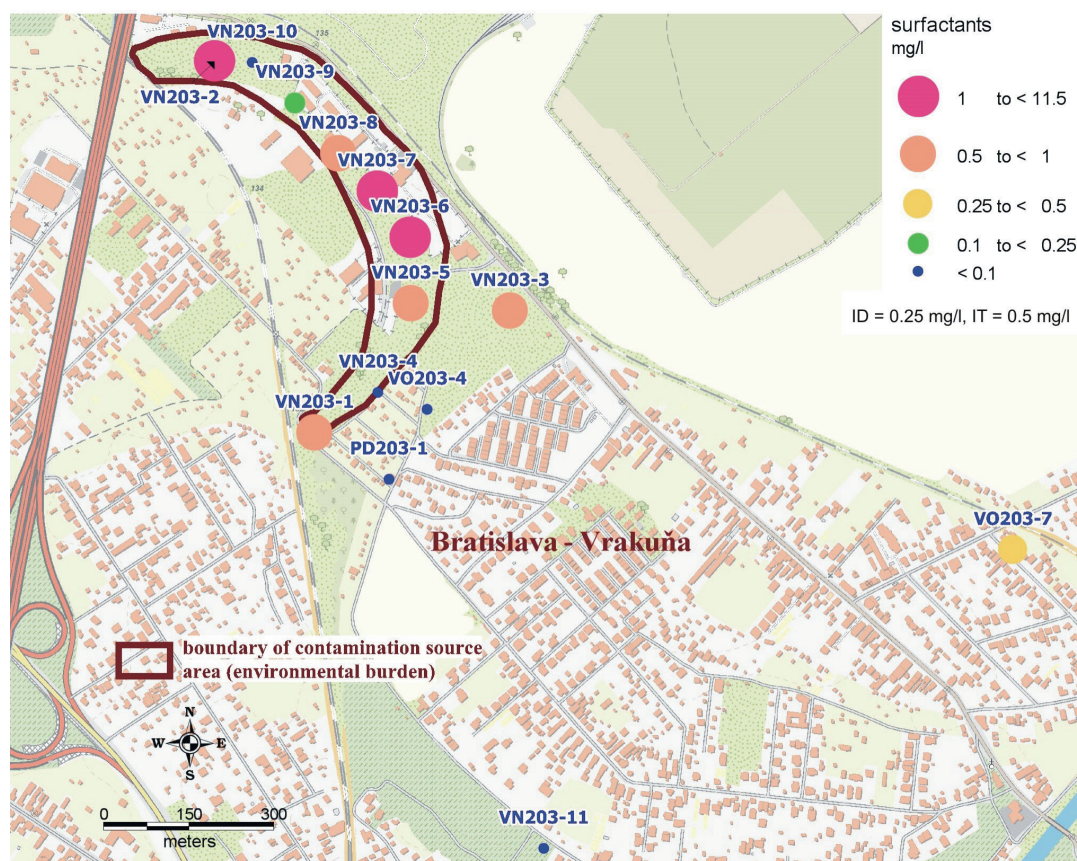


Fig. 1.24 Distribution of surfactants in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

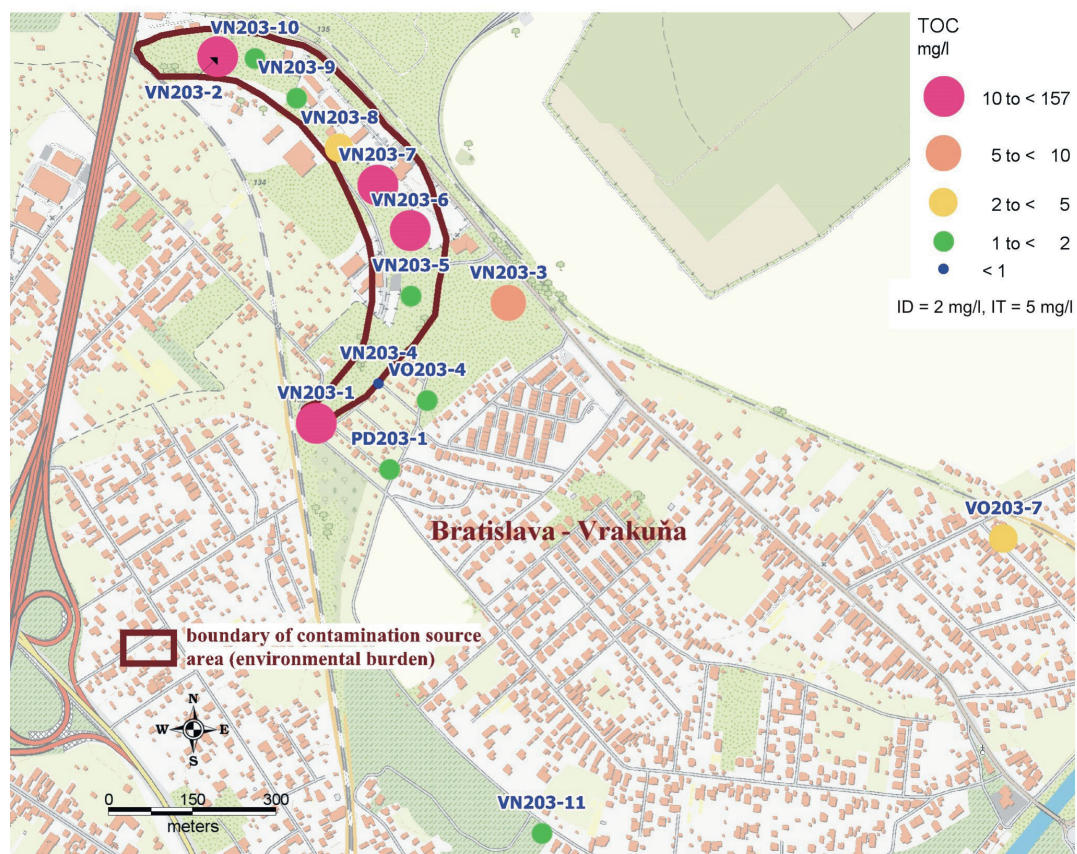


Fig. 1.25 Distribution of TOC in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

The Žitný ostrov is an important water management area of Slovakia. Substances with low sorption and poor degradation tend to spread over the greatest distances. Such substances are e.g. certain herbicides, chlorinated hydrocarbons and BTEX, which are typical of pollution from the CHZJD dump area.

Given the level and extent of groundwater contamination observed, the risk analysis has shown the relevance of the risk of groundwater contamination spreading, and practically of all main landfill contaminant groups (BTEX, chlorinated hydrocarbons, pesticides, herbicides, metals, PCBs; Urban et al., 2015a).

Maps of distribution of selected parameters (median concentrations) in groundwaters are presented in Figs. 1.19 to 1.25.

### 1.3.7 Smolník – pyrite ores (loc. No. 207)

The site of Smolník and its surroundings is significantly influenced by the long-term mining activity, which lasted from the 13<sup>th</sup> century until 1991, when the mining activity was terminated. The deposit is spread over a length of more than 3 km, in the eastern part it was mined to a depth of 360 m. During centuries of the mining activity, it provided around 150,000 tonnes of pure copper and over a million tonnes of pyrite. Silver, gold, copper and iron were abundantly extracted from the deposit in the Middle Ages.

NW and NE part of the area of interest build the rocks of the Bystrý potok Fm. (Late Silurian), the rest the rock of the Drnava Fm. (Early Devonian). Both strata are part of the Gelnica Group of the Gemericum (Cambrian – Early Devonian). The Bystrý potok Fm. consists mainly of quartz-sericitic, graphitic-sericitic and sericitic-chlorite phyllites. The Drnava Fm. north of the Smolnícky potok Brook is represented by strips of rhyolite metatuffites and coarse-grained rhyolite metatuffs. Metamorphic quartz graywackes and quartz phyllites, laminated chloritic-sericitic and graphitic-sericitic phyllites are developed

more southern of the area (Grecula, 1972; Jaško et al., 1996).

Monitoring confirmed the bad state of the environment affected by long-term mining activities. Groundwater contamination is mainly due to the infiltration of meteoric water through the tailings and dumps material. During the infiltration process, water changes its physico-chemical properties (mainly pH), dissolves several metals and enriches their contents (especially As, Cu, Al, Ni, Zn) and thus acts as a migration medium of pollutants in solution.

The most polluted are surface waters originating from the outflows of old mining works. Particularly contaminated are the discharges from the Pech and Karitas mining works and the outflow under the old railway station. High concentrations were recorded mainly in the indicators As, Ba, Cd, Cu, Ni, Pb, Co, Zn, Fe<sub>total</sub>, Mn, Al, SO<sub>4</sub><sup>2-</sup> (Tab. 1.8). Important problem is the acid mine water (AMD) with pH usually lower than 4.5, which is an extremely dangerous type of water (mobilizing of extreme high concentrations of toxic metals). AMDs are one of the causes of the mobilization of extremely high concentrations of toxic metals. The effluent mining waters have a direct impact on the individual components of the environment, especially the water in the Smolník stream. In addition, these waters cause the formation of ochre precipitates, i.e. iron oxyhydroxides and iron oxyhydrosulphates.

Migration of pollutants is possible to follow through the Smolnícky potok Brook to the Hnilec River with their subsequent accumulation in the sediments of the Ružín water reservoir. The transport of the polluted mining waters and infiltration of contaminated groundwaters into the Smolník River is clear. Exceedances of the limits given in Annex No. 1 of the Government Ordinance No. 269/2010 Coll., were recorded in indicators As, Cu, Zn, Ba, Mn, Al, Fe<sub>total</sub>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, COD<sub>Mn</sub> and hydrocarbon index (C<sub>10</sub>-C<sub>40</sub>). Ecotoxicity tests have shown poor quality of the Smolník stream (Auxt et al., 2015a), which can also

Table 1.8 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Smolník – pyrite ores

|                               | unit               | mean  | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples >ID | number of samples >IT |
|-------------------------------|--------------------|-------|--------|--------------------|---------|---------|--------|----------|----------|-----------------------|-----------------------|
| SO <sub>4</sub> <sup>2-</sup> | mg.l <sup>-1</sup> | 1,265 | 203    | 1,634              | 17.7    | 5,900   | 30     |          |          |                       |                       |
| Fe <sub>total</sub>           | mg.l <sup>-1</sup> | 79.6  | 5.68   | 154                | 0.021   | 590     | 30     |          |          |                       |                       |
| Mn <sup>2+</sup>              | mg.l <sup>-1</sup> | 6.26  | 1.59   | 8.03               | 0.021   | 25.6    | 30     |          |          |                       |                       |
| Al <sup>3+</sup>              | mg.l <sup>-1</sup> | 17.1  | 0.09   | 33.2               | <0.01   | 110     | 30     | 0.25     | 0.4      | 1                     | 10                    |
| As                            | µg.l <sup>-1</sup> | 23.2  | 0.95   | 44.1               | <0.5    | 178     | 30     | 50       | 100      | 2                     | 2                     |
| Cd                            | µg.l <sup>-1</sup> | 2.89  | 0.4    | 5.40               | <0.1    | 17.6    | 30     | 5        | 20       | 4                     | 0                     |
| Cu                            | µg.l <sup>-1</sup> | 853   | 34.5   | 1,885              | <2      | 5,670   | 30     | 1,000    | 2,000    | 1                     | 4                     |
| Ni                            | µg.l <sup>-1</sup> | 62.7  | 35     | 77.6               | <2      | 232     | 30     | 100      | 200      | 4                     | 4                     |
| Pb                            | µg.l <sup>-1</sup> | 5.91  | 0.5    | 13.8               | <0.5    | 59.9    | 30     | 100      | 200      | 0                     | 0                     |
| Co                            | µg.l <sup>-1</sup> | 77    | 20     | 117                | <2      | 478     | 30     | 100      | 200      | 2                     | 4                     |
| Zn                            | µg.l <sup>-1</sup> | 1,717 | 199    | 3,053              | 14      | 9,990   | 30     | 1,500    | 5,000    | 4                     | 4                     |







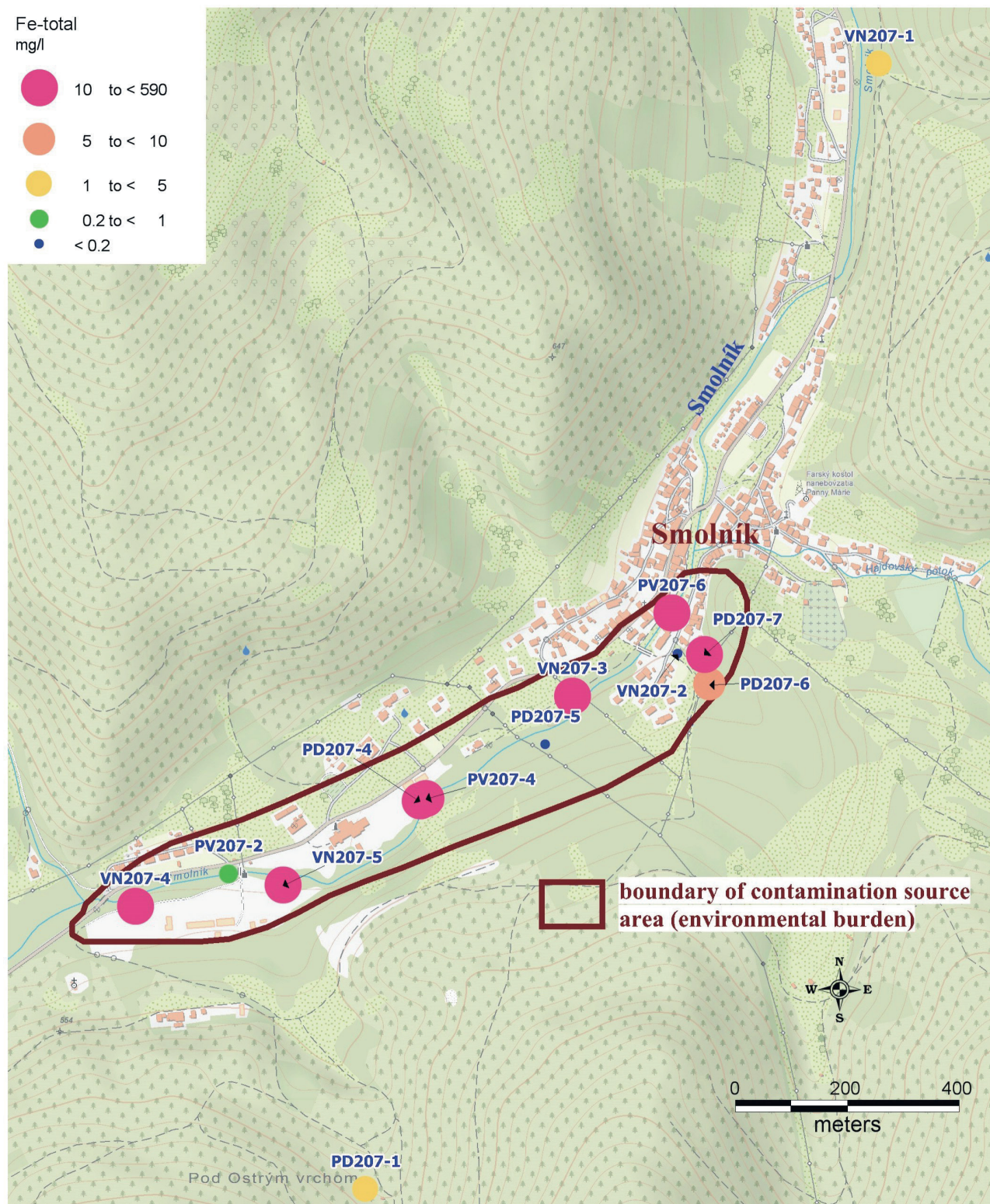


Fig. 1.27 Distribution of Fe in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



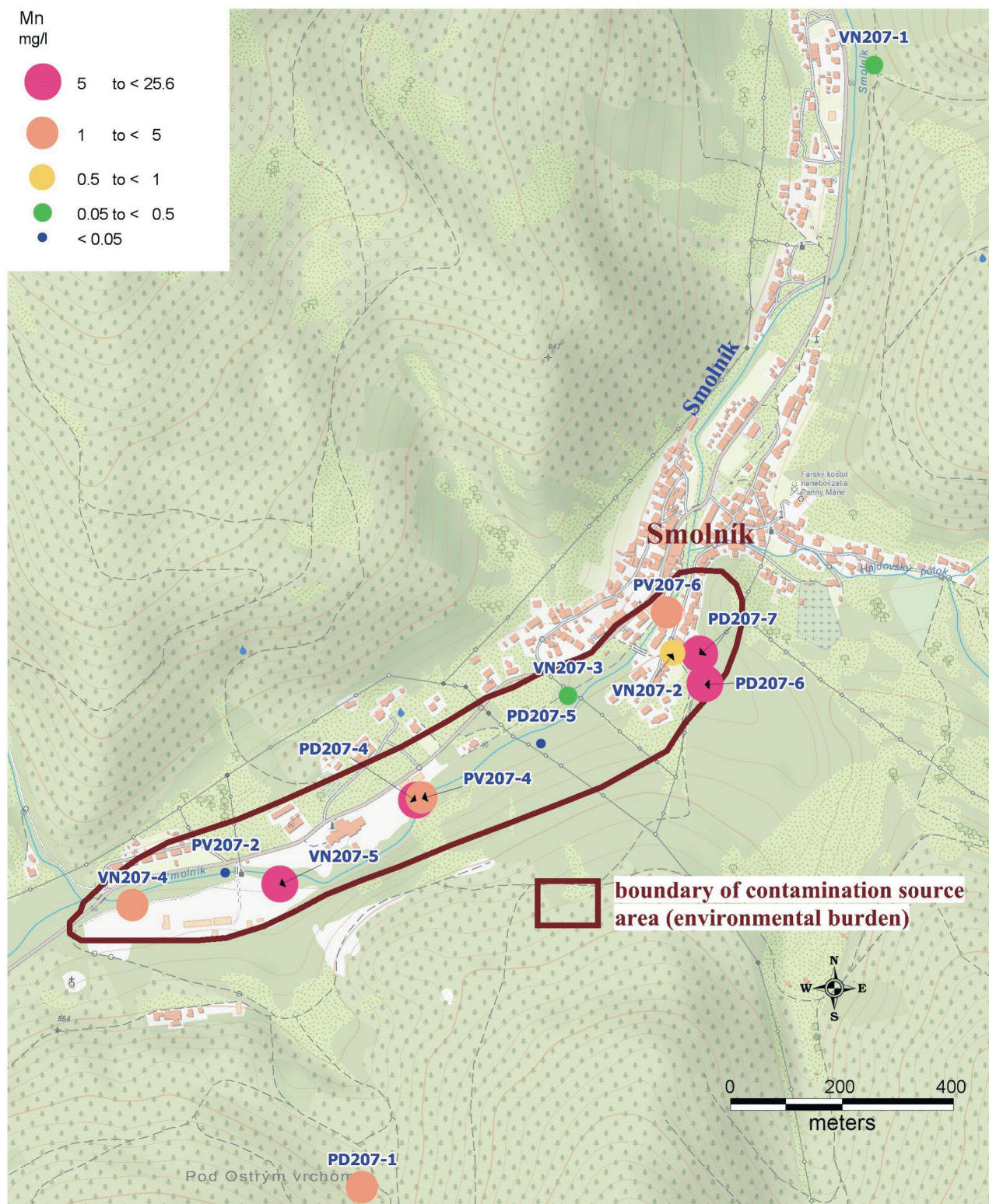


Fig. 1.28 Distribution of Mn in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



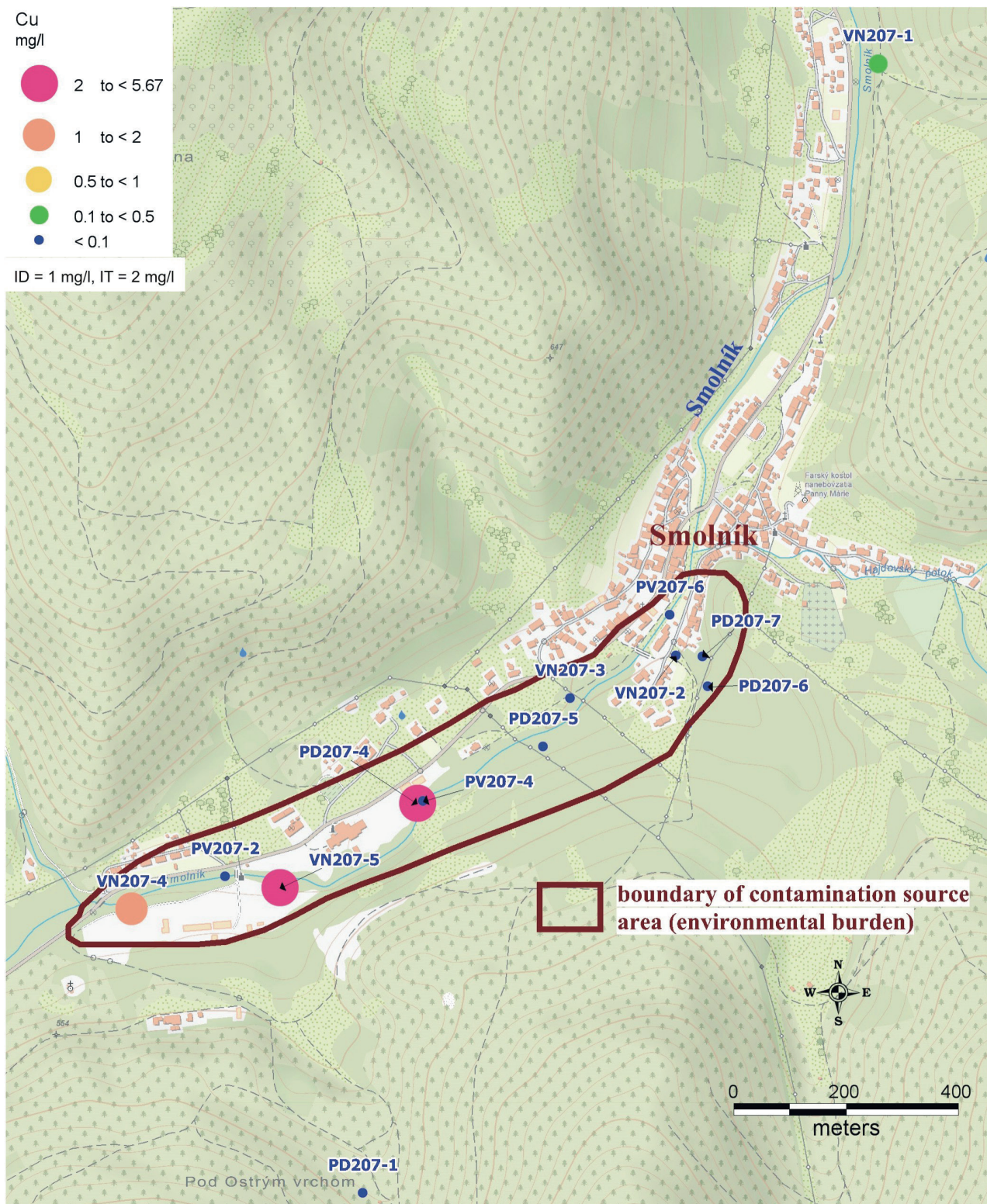


Fig. 1.29 Distribution of Cu in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



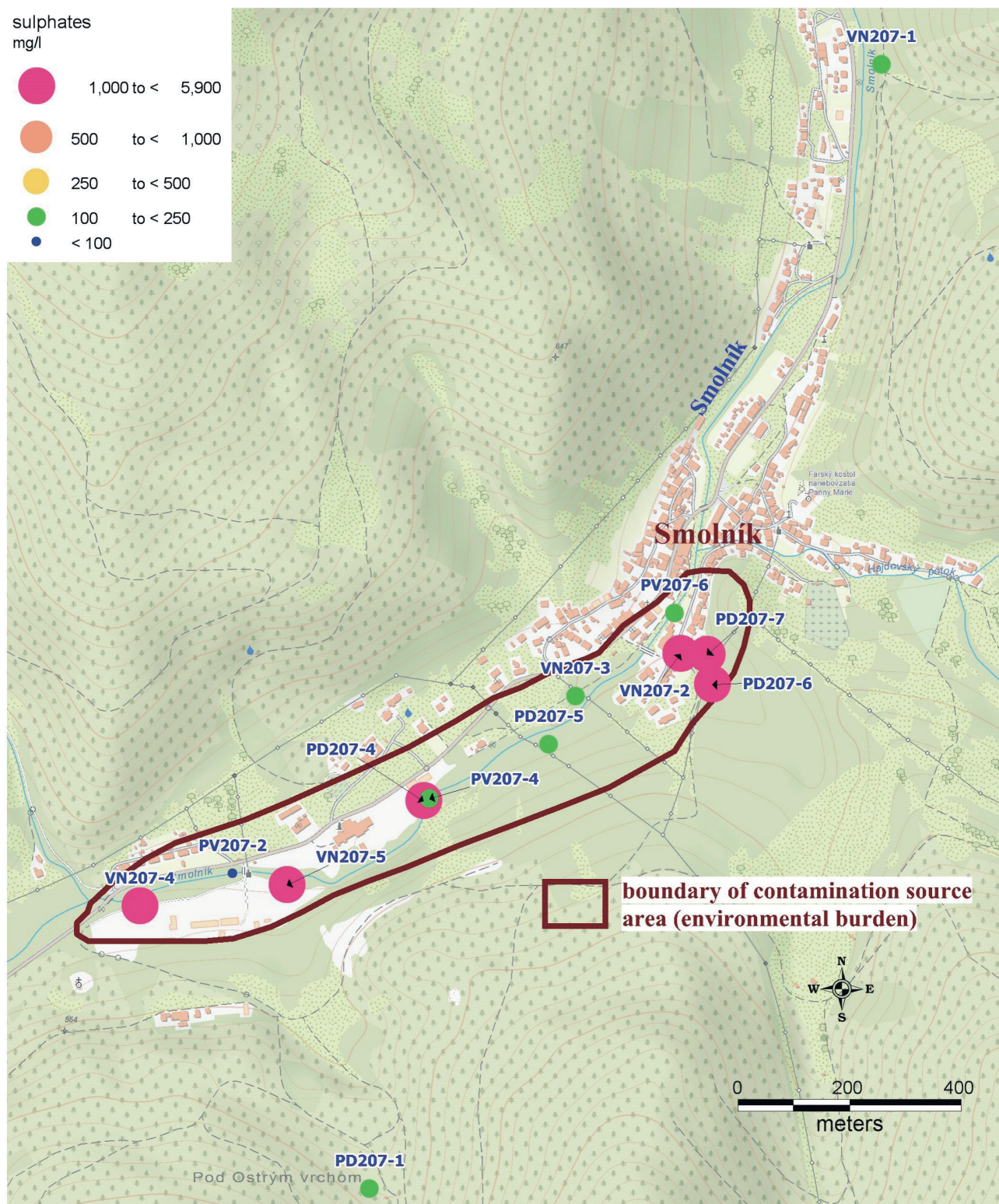


Fig. 1.30 Distribution of sulphates in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



be seen visually, both the rusty colour of the stream in the profile from the old mining plant in Smolnícka Huta to confluence with the Hnilec River and the lack of nektonic life (especially fish). Pollution of the Hnilec River is on the one hand related to the flow along populated areas and on the other hand to the drainage of other ore fields of the Spišsko-gemerské Rudohorie subregion (Švedlár, Prakovce, Gelnica).

Maps of distribution of selected parameters (median concentrations) in groundwaters are presented in Figs. 1.26 to 1.30.

The issue of environmental pollution and acid mine drainage waters in the Smolník area is described in detail in Lintnerová et al. (2006, 2009) and Šoltés (2007).

### 1.3.8 Poproč – Petrova dolina Valley (loc. No. 213)

Antimony ore extraction at Poproč began in the 17<sup>th</sup> century and was finally completed in 1965. The most intensive mining took place between 1931 and 1965, when 10,000 metric tons of antimony and 80 kg of gold were extracted (Grecula et al., 1995).

The Poproč deposit is situated in Old Palaeozoic metapelites and acidic pyroclastics, into which Permian granites intruded later (Grecula et al., 1995). The main minerals of hydrothermal veins are quartz and antimonite with less frequent pyrite, arsenopyrite, berthierite, tetrahedrite, sphalerite, zinkenite and fülöpite (Klimko et al., 2009). On the entire defined area there are mining heaps and tailings, which are a significant source of contamination of individual components of the environment, especially by potentially toxic elements – As, Sb, Pb and Zn.

Within the site monitoring, large amounts of contaminants and risk of pollution spreading were proven in the environment. Most dangerous contaminants in the area represent As and Sb (Tab. 1.9) with very high average (320 µg.l<sup>-1</sup> for As, 406 µg.l<sup>-1</sup> for Sb) and maximum (7,250 µg.l<sup>-1</sup> for As, 7,176 µg.l<sup>-1</sup> for Sb) concentrations. Pollution of waters and other environmental compartments by inorganic contaminants is the result of two processes – anthropogenic activities related to mining and processing of Sb-ores in Petrova dolina Valley (deposited tailings sludge and sediments, mining heaps, galleries water outflows) and natural weathering of parental rocks with higher contents of several elements (arsenic, antimony, lead, zinc, cadmium). A specific problem of this site is groundwater contamination in the northern part of the Petrova dolina Valley, which is represented by the outflowing mining waters from the Agnes and Anna adits (Auxt et al., 2015b).

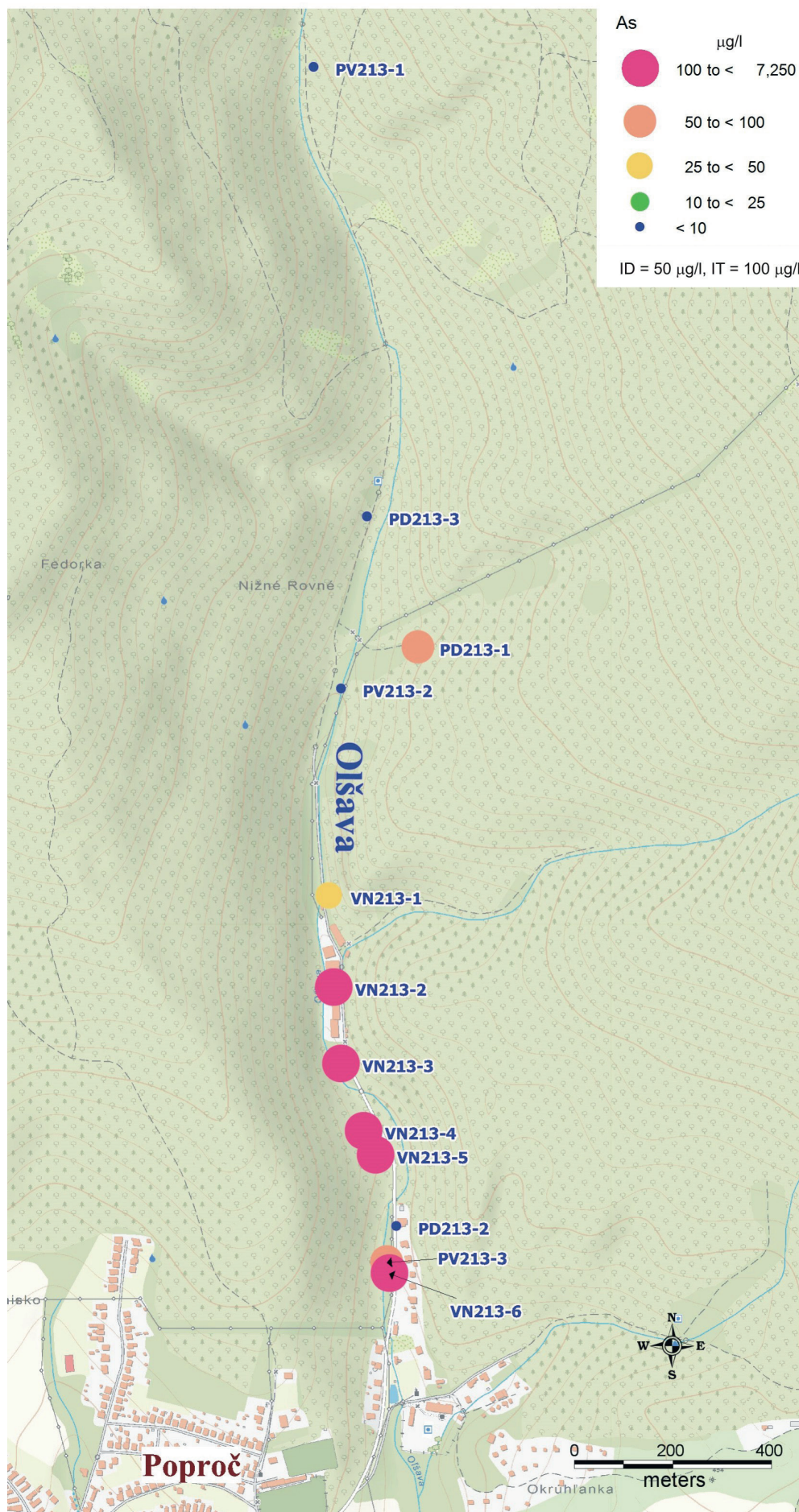
At the site, the environmental risk from the spread of groundwater contamination by arsenic and antimony has been demonstrated. Similarly, the health risk identified in several exposure scenarios has been identified (water ingestion from wells, soil ingestion, long-term dermal contact with water and soil, vegetable ingestion when using groundwater for irrigation), both the risk of carcinogenic and non-carcinogenic effects for both the individual and the population (Auxt et al., 2015b).

Maps of distribution of As and Sb (median concentrations) in groundwaters are presented in Figs. 1.31 and 1.32.

The issue of environmental pollution in the Poproč area is described in detail in many works, e.g. Fláková et al. (2009), Jurkovič et al. (2010, 2015), Klimko et al. (2014).

Table 1.9 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Poproč – Petrova dolina Valley

|                               | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples >ID | number of samples >IT |
|-------------------------------|--------------------|------|--------|--------------------|---------|---------|--------|----------|----------|-----------------------|-----------------------|
| SO <sub>4</sub> <sup>2-</sup> | mg.l <sup>-1</sup> | 137  | 87     | 167                | 11.1    | 863     | 38     |          |          |                       |                       |
| Fe <sub>total</sub>           | mg.l <sup>-1</sup> | 9.11 | 0.371  | 28.4               | 0.004   | 213     | 65     |          |          |                       |                       |
| Mn                            | mg.l <sup>-1</sup> | 0.92 | 0.209  | 1.82               | 0.002   | 10.5    | 65     |          |          |                       |                       |
| Al                            | mg.l <sup>-1</sup> | 1.23 | 0.05   | 4.33               | <0.01   | 30.5    | 65     | 0.25     | 0.4      | 0                     | 13                    |
| As                            | µg.l <sup>-1</sup> | 320  | 24.6   | 1,071              | <0.5    | 7,250   | 65     | 50       | 100      | 8                     | 19                    |
| Sb                            | µg.l <sup>-1</sup> | 406  | 199    | 922                | <1      | 7,176   | 65     | 25       | 50       | 2                     | 56                    |
| Cd                            | µg.l <sup>-1</sup> | 3.75 | 0.3    | 14.1               | <0.1    | 107     | 65     | 5        | 20       | 3                     | 3                     |
| Ni                            | µg.l <sup>-1</sup> | 27.3 | 2      | 69.3               | <2      | 354     | 45     | 100      | 200      | 1                     | 2                     |
| Pb                            | µg.l <sup>-1</sup> | 163  | 0.7    | 999                | <0.5    | 7,810   | 65     | 100      | 200      | 1                     | 2                     |
| Co                            | µg.l <sup>-1</sup> | 30.5 | 4      | 59.7               | <2      | 258     | 39     | 100      | 200      | 4                     | 1                     |
| Zn                            | µg.l <sup>-1</sup> | 536  | 19     | 1,693              | <2      | 12,100  | 65     | 1,500    | 5,000    | 5                     | 2                     |





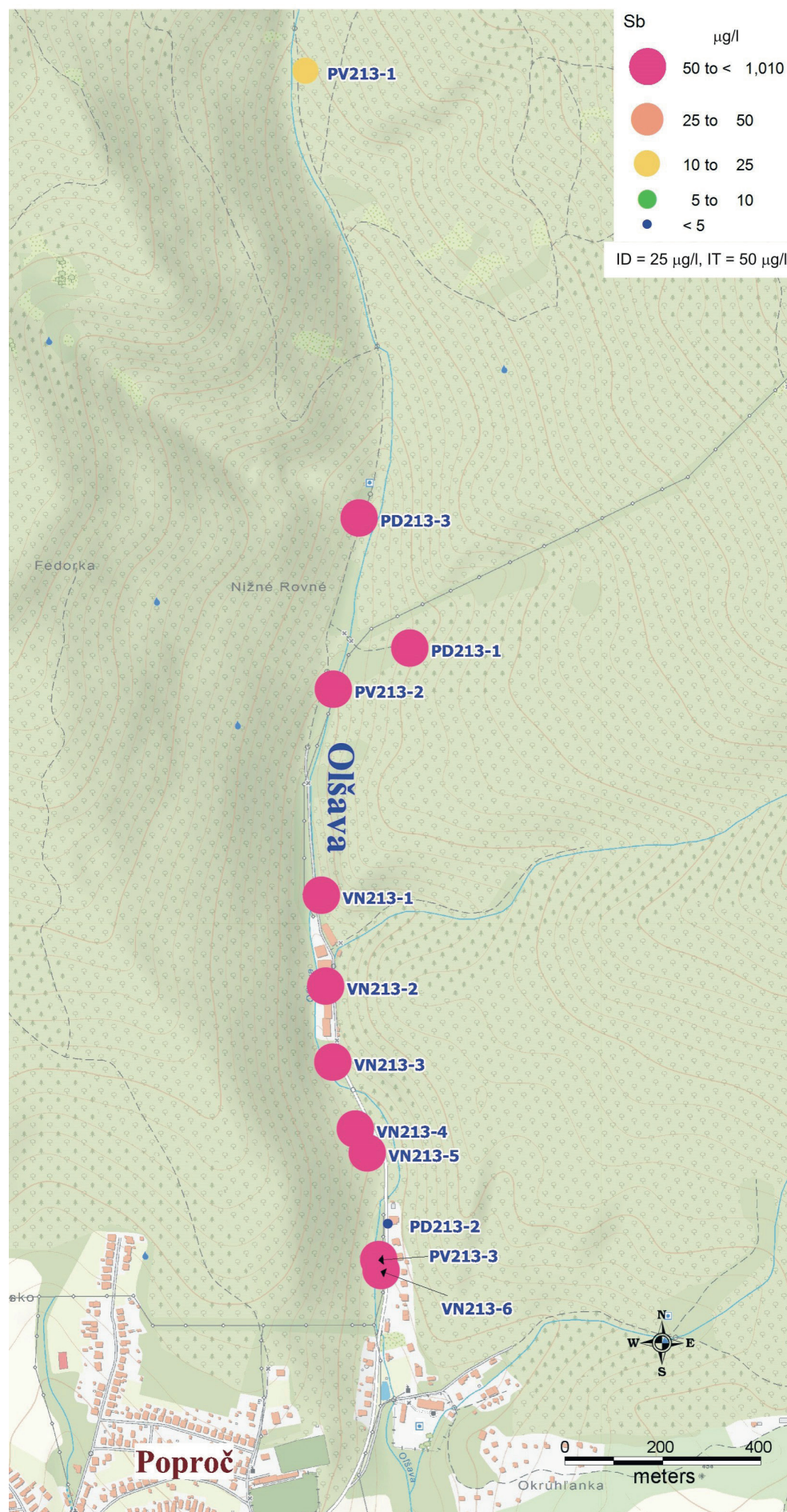


Fig. 1.32 Distribution of Sb in groundwaters (median concentrations) – site Poproč – Petrova dolina Valley (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

### 1.3.9 Čierna nad Tisou – transshipment station (loc. No. 248)

Site Čierna nad Tisou – transshipment station is considered to be one of the most important sources of groundwater contamination within the Eastern Slovakia region. The release of contaminants into the rock environment and groundwaters occurred mainly during the period of the most intensive operation in the transshipment station, which lasted until about 1985. Then the Družba pipeline was built, which led to a gradual reduction of the pumping. During this period, a wastewater treatment plant was put into trial operation and the wastewater discharge into the “biological pond” was stopped. The site is currently handling hazardous substances, which can be identified as potential contaminants (petrol, diesel, technical gasoline, oils and others).

The area of interest is a flat relief, covering several tens of meters of thick layers of the Quaternary Holocene sediments: the top layer consists mainly of clays, to a lesser extent fine sands. In the near and wider surroundings there is also a significant representation of loams, in places

with relics of oxbow clogged with flood loams (Baňacký et al., 1988).

In the area of interest the monitoring confirmed groundwater contamination caused by the presence of oil substances (Tab. 1.10) with very high average (16.2 mg.l<sup>-1</sup> for hydrocarbon index, 67.0 mg.l<sup>-1</sup> for NEL-UV) and maximum (689 mg.l<sup>-1</sup> for hydrocarbon index, 2,775 mg.l<sup>-1</sup> for NEL-UV) concentrations. Elevated concentrations of BTEX, tetrachloroethane and tetrachloromethane were observed as well. In the long term, groundwater contamination in the area of interest is permanent and relatively stable (the values do not show significant trends of increasing or decreasing concentrations in individual boreholes) and spatially connected with handling areas of the transshipment station (currently the pumping complex and its surroundings). The differences in the recorded free phase thickness and the non-polar extractables contents in groundwater are mainly attributed to seasonal temperature effects (Auxt et al., 2015c).

Map of distribution of NEL-UV (sampled in 2018) in groundwaters is presented in Fig. 1.33.

Table 1.10 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Čierna nad Tisou – transshipment station

|                                                       | unit               | mean   | median | standard deviation | minimum | maximum   | number | ID value | IT value | number of samples >ID | number of samples >IT |
|-------------------------------------------------------|--------------------|--------|--------|--------------------|---------|-----------|--------|----------|----------|-----------------------|-----------------------|
| NO <sub>3</sub> <sup>-</sup>                          | mg.l <sup>-1</sup> | 12.2   | 1.37   | 47.7               | 1       | 335       | 72     |          |          |                       |                       |
| Cl <sup>-</sup>                                       | mg.l <sup>-1</sup> | 76.8   | 24.5   | 216                | 1       | 1,782     | 72     | 150      | 250      | 2                     | 5                     |
| SO <sub>4</sub> <sup>2-</sup>                         | mg.l <sup>-1</sup> | 78.6   | 43.5   | 153                | 1.62    | 1,060     | 72     |          |          |                       |                       |
| Fe <sub>total</sub>                                   | mg.l <sup>-1</sup> | 9.49   | 0.53   | 16.9               | 0.018   | 67.3      | 71     |          |          |                       |                       |
| Mn                                                    | mg.l <sup>-1</sup> | 1.07   | 0.637  | 1.22               | 0.003   | 5.98      | 72     |          |          |                       |                       |
| hydrocarbon index (C <sub>10</sub> -C <sub>40</sub> ) | mg.l <sup>-1</sup> | 16.2   | 0.03   | 96.6               | 0.02    | 689       | 72     | 0.25     | 0.5      | 2                     | 6                     |
| NEL-UV                                                | mg.l <sup>-1</sup> | 67.0   | 0.105  | 395                | 0.05    | 2,775     | 72     | 0.5      | 1        | 9                     | 16                    |
| tetrachloroethane                                     | µg.l <sup>-1</sup> | 278    | <0.2   | 2,359              | <0.2    | 20,016    | 72     |          |          |                       |                       |
| dichloromethane                                       | µg.l <sup>-1</sup> | 1.43   | <0.2   | 4.01               | <0.2    | 18.9      | 72     | 15       | 30       | 2                     | 0                     |
| tetrachloromethane                                    | µg.l <sup>-1</sup> | 16,099 | <0.2   | 136,298            | <0.2    | 1,156,560 | 72     | 5        | 10       | 1                     | 3                     |
| trichloroethene                                       | µg.l <sup>-1</sup> | 0.77   | <0.2   | 3.26               | <0.2    | 20.5      | 72     | 25       | 50       | 0                     | 0                     |
| chloroethene                                          | µg.l <sup>-1</sup> | 0.44   | <0.2   | 1.06               | <0.2    | 8         | 72     | 5        | 10       | 1                     | 0                     |
| chloroform                                            | µg.l <sup>-1</sup> | 3,405  | <0.2   | 28,885             | <0.2    | 245,100   | 72     |          |          |                       |                       |
| benzene                                               | µg.l <sup>-1</sup> | 4,108  | <0.2   | 33,975             | <0.2    | 288,350   | 72     | 15       | 30       | 0                     | 4                     |
| ethylbenzene                                          | µg.l <sup>-1</sup> | 95.5   | <0.2   | 764                | <0.2    | 6,480     | 72     | 150      | 300      | 1                     | 1                     |
| chlorobenzene                                         | µg.l <sup>-1</sup> | 83.2   | <0.2   | 703                | <0.2    | 5,965     | 72     | 15       | 30       | 0                     | 1                     |
| toluene                                               | µg.l <sup>-1</sup> | 47.5   | <0.2   | 394                | <0.2    | 3,340     | 72     | 350      | 700      | 0                     | 1                     |
| styrene                                               | µg.l <sup>-1</sup> | 0.2    | <0.2   | 0.00               | <0.2    | 0.2       | 72     | 20       | 50       | 0                     | 0                     |
| xylene                                                | µg.l <sup>-1</sup> | 3,703  | <0.2   | 30,912             | <0.2    | 262,340   | 72     | 250      | 500      | 0                     | 4                     |



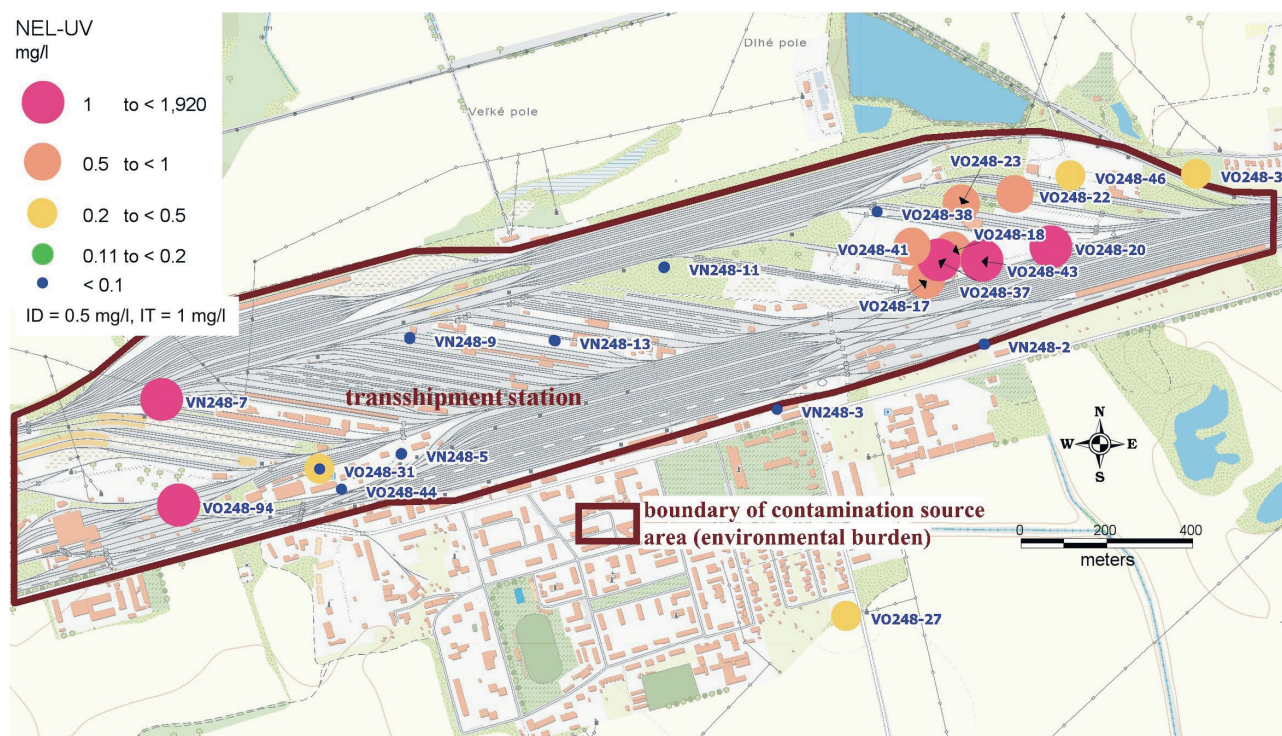


Fig. 1.33 Distribution of NEL-UV in groundwaters (sampled in 2018) – site Čierna nad Tisou – transshipment station (most contaminated boreholes; Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

### 1.3.10 Bánovce nad Bebravou – Railway station (loc. No. 252)

At the Bánovce nad Bebravou railway station, in 2004, contamination of groundwater with aliphatic chlorinated hydrocarbons dominated by tetrachloroethene was detected in connection with the accidental leakage of diesel fuel from the locomotives (Matiová, 2005). Subsequent monitoring of the development of groundwater quality in the years 2006 – 2007 showed a permanent occurrence of concentrations of non-polar extractables and tetrachloroethene indicators in excess of the currently valid intervention criteria (Matiová, 2007).

The Quaternary rock complex and the Pliocene sediments in contact with the Quaternary base are particularly important in terms of the depth of impact of possible pollution. At the surface the Quaternary consists mostly of anthropogenic soils with a maximum documented

thickness of 3.85 m. The anthropogenic sediments consist predominantly of redeposited sandy clays, clays with low to medium plasticity and silts with admixture of gravel and fragments of building materials. Materials with the character of municipal waste are deposited locally. The presence of organic soils has been documented under the anthropogenic soils, suggesting that in the past there was an oxbow of the surface stream, which was completely filled with excavated soils and waste. Fluvial sediments of Radiša and Bebrava streams are located under the anthropogenic sediments (Pristaš et al., 2000).

The pollutants (chlorinated hydrocarbons) are found in an artesian aquifer bound to fluvial gravel sediments. The dominant pollutants in groundwater are 1,2 cis-dichloroethene, tetrachloroethene and trichloroethene (Tab. 1.11) with very high average (15.4  $\mu\text{g.l}^{-1}$  for cis 1,2-dichloroethene, 57.3  $\text{mg.l}^{-1}$  for tetrachloroethene,

Table 1.11 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Bánovce nad Bebravou – Railway station

|                        | unit                 | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples $\wedge$ ID | number of samples $\wedge$ IT |
|------------------------|----------------------|------|--------|--------------------|---------|---------|--------|----------|----------|-------------------------------|-------------------------------|
| $\text{NH}_4^+$        | $\text{mg.l}^{-1}$   | 0.82 | 0.115  | 1.88               | <0.03   | 7.7     | 34     | 1.2      | 2.4      | 0                             | 4                             |
| TOC                    | $\text{mg.l}^{-1}$   | 2.74 | 2.55   | 1.16               | 1.1     | 5.9     | 34     | 2        | 5        | 20                            | 2                             |
| cis 1,2-dichloroethene | $\mu\text{g.l}^{-1}$ | 15.4 | 9.05   | 17.7               | <0.2    | 61.8    | 34     | 25       | 50       | 5                             | 3                             |
| tetrachloroethene      | $\mu\text{g.l}^{-1}$ | 57.3 | 5      | 111                | <0.2    | 413     | 34     | 10       | 20       | 2                             | 14                            |
| trichloroethene        | $\mu\text{g.l}^{-1}$ | 50.2 | 6.45   | 95.0               | <0.2    | 421     | 34     | 25       | 50       | 4                             | 8                             |
| chloroethene           | $\mu\text{g.l}^{-1}$ | 1.36 | <0.2   | 2.51               | <0.2    | 9.1     | 34     | 5        | 10       | 4                             | 0                             |

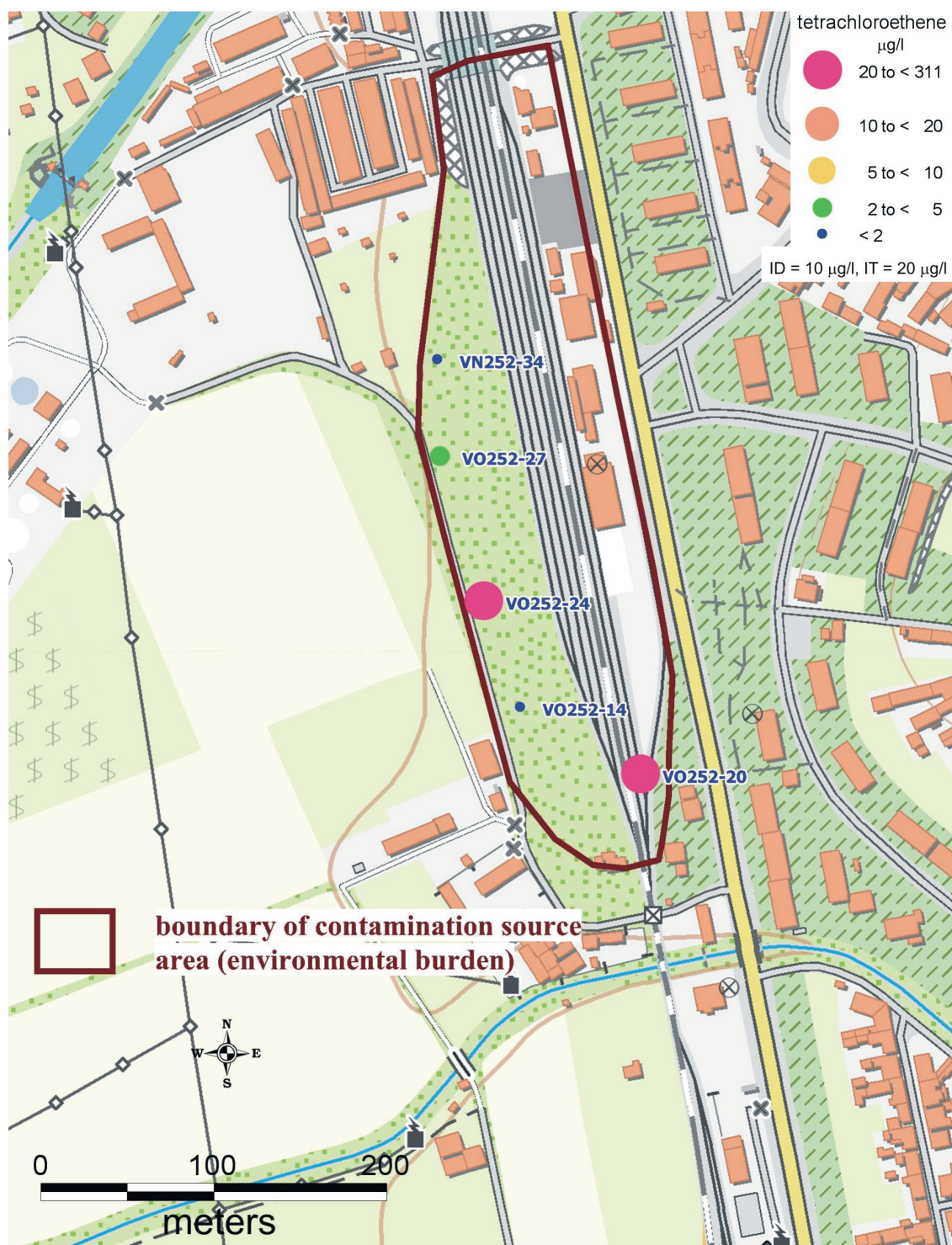


Fig. 1.34 Distribution of tetrachloroethene in groundwaters (median concentrations) – site Bánovce nad Bebravou – Railway station (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

50.2 mg.l<sup>-1</sup> for trichloroethene) and maximum (61.8 µg.l<sup>-1</sup> for cis 1,2-dichloroethene, 413 µg.l<sup>-1</sup> for tetrachloroethene, 421 µg.l<sup>-1</sup> for trichloroethene) concentrations. Maps of distribution of tetrachloroethene (median concentrations) in groundwaters are presented in Fig. 1.34.

### 1.3.11 Komárno – area after the Soviet Army (loc. No. 253)

Until 1968 the territory of interest was used by the Czechoslovak Army, after 1968 by the Soviet Army and

since 1990 again by the Czechoslovak/Slovak Army. Long-term maintenance, repair of military equipment, replacement of used oils and their storage resulted in pollution that spread to the surrounding environment. The pollution was mainly caused by substances of petroleum origin and in some buildings by aliphatic and aromatic chlorinated hydrocarbons (Klago et al., 1991).

The geological evolution of the evaluated area during the Quaternary follows the development of the Tertiary, especially the Late Pliocene, when the tectonic elevation



of the lowland territory was recorded. The Quaternary reaches a thickness of approx. 15 – 20 m. The lithological types are represented by clays, clayey sands, sandy gravels, gravels (Pleistocene – Holocene), sands with gravels (Pleistocene) and sands. Sandy gravels occur on the surface and form accumulation in the confluence of the Váh and Danube Rivers (Pristaš et al., 1996).

Permanent pollution has also been confirmed by regular groundwater monitoring in recent years (Tab. 1.12). According to MoE Directive No. 1/2015-7 exceeding of ID and/or IT criteria has been found mainly for  $\text{NH}_4^+$ , TOC, hydrocarbon index ( $\text{C}_{10}\text{-C}_{40}$ ), tetrachloroethene, benzene, benzo(b)fluoranthene, benzo(g,h,i)perylene, phenanthrene and chrysene. The extremely high concentrations of  $\text{NH}_4^+$ ,

Table 1.12 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Komárno – area after the Soviet Army

|                                                     | unit                 | mean   | median | standard deviation | minimum | maximum   | number | ID value | IT value | number of samples $\wedge$ ID | number of samples $\wedge$ IT |
|-----------------------------------------------------|----------------------|--------|--------|--------------------|---------|-----------|--------|----------|----------|-------------------------------|-------------------------------|
| $\text{NH}_4^+$                                     | $\text{mg.l}^{-1}$   | 3.67   | 0.425  | 6.27               | <0.02   | 34.6      | 226    | 1.2      | 2.4      | 6                             | 84                            |
| TOC                                                 | $\text{mg.l}^{-1}$   | 20.8   | 10.8   | 79.0               | 0.862   | 1,460     | 370    | 2        | 5        | 89                            | 270                           |
| hydrocarbon index ( $\text{C}_{10}\text{-C}_{40}$ ) | $\text{mg.l}^{-1}$   | 10,285 | 0.1    | 101,541            | <0.005  | 1,193,000 | 388    | 0.25     | 0.5      | 20                            | 65                            |
| tetrachloroethene                                   | $\mu\text{g.l}^{-1}$ | 1.04   | <0.1   | 5.98               | <0.1    | 107       | 423    | 10       | 20       | 15                            | 2                             |
| tetrachloromethane                                  | $\mu\text{g.l}^{-1}$ | 0.21   | <0.1   | 1.12               | <0.1    | 19.3      | 404    | 5        | 10       | 2                             | 1                             |
| trichloroethene                                     | $\mu\text{g.l}^{-1}$ | 0.44   | <0.1   | 2.46               | <0.1    | 29.1      | 423    | 25       | 50       | 3                             | 0                             |
| chloroethene                                        | $\mu\text{g.l}^{-1}$ | 0.25   | <0.1   | 1.05               | <0.1    | 12.7      | 423    | 5        | 10       | 2                             | 2                             |
| benzene                                             | $\mu\text{g.l}^{-1}$ | 2.26   | <0.1   | 13.3               | <0.1    | 153       | 385    | 15       | 30       | 4                             | 8                             |
| ethylbenzene                                        | $\mu\text{g.l}^{-1}$ | 1.96   | <0.1   | 12.4               | <0.1    | 147       | 385    | 150      | 300      | 0                             | 0                             |
| xylene                                              | $\mu\text{g.l}^{-1}$ | 15.9   | <0.1   | 102                | <0.1    | 1,405     | 385    | 250      | 500      | 3                             | 4                             |
| benzo(a)pyrene                                      | $\mu\text{g.l}^{-1}$ | 0.01   | <0.001 | 0.02               | <0.001  | 0.133     | 385    | 0.1      | 0.2      | 1                             | 0                             |
| benzo(b)fluoranthene                                | $\mu\text{g.l}^{-1}$ | 0.09   | <0.001 | 0.61               | <0.001  | 8.64      | 385    | 0.25     | 0.5      | 2                             | 12                            |
| benzo(g,h,i)perylene                                | $\mu\text{g.l}^{-1}$ | 0.01   | <0.001 | 0.04               | <0.001  | 0.4       | 385    | 0.1      | 0.2      | 12                            | 2                             |
| benzo(k)fluoranthene                                | $\mu\text{g.l}^{-1}$ | 0.01   | <0.001 | 0.06               | <0.001  | 0.85      | 385    | 0.1      | 0.2      | 3                             | 3                             |
| phenanthrene                                        | $\mu\text{g.l}^{-1}$ | 3.49   | 0.003  | 22.9               | <0.001  | 297       | 385    | 5        | 10       | 4                             | 15                            |
| chrysene                                            | $\mu\text{g.l}^{-1}$ | 0.44   | <0.001 | 2.93               | <0.001  | 37.5      | 385    | 0.1      | 0.2      | 4                             | 21                            |
| naphthalene                                         | $\mu\text{g.l}^{-1}$ | 2.12   | <0.001 | 14.2               | <0.001  | 182       | 385    | 25       | 50       | 2                             | 7                             |
| pyrene                                              | $\mu\text{g.l}^{-1}$ | 0.798  | 0.004  | 5.79               | <0.001  | 74.1      | 385    | 25       | 50       | 1                             | 2                             |

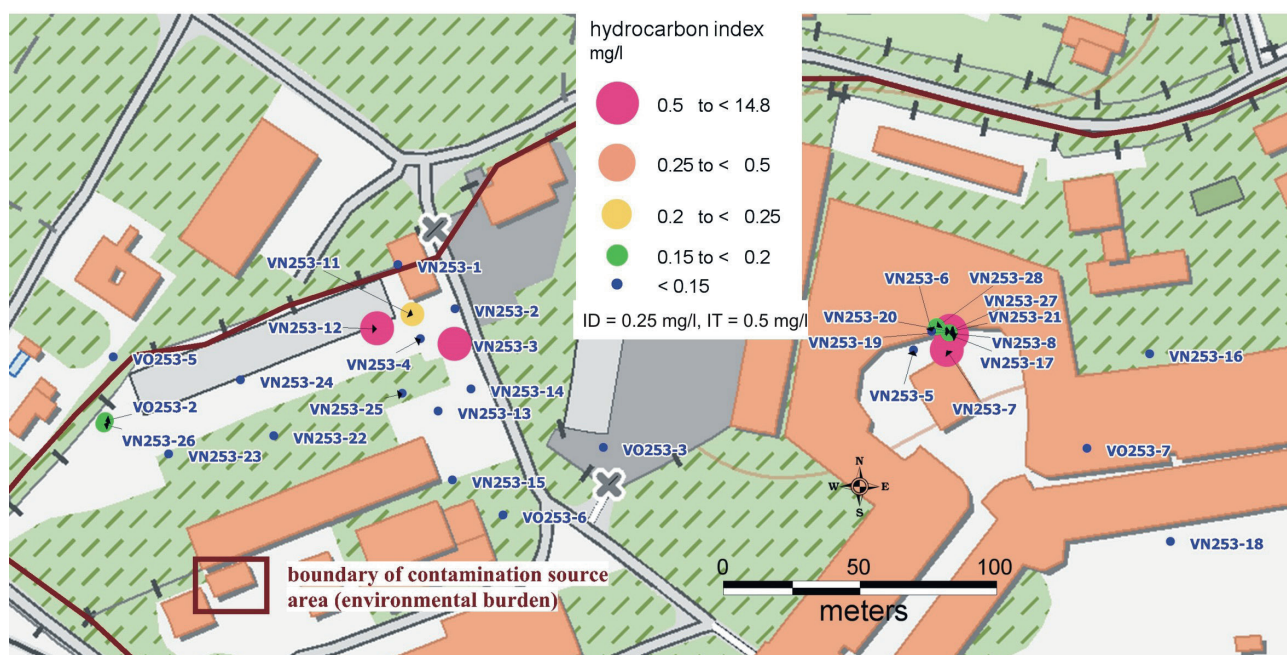


Fig. 1.35 Distribution of hydrocarbon index in groundwaters (median concentrations) – site Komárno – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

TOC, hydrocarbon index and xylene in groundwater (Tab. 1.12) were observed (maximum values 34.6 mg.l<sup>-1</sup> for NH<sub>4</sub><sup>+</sup>, 1,460 mg.l<sup>-1</sup> for TOC, 1,193,000 µg.l<sup>-1</sup> for hydrocarbon index, 1,405 µg.l<sup>-1</sup> for xylene).

Maps of distribution of selected parameters (median concentrations) in groundwaters are presented in Figs. 1.35 to 1.37.

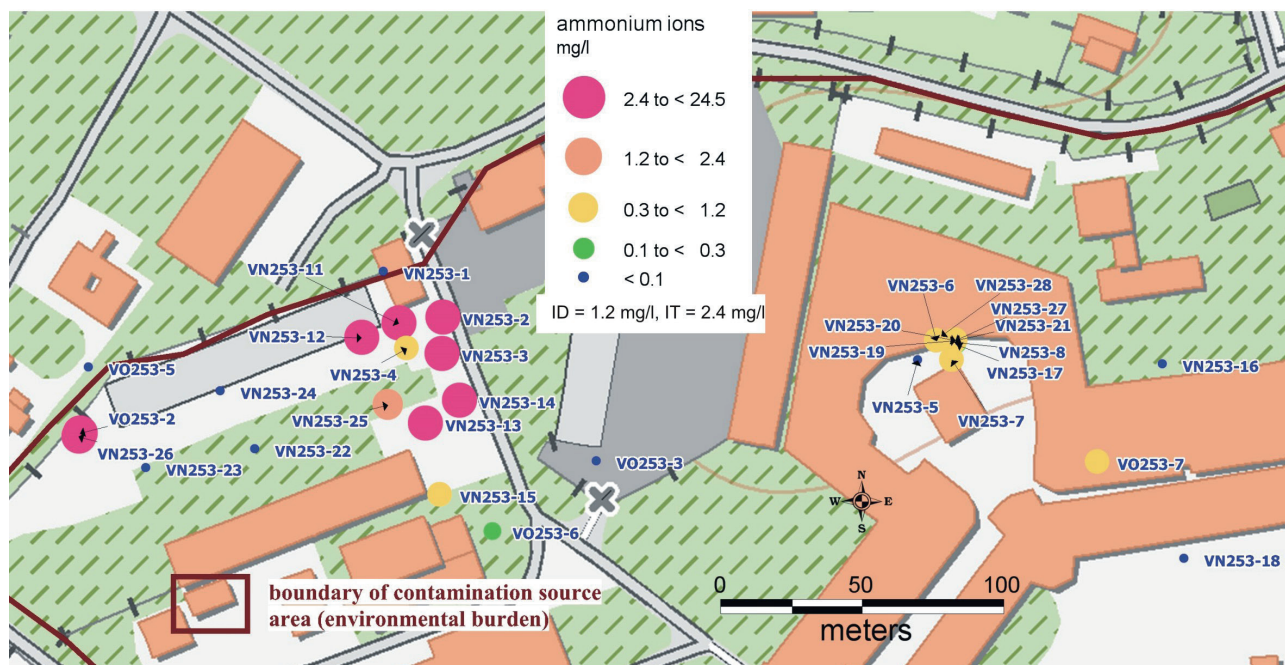


Fig. 1.36 Distribution of NH<sub>4</sub><sup>+</sup> in groundwaters (median concentrations) – site Komárno – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

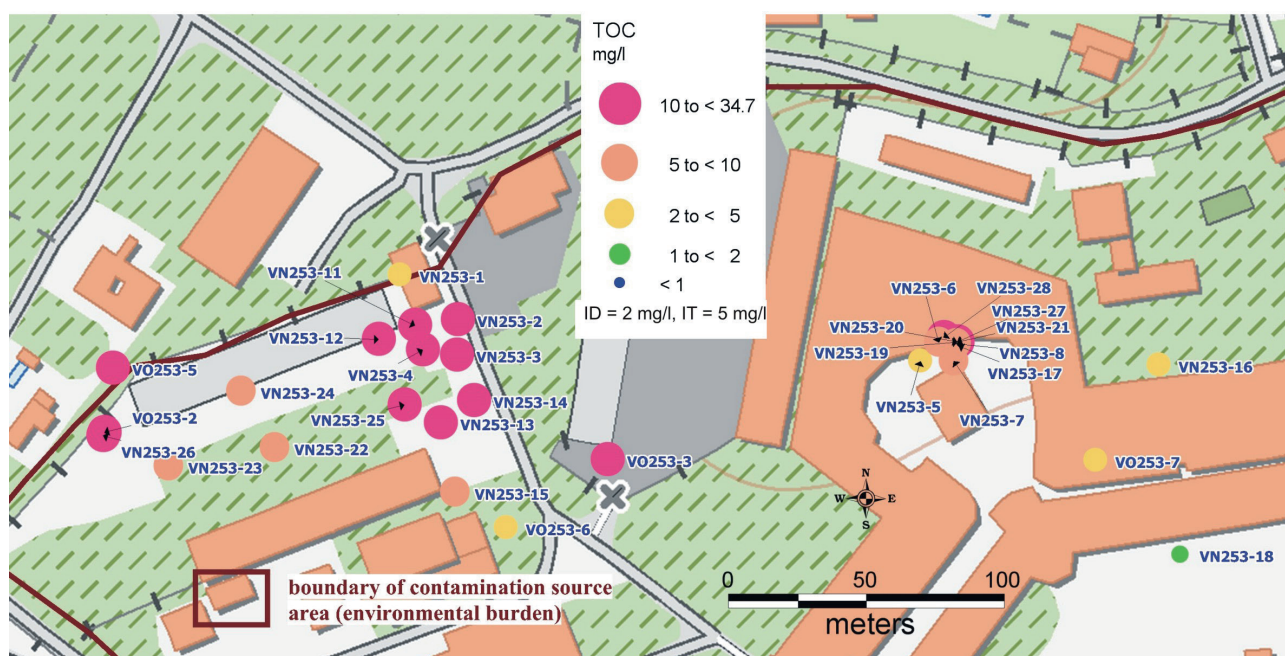


Fig. 1.37 Distribution of TOC in groundwaters (median concentrations) – site Komárno – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



### 1.3.12 Rimavská Sobota – area after the Soviet Army (loc. No. 256)

Environmental burden is caused by the long-term operation of the Soviet Army in barracks, namely inappropriate storage and handling of fuel, oils (tanks were overfilled and the terrain in their vicinity was seeped with oil) and solvents, handling with repaired and washed heavy equipment (waste water flushes into the rain sewer), etc. Several investigations in the area have shown significant groundwater pollution, with aliphatic chlorinated hydrocarbons currently being the main contaminant.

The area of interest is built of Tertiary and Quaternary sediments. The Tertiary is represented by siltstones, calcareous claystones and calcareous siltstones to siltstones with sand and clay positions (Lučenec Formation). Directly in the study area, the Tertiary sediments were found at a depth of 4.7 – 5.7 m (average), occasionally also at a depth of 6.5 – 6.9 m. They are represented by fine-grained

clayey sands to sandy clays compacted into intercalations of small thickness (1 – 5 cm; Klúz et al., 1991). In the immediate overburden of the Tertiary sediments, the fluvial sandy gravels are discordantly deposited. Their thickness is relatively small, ranging from 1.3 to 4.6 m, most often around 2.5 – 3.5 m. These are covered with a continuous position of alluvial sandy loams. The clays were drilled underneath the anthropogenic layers at a depth of 0.1 – 2.0 m and reached a thickness of 1 – 2 m on average. Almost the entire surface of the exploration area is covered by anthropogenic sediments (concrete, asphalt, quarry stones, loams, sand, brick fragments) with a maximum thickness of 2.8 m (Elečko et al., 1985; Vass et al., 1986).

Permanent pollution has also been confirmed by regular groundwater monitoring in recent years (Tab. 1.13). According to MoE Directive No. 1/2015-7 exceeding of ID and/or IT criteria was found mainly for cis 1,2-dichloroethene, tetrachloroethene, trichloroethene,

Table 1.13 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Rimavská Sobota – area after the Soviet Army

|                                           | unit               | mean | median | standard deviation | minimum | maximum | number | ID value | IT value | number of samples > ID | number of samples > IT |
|-------------------------------------------|--------------------|------|--------|--------------------|---------|---------|--------|----------|----------|------------------------|------------------------|
| hydrocarbon index ( $C_{10}$ - $C_{40}$ ) | mg.l <sup>-1</sup> | 0.03 | 0.02   | 0.04               | 0.02    | 0.32    | 91     | 0.25     | 0.5      | 2                      | 0                      |
| cis 1,2-dichloroethene                    | µg.l <sup>-1</sup> | 38.9 | 1.8    | 111                | <0.2    | 770     | 91     | 25       | 50       | 2                      | 16                     |
| tetrachloroethene                         | µg.l <sup>-1</sup> | 7.10 | <0.2   | 27.1               | <0.2    | 213     | 91     | 10       | 20       | 0                      | 8                      |
| trichloroethene                           | µg.l <sup>-1</sup> | 6.69 | <0.2   | 31.4               | <0.2    | 275     | 91     | 25       | 50       | 2                      | 4                      |
| chloroethene                              | µg.l <sup>-1</sup> | 7.73 | 1.6    | 16.0               | <0.2    | 103     | 91     | 5        | 10       | 10                     | 17                     |

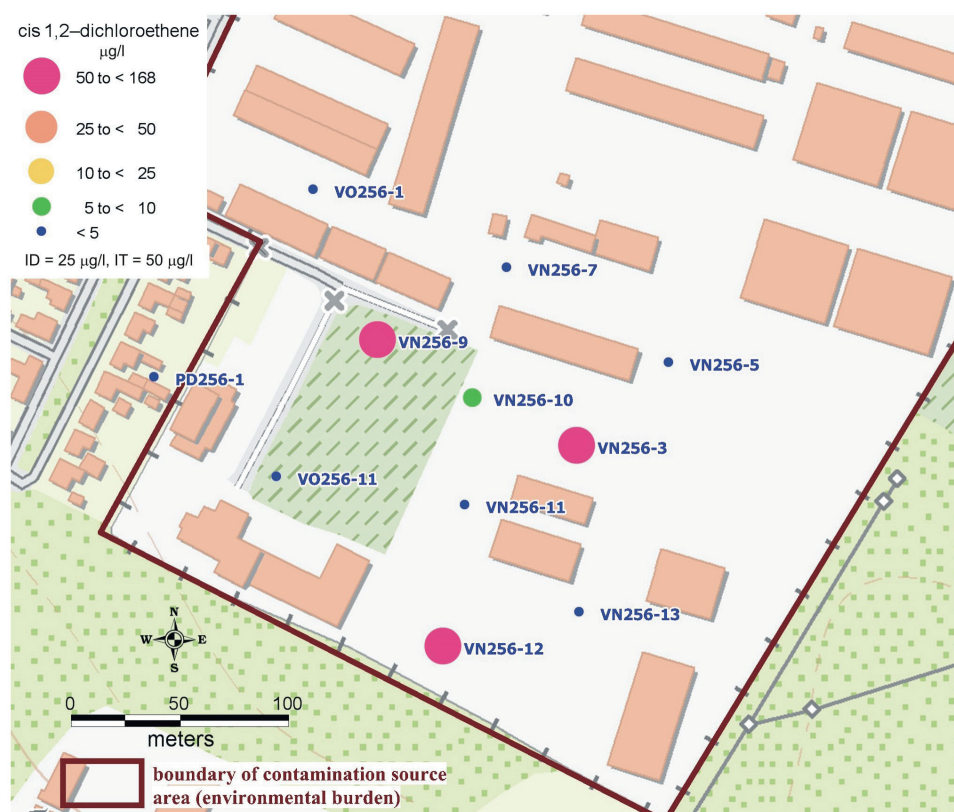


Fig. 1.38 Distribution of cis 1,2-dichloroethene in groundwaters (median concentrations) – site Rimavská Sobota – area after the Soviet Army (Topographic background: ZB-GIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

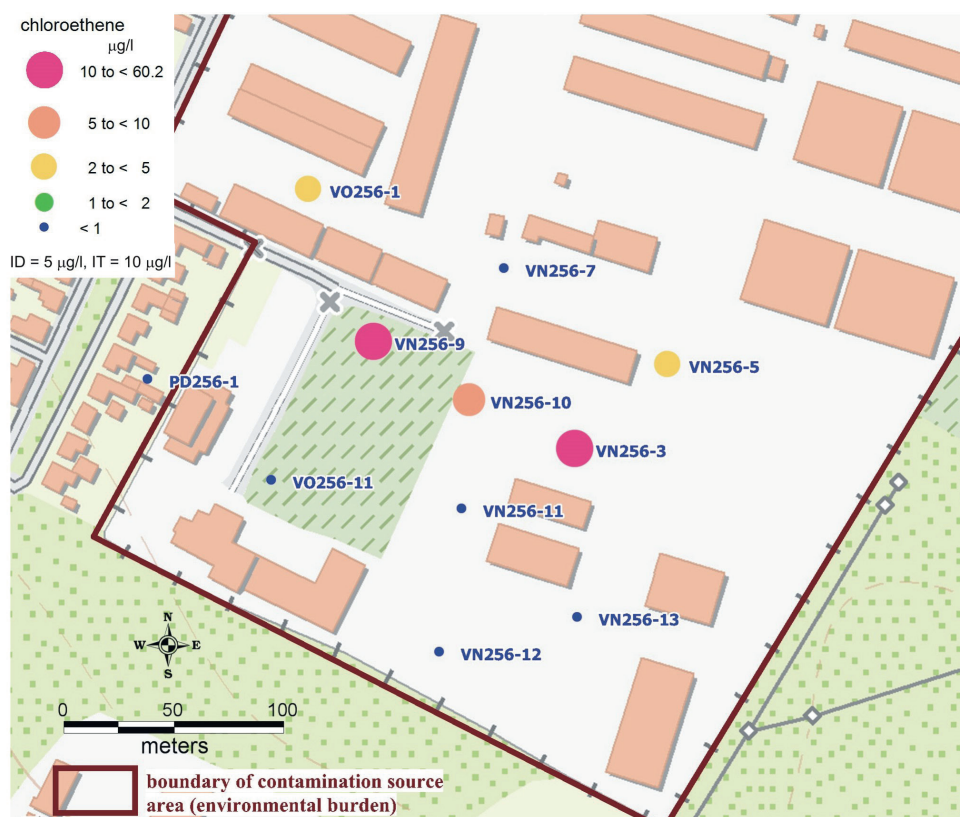


Fig. 1.39 Distribution of chloroethene in groundwaters (median concentrations) – site Rimavská Sobota – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

chloroethene. Elevated maximum concentrations of cis 1,2-dichloroethene (770 mg.l<sup>-1</sup>), tetrachloroethene (213 mg.l<sup>-1</sup>), trichloroethene (275 mg.l<sup>-1</sup>) and chloroethene (103 mg.l<sup>-1</sup>) were found in groundwater.

Maps of distribution of cis 1,2-dichloroethene and chloroethene (median concentrations) in groundwaters are presented in Figs. 1.38 and 1.39.

### 1.3.13 Krompachy – Kovohuty (loc. No. 314)

In the Kovohuty Krompachy plant there were processed ores and produced mainly copper and sulphuric acid. The copper production continues today in the form of copper wire and copper anode fabrication, sulphuric acid production was stopped.

The Quaternary sediments located in the area of interest consist of anthropogenic fillings, the bedrock of which is formed by fluvial sediments (mainly terrace loamy-sandy gravels and loams) and in upper position by incoherent layer of deluvial clayey-sandy silts. In the northern and north-eastern part of the investigated area loamy to clayey gravels of fluvial plain have been described. The thickness of these gravels ranges from 1 to 8 m depending on the distance from the channel of the Hornád River. The terrace gravels contain more clayey components, have a thickness of 2 – 3 m and their occurrence was recorded only in the south-western part of the studied area. Anthropogenic materials are represented in the operated area by blast furnace slag and artificial aggregates (products of current production). The layer thickness increases from south to north, reaching a maximum of 11 meters in the northern part of the enterprise (Polák et al., 1997).

Since 2016, 24 boreholes in the pollution area of the environmental burden have been monitored at various

frequencies. Moreover, 4 surface water profiles in the Hornád River have been monitored because of expected spreading of groundwater pollution from the assessed site. In addition, archive data from 29 boreholes have been taken into consideration according to Pospiechová et al. (2015). The monitoring showed the persistence of significant groundwater pollution at the site (Tab. 1.14). According to MoE Directive No. 1/2015-7 exceeding of ID and/or IT criteria was found mainly for TOC, NH<sub>4</sub><sup>+</sup> and several trace elements (As, Sb, Cd, Cu, Ni, Zn).

Mean values of selected parameters determined in groundwaters of monitoring boreholes are presented in Tab. 1.15. Very high mean values of specific conductivity were found in boreholes VN314-1 (374.9 mS.m<sup>-1</sup>), VO314-23 (917.7 mS.m<sup>-1</sup>), VN314-2 (278 mS.m<sup>-1</sup>), VO314-28 (293.3 mS.m<sup>-1</sup>). Mean sulphate concentrations above extremely high value of 1,000 mg.l<sup>-1</sup> were observed in many monitored boreholes: VN314-1, VN314-2, VN314-10, VN314-19, VO314-23 (the highest mean value of about 5,020 mg.l<sup>-1</sup>), VO314-24, VO314-25, VO314-26, VO314-28, VO314-30. Elevated mean contents of arsenic (above 100 µg.l<sup>-1</sup>) were monitored in boreholes VN314-17, VO314-26 and VO314-30 (the highest mean value of about 1,774 µg.l<sup>-1</sup>). Extremely high mean concentration was observed in borehole VO314-26 (2,254 µg.l<sup>-1</sup>) for antimony, in borehole VO314-23 (4,367 µg.l<sup>-1</sup>) for cadmium, in boreholes VN314-17 (6,436 µg.l<sup>-1</sup>) and VO314-26 (13,533 µg.l<sup>-1</sup>) for copper. Mean nickel contents above very high value of 1,000 µg.l<sup>-1</sup> were observed in monitored boreholes: VN314-1, VN314-2 (the highest mean value at level 9,405 µg.l<sup>-1</sup>), VN314-10, VO314-24, VO314-25, VO314-26. In case of zinc, extremely high



Table 1.14 Basic statistical parameters of selected parameters determined in waters and number of exceedances IT and ID values according to MoE Directive No. 1/2015-7 – site Krompachy – Kovohuty

|                                                       | unit               | mean    | median | standard deviation | minimum | maximum   | number | ID value            | IT value        | number of samples > ID | number of samples > IT |
|-------------------------------------------------------|--------------------|---------|--------|--------------------|---------|-----------|--------|---------------------|-----------------|------------------------|------------------------|
| pH                                                    |                    | 7.04    | 7.09   | 0.41               | 5.4     | 8.25      | 234    | 6.0-6.5 and 8.5-9.0 | < 6.0 and > 9.0 | 6                      | 12                     |
| conductivity                                          | mS.m <sup>-1</sup> | 208     | 169    | 180                | 37      | 1,170     | 243    | 200                 | 300             | 82                     | 21                     |
| NH <sub>4</sub> <sup>+</sup>                          | mg.l <sup>-1</sup> | 1.95    | 0.21   | 3.81               | <0.05   | 19.2      | 99     | 1.2                 | 2.4             | 2                      | 21                     |
| Cl <sup>-</sup>                                       | mg.l <sup>-1</sup> | 86      | 35     | 164                | 2.12    | 1,490     | 146    | 150                 | 250             | 12                     | 10                     |
| F <sup>-</sup>                                        | mg.l <sup>-1</sup> | 0.73    | 0.17   | 1.62               | <0.1    | 8.4       | 81     | 2                   | 4               | 4                      | 5                      |
| SO <sub>4</sub> <sup>2-</sup>                         | mg.l <sup>-1</sup> | 1,140   | 750    | 1,446              | 28      | 12,649    | 155    |                     |                 |                        | 116*                   |
| Fe-total                                              | mg.l <sup>-1</sup> | 12.1    | 0.12   | 42.6               | <0.002  | 257       | 146    |                     |                 |                        | 43**                   |
| Mn                                                    | mg.l <sup>-1</sup> | 4.92    | 2.29   | 6.56               | 0.001   | 31.8      | 146    |                     |                 |                        | 107***                 |
| Al                                                    | mg.l <sup>-1</sup> | 0.15    | 0.05   | 0.24               | 0.01    | 1.44      | 116    | 0.25                | 0.4             | 4                      | 15                     |
| B                                                     | mg.l <sup>-1</sup> | 0.53    | 0.21   | 0.63               | 0.02    | 2.24      | 116    | 0.5                 | 5               | 32                     | 0                      |
| As                                                    | µg.l <sup>-1</sup> | 46.3    | 5      | 208                | <0.5    | 2,010     | 232    | 50                  | 100             | 15                     | 15                     |
| Sb                                                    | µg.l <sup>-1</sup> | 57.3    | 2.4    | 274                | <0.5    | 2,410     | 213    | 25                  | 50              | 9                      | 25                     |
| Cd                                                    | µg.l <sup>-1</sup> | 215     | 1.1    | 977                | <0.1    | 6,680     | 232    | 5                   | 20              | 40                     | 31                     |
| Cu                                                    | µg.l <sup>-1</sup> | 778     | 32     | 2,619              | <2      | 16,700    | 232    | 1,000               | 2,000           | 4                      | 14                     |
| Ni                                                    | µg.l <sup>-1</sup> | 865     | 18     | 2,329              | <2      | 12,200    | 232    | 100                 | 200             | 12                     | 76                     |
| Zn                                                    | µg.l <sup>-1</sup> | 189,752 | 136    | 936,162            | 3       | 7,090,000 | 232    | 1,500               | 5,000           | 29                     | 16                     |
| Pb                                                    | µg.l <sup>-1</sup> | 19      | 1      | 78                 | <0.05   | 862       | 232    | 100                 | 200             | 5                      | 7                      |
| Co                                                    | µg.l <sup>-1</sup> | 28.7    | 1      | 82                 | <2      | 532       | 167    | 100                 | 200             | 6                      | 7                      |
| Hg                                                    | µg.l <sup>-1</sup> | 1.1     | 0.2    | 3.2                | <0.1    | 23.5      | 230    | 2                   | 5               | 8                      | 15                     |
| TOC                                                   | mg.l <sup>-1</sup> | 32      | 7      | 92                 | 0.5     | 513       | 79     | 2                   | 5               | 10                     | 44                     |
| hydrocarbon index (C <sub>10</sub> -C <sub>40</sub> ) | mg.l <sup>-1</sup> | 0.07    | <0.02  | 0.12               | <0.02   | 0.74      | 161    | 0.25                | 0.5             | 9                      | 3                      |

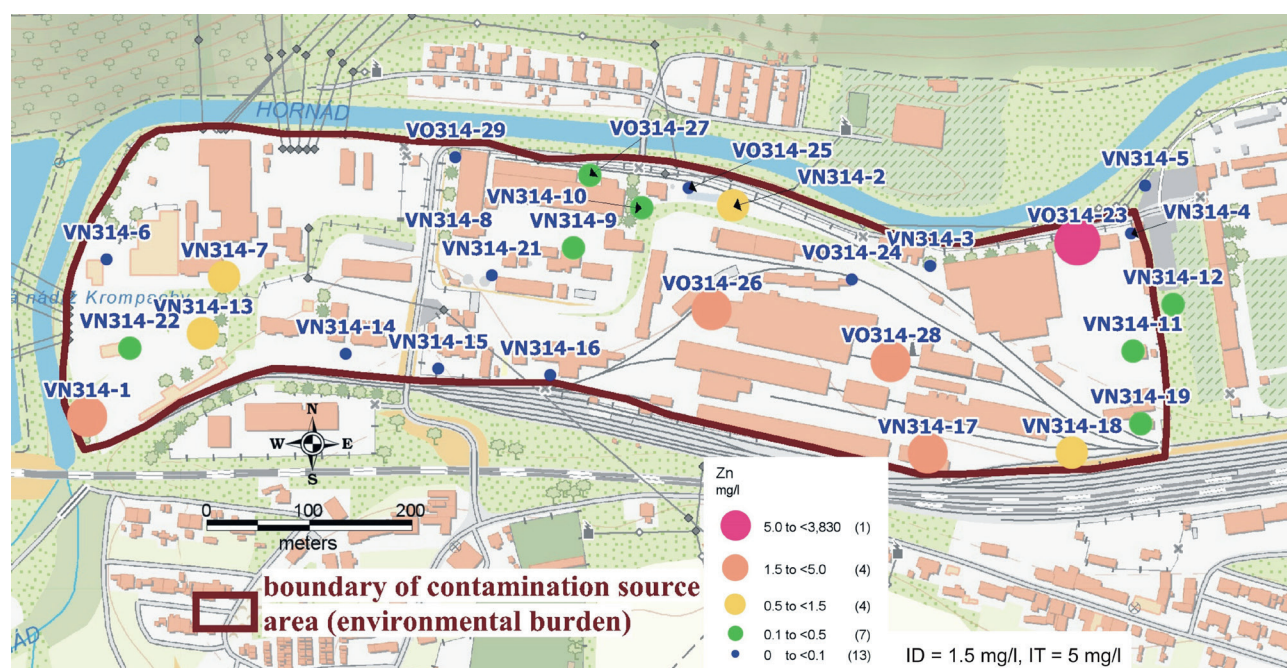
\* Number of samples > 250 mg.l<sup>-1</sup> (national normative value according to 247/2017 Coll.)\*\* Number of samples > 0.5 mg.l<sup>-1</sup> (national normative value according to 247/2017 Coll.)\*\*\* Number of samples > 0.2 mg.l<sup>-1</sup> (national normative value according to 247/2017 Coll.)

Fig. 1.40 Distribution of Zn in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

Table 1.15 Mean values of selected parameters determined in groundwaters of monitoring boreholes

| Borehole | conductivity       | NH <sub>4</sub> <sup>+</sup> | Cl <sup>-</sup>    | SO <sub>4</sub> <sup>2-</sup> | As                 | Sb                 | Cd                 | Cu                 | Ni                 | Zn                 | B                  | TOC                |
|----------|--------------------|------------------------------|--------------------|-------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
|          | mS.m <sup>-1</sup> | mg.l <sup>-1</sup>           | mg.l <sup>-1</sup> | mg.l <sup>-1</sup>            | µg.l <sup>-1</sup> | µg.l <sup>-1</sup> | µg.l <sup>-1</sup> | µg.l <sup>-1</sup> | µg.l <sup>-1</sup> | µg.l <sup>-1</sup> | mg.l <sup>-1</sup> | mg.l <sup>-1</sup> |
| VN314-1  | 374.9              | 1.31                         | 95                 | 2,441                         | 25.8               | 93.8               | 18.6               | 519                | 1,050              | 2,394              | 0.16               | 3.1                |
| VN314-2  | 278                | 7.25                         | 33                 | 1,646                         | 1.7                | 1.2                | 6.4                | 793                | 9,405              | 908                | 0.15               | 2.3                |
| VN314-3  | 201.5              | 1.04                         | 665                | 490                           | 3.6                | 1.7                | 0.8                | 35                 | 214                | 242                | 0.45               | 9.2                |
| VN314-4  | 186.5              | 0.13                         | 33                 | 768                           | 1.8                | 0.8                | 2.1                | 16                 | 4                  | 968                | 0.31               | 3.3                |
| VN314-5  | 150                | 0.08                         | 57                 | 459                           | 2.6                | 1.5                | 0.4                | 8                  | 2                  | 47                 | 0.29               | 9.4                |
| VN314-6  | 101.3              | 0.03                         | 94                 | 195                           | 3.3                | 16.5               | 0.4                | 40                 | 4                  | 24                 |                    | 7.7                |
| VN314-7  | 64.7               | 0.03                         | 74                 | 110                           | 3.1                | 6                  | 0.4                | 41                 | 7                  | 602                |                    | 6.8                |
| VN314-8  | 232.5              | 0.03                         | 124                | 983                           | 35.5               | 17.8               | 0.4                | 8                  | 2                  | 17                 | 0.47               | 8.4                |
| VN314-9  | 128.3              | 0.41                         | 38                 | 468                           | 27.6               | 6.5                | 53.4               | 18                 | 4                  | 488                | 0.17               | 6.9                |
| VN314-10 | 247.2              | 0.12                         | 34                 | 1,562                         | 2.7                | 1.5                | 2.8                | 158                | 1,013              | 155                | 0.11               | 7.8                |
| VN314-11 | 120.9              | 0.24                         | 53                 | 491                           | 18.4               | 36.9               | 1.1                | 47                 | 21                 | 136                | 2.13               | 4                  |
| VN314-12 | 221.9              | 0.87                         | 94                 | 922                           | 64.5               | 1.1                | 1.9                | 5                  | 6                  | 185                | 1.51               | 11.3               |
| VN314-13 | 74.9               | 0.03                         | 6                  | 203                           | 10.2               | 1.6                | 14.8               | 1,934              | 96                 | 7,630              | 0.12               | 3.3                |
| VN314-14 | 91.4               | 0.03                         | 21                 | 116                           | 1.7                | 1.3                | 0.6                | 17                 | 2                  | 31                 | 0.07               | 6.9                |
| VN314-15 | 76.2               | 0.16                         | 11                 | 68                            | 1.6                | 1.9                | 0.2                | 9                  | 6                  | 26                 | 0.09               | 17.7               |
| VN314-16 | 70.5               | 0.03                         | 37                 | 87                            | 2.5                | 3.8                | 0.2                | 28                 | 2                  | 19                 | 0.07               | 2.8                |
| VN314-17 | 103.2              | 0.2                          | 17                 | 305                           | 115                | 229                | 17                 | 6,436              | 50                 | 2,476              | 0.23               | 221                |
| VN314-18 | 85.2               | 0.18                         | 16                 | 156                           | 50.2               | 24.7               | 7.7                | 70                 | 13                 | 476                | 0.28               | 3.4                |
| VN314-19 | 234.1              | 0.1                          | 40                 | 1,152                         | 17.5               | 12.5               | 1.6                | 33                 | 121                | 276                | 1.18               | 3.3                |
| VN314-21 | 93.5               | 0.09                         | 65                 | 298                           | 0.8                | 1.1                | 0.2                | 4                  | 2                  | 10                 | 0.12               | 7.3                |
| VN314-22 | 84.8               | 0.03                         | 115                | 130                           | 3.2                | 13.2               | 0.4                | 51                 | 19                 | 168                |                    | 8.9                |
| VO314-23 | 917.7              | 1.53                         | 250                | 5,020                         | 14.8               | 2.1                | 4,367              | 631                | 894                | 3,980,455          | 1.77               | 9.8                |
| VO314-24 | 198.4              | 0.88                         | 44                 | 1,208                         | 2.4                | 8.1                | 0.4                | 333                | 1,280              | 64                 | 0.07               | 4.5                |
| VO314-25 | 261.5              | 3.36                         | 63                 | 1,588                         | 5.3                | 1.1                | 0.2                | 8                  | 1,361              | 40                 | 0.13               | 1.3                |
| VO314-26 | 234.4              |                              | 90                 | 2,000                         | 235                | 2,254              | 42                 | 13,533             | 1,173              | 2,317              | 0.19               |                    |
| VO314-27 | 167.4              | 15.95                        | 66                 | 631                           | 1.3                | 1.5                | 0.4                | 10                 | 579                | 137                | 0.21               | 1.9                |
| VO314-28 | 293.3              | 0.57                         | 255                | 1,485                         | 5.1                | 1.8                | 3.5                | 19                 | 10                 | 7,284              | 0.79               | 2.5                |
| VO314-29 | 127.9              | 0.43                         | 55                 | 337                           | 2.5                | 7.2                | 1.8                | 13                 | 3                  | 95                 |                    | 7.3                |
| VO314-30 | 239.2              | 4.14                         | 28                 | 1,662                         | 1,774              | 220                | 0.3                | 169                | 333                | 79                 |                    | 7.6                |

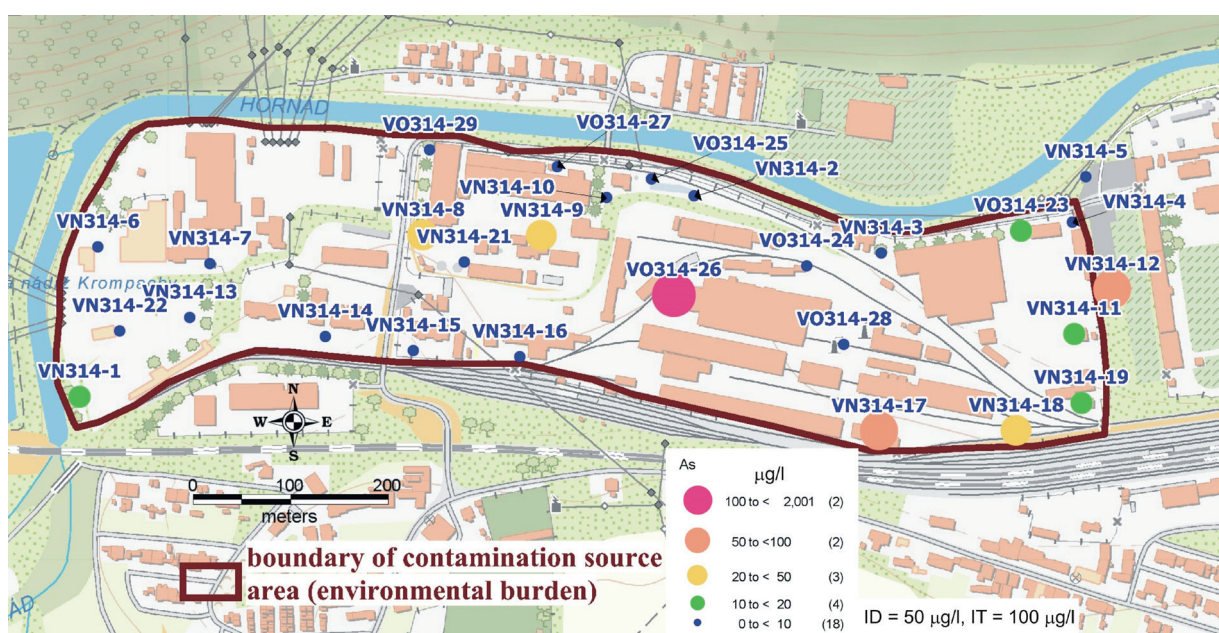


Fig. 1.41 Distribution of As in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



mean concentration was calculated in borehole VO314-23 ( $3,980,455 \mu\text{g.l}^{-1}$ ). Mean zinc contents above  $1,000 \mu\text{g.l}^{-1}$  were found also in monitored boreholes: VN314-1, VN314-13, VN314-17, VO314-26 and VO314-28.

For most of the pollutants the risk of spreading of groundwater pollution in both the western and eastern

parts of the assessed site is expected (Pospiechová et al., 2015). In the eastern part of the assessed site, in the case of arsenic, cadmium, nickel and zinc, it is assumed that groundwater pollution will spread and the quality criteria will be exceeded at the boundary of the industrial site

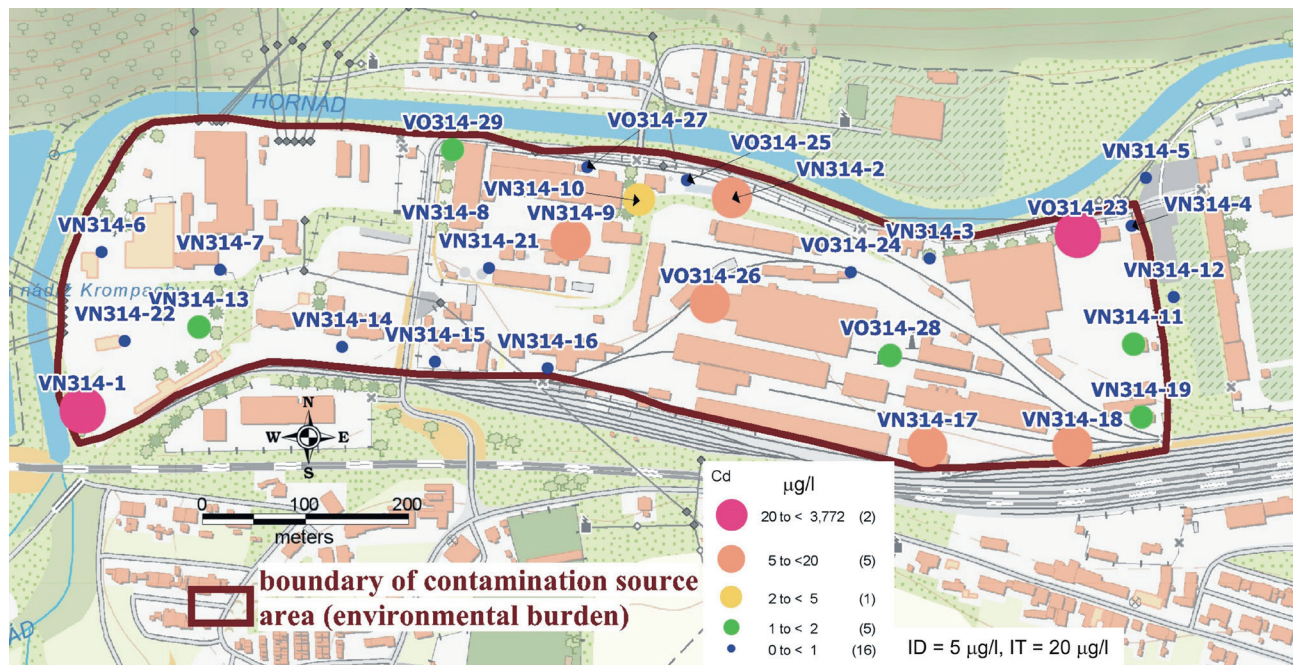


Fig. 1.42 Distribution of Cd in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

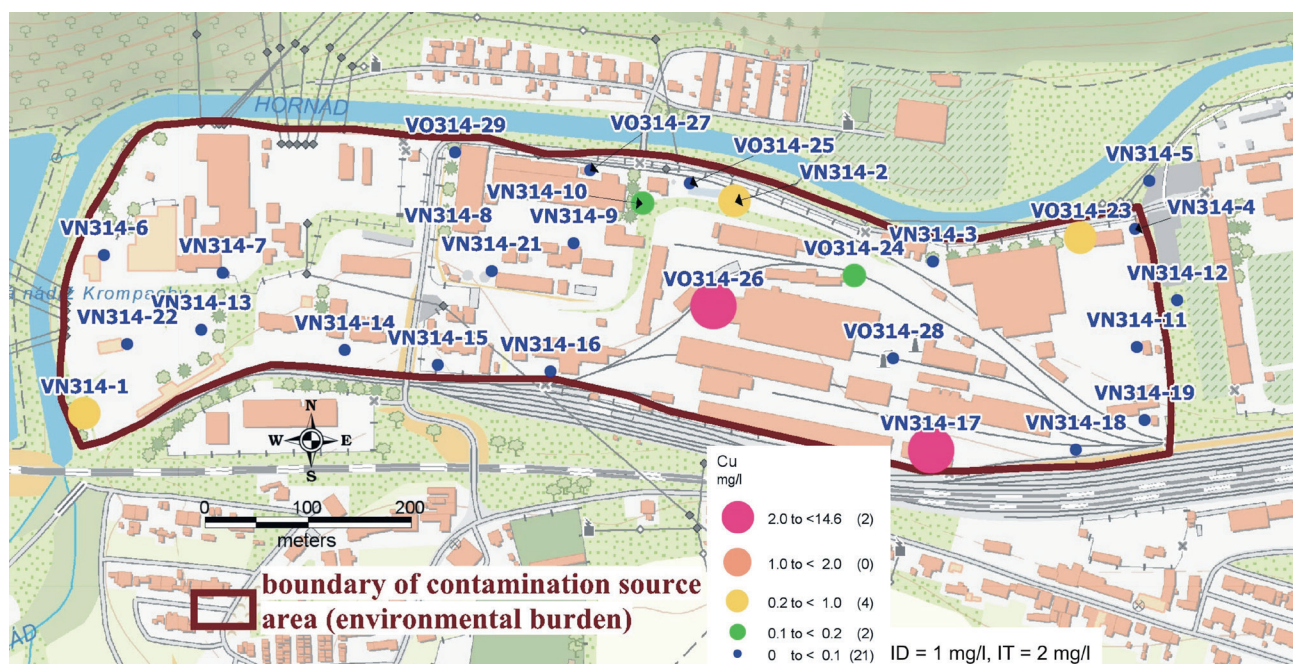


Fig. 1.43 Distribution of Cu in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



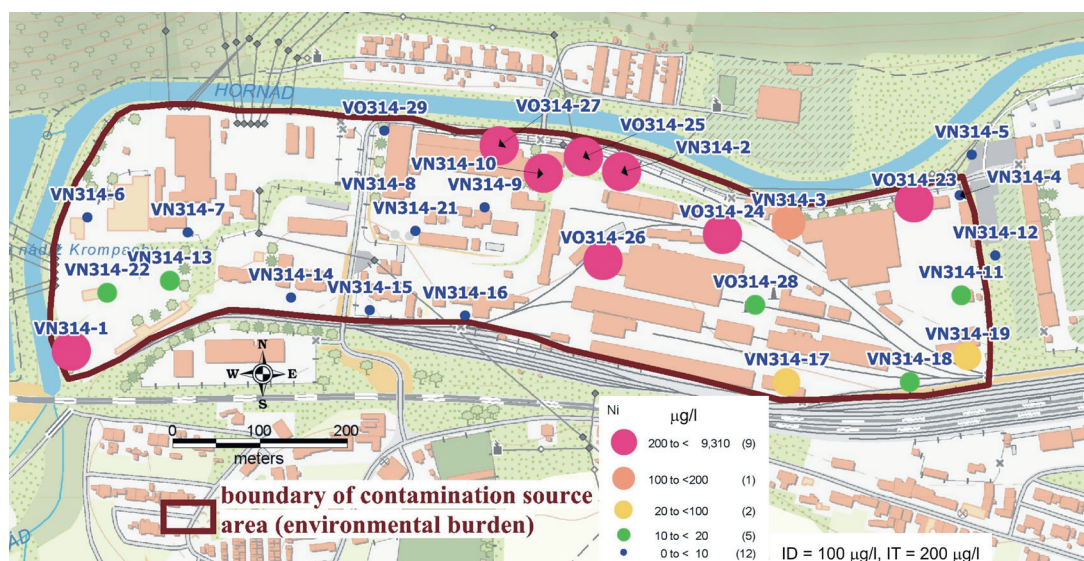


Fig. 1.44 Distribution of Ni in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

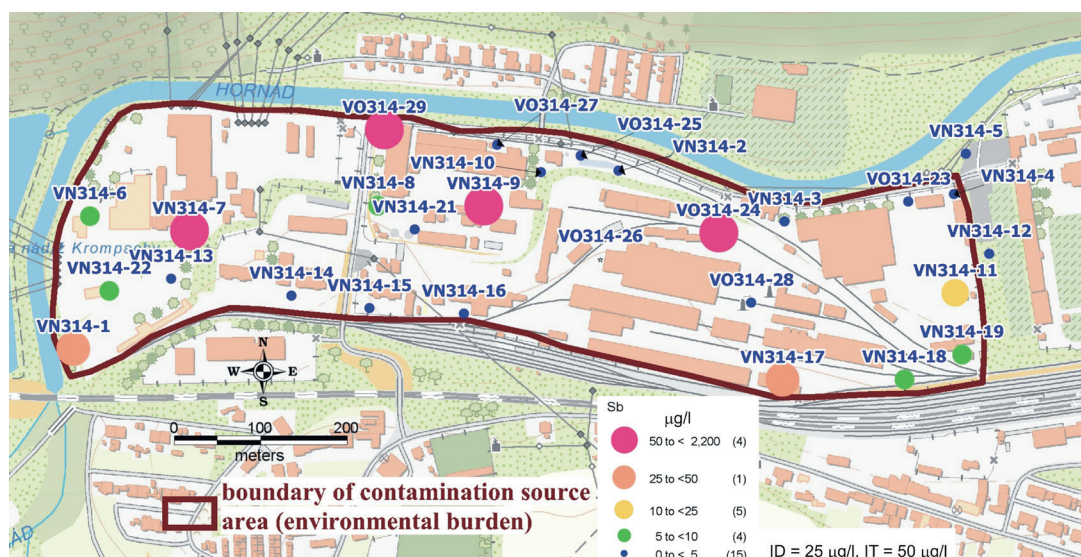


Fig. 1.45 Distribution of Sb in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

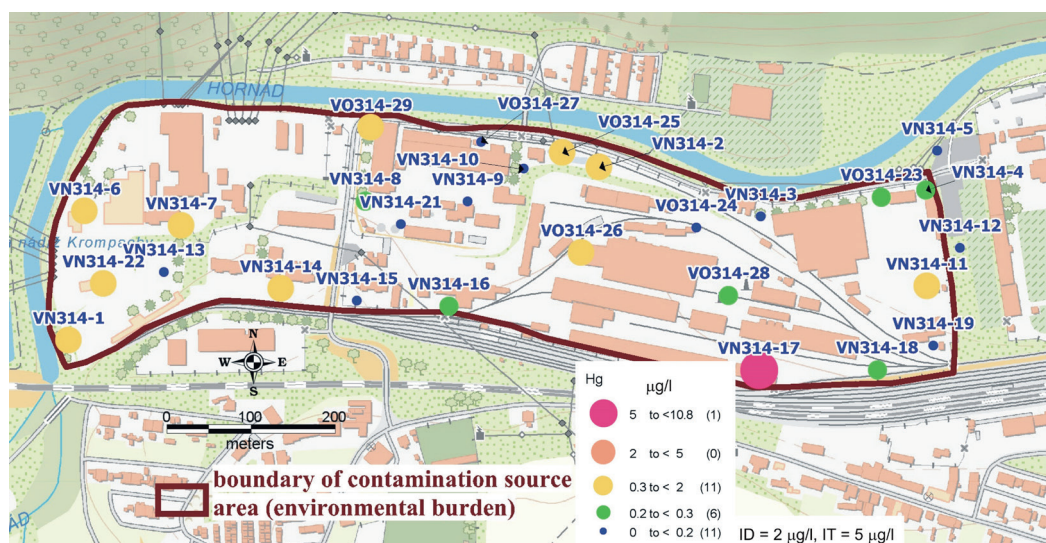


Fig. 1.46 Distribution of Hg in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)



even after the dilution of pollution in the Hornád River (at minimum water levels). Maps of distribution of selected parameters (median concentrations) in groundwaters are presented in Figs. 1.40 to 1.46.

#### 1.4 Conclusion

Since 2012, the State Geological Institute of Dionýz Štúr has been carrying out tasks related to the monitoring of environmental burdens, currently in more than 300 sites. Results of groundwater and surface water quality monitoring in selected heavily polluted sites representing a wide range of economic activities are commented in this paper. Pollution from landfills is typically associated with the occurrence of high levels (above IT criteria) of boron, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup> and conductivity. As an example, extremely high contents of B (above 5 mg.l<sup>-1</sup>) and NH<sub>4</sub><sup>+</sup> (above 100 mg.l<sup>-1</sup>) were observed at the site Bojná – landfill – part A.

Pollution with organic substances (which is indicated by TOC and COD<sub>Mn</sub>) is relatively frequent in Slovakia, especially at sites such as municipal landfills and oil pollution areas or other contamination sources. The highest content of TOC (1,460 mg.l<sup>-1</sup>) was found at the site Komárno – area after the Soviet Army. Extremely high levels of TOC (above 50 mg.l<sup>-1</sup>) were also determined at the sites Bojná – landfill – part A and Bratislava – Vrakuňa – CHZJD landfill. Extremely high levels of COD<sub>Mn</sub> (above 50 mg.l<sup>-1</sup>) were found for instance at the site Bojná – landfill – part A.

Among the organic substances, chlorinated hydrocarbons (concentrations above the IT limits) appear to be problematic specifically within the industrial EBs, especially cis 1,2-dichloroethene, dichloromethane, tetrachloroethene, trichloroethene and chloroethene. Very high contents of cis 1,2-dichloroethene (above 1 mg.l<sup>-1</sup>), trichloroethene (above 1 mg.l<sup>-1</sup>), tetrachloroethene (above 1 mg.l<sup>-1</sup>) and chloroethene (above 0.1 mg.l<sup>-1</sup>) were found at the site Zlaté Moravce – Calex. Very high concentrations of chloroethene (above 0.1 mg.l<sup>-1</sup>) and dichloromethane (above 0.02 mg.l<sup>-1</sup>) were observed at the site Piešťany – Chirana. Very high contents of dichloromethane (above 0.02 mg.l<sup>-1</sup>) were determined at the site Bratislava – Vrakuňa – CHZJD landfill. Extremely high levels of C<sub>10</sub>-C<sub>40</sub> (above 10 mg.l<sup>-1</sup>) were observed at the sites Bratislava – Chemika, Bratislava – Gumon, Čierna nad Tisou – transshipment station, Komárno – area after the Soviet Army (loc. No. 253).

Specific organic substances were found also in surface water at above-limit concentrations: cis 1,2-dichloroethene (Piešťany – Chirana, Zlaté Moravce – Calex), chlorobenzene (Bratislava – CHZJD chemical plants, dichloromethane (Piešťany – Chirana), perchloroethylene (Zlaté Moravce – Calex), trichloroethene (Zlaté Moravce – Calex).

Some trace inorganic elements, also due to the inclusion of mining sites in monitoring, exceed IT criteria in groundwaters. Very high concentrations of As (above 1 mg.l<sup>-1</sup>) are mainly associated with industrial (Bojná – landfill – part A, Bratislava – Vrakuňa – CHZJD landfill, Krompachy – Kovohuty) or mining activities (Poproč

– Petrova dolina Valley). Very high concentrations of Sb (above 0.3 mg.l<sup>-1</sup>) were observed at the sites Poproč – Petrova dolina Valley and Krompachy – Kovohuty.

The data obtained and the results of extensive monitoring contribute to the overall awareness of the effects of the environmental burdens on the quality of groundwater or surface water. The results of monitoring of environmental burdens allow relevant authorities to take flexible measures to minimize risks and damages, set targets and scope for a detailed or additional investigation of the EBs and propose preventive or remedial measures.

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## 2. Application of Microchemical Research in Environmental Burdens Investigation

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**Abstract:** The presented work offers an overview of the microchemical applications of solid and non-cohesive, synthetic and natural materials realized by electron microanalysis. Microchemical study of materials for the purpose of research and monitoring of environmental burdens aims to identify potential contamination in the source area or its spread in the natural environment. In addition to the direct identification of the chemical elements of interest or mineral phases, the results of the electron probe micro-analysis analysis provide information on the physical and chemical stability conditions of the system under investigation. The work gradually presents solved examples selectively for various types of materials such as waste sludge, metallurgical waste, organic material, sands, ash, soils and river sediments. The analysed materials are in natural conditions in direct interaction with surface waters, atmosphere and biosphere and their interaction determines various variants of migration of pollutants in hypergenic environment. Migration is not always controlled by the active form of transport in the aquatic environment, as demonstrated by several examples. Migration of pollutants by mechanical or aeolian form of transport is frequent and may be unidentifiable by classical hydrochemical monitoring methods. The use of a microchemical study for the analysis of solid materials in a hypergenic environment utilizes their natural physical and chemical properties with respect to sorption capacity and their function as a natural geochemical barrier in the area of the migration route. The systematic analysis of the organic material of decaying plant tissues and the autogenous phases of FeOOH proves their effective usability as natural time-sensitive monitoring probes throughout their lifetime. Identifying elements of interest or pollutants on autogenous minerals directly identifies the distribution of contamination in the environment and their form of migration. The knowledge gained from the results of the microchemical EPMA study serves as a direct basis for the reconstruction of distribution, the form and extent of migration and the prognosis of the development of contamination in the environment.

**Key words:** microchemical investigation, EPMA analysis, environmental burdens

### 2.1 Introduction

Tackling the problem of environmental burdens “EB” or environmental damage “ED” is the forced response of society to the negative environmental impact of industrial and agricultural activity. The entry of contamination into the natural system can be simple, but its interaction with environmental components is virtually always complex. An example is the entry of contamination into groundwater and surface waters, which are in direct interaction with the rock environment, soils and with the inseparable part

of the biota present everywhere. There is a set of direct links between environmental components that control the further chain of direct and feedback relations.

The basic methods for the investigation and monitoring of environmental burdens are chemical research based on full-surface analyses of the substrate in which contamination is assumed or identified along with groundwater and surface water analyses. The monitoring phase itself is based primarily on the analysis of the surface and groundwaters, as these are the main transport medium for the spread of contamination in the environment. The practice of the solution itself is pragmatic, but it does not cover the solution of the distribution of contamination in the contaminated environment and it cannot solve the physico-chemical stability of the contaminated source and its surroundings. An important aspect of the investigation and monitoring of the EBs is monitoring itself, which is intended to provide answers to the issues of contamination mobility and spread. The problem lies in the complexity of natural processes, since the movement of contamination does not have to take place only in the active form of transport of dissolved substances in water, but in a form as, for instance, mechanical transport.

The mechanically transported contamination can often be highly effective, but may not be identifiable by hydrochemistry.

Part of the above shortcomings of the research and monitoring of the EBs can be solved by targeted petrographic work and the application of electron microanalysis “EPMA” (Electron Probe Micro-Analyser).

The application of the EPMA microanalysis to solve the problem of environmental burdens enables microchemical study of rocks, soils, stream sediments, synthetic solid waste or even organic material. The aim of this paper is to provide an overview of the possibilities of applying the EMF study of solid materials on examples that were solved within the tasks focused on the EBs monitoring at the State Geological Institute of Dionýz Štúr (Kordík & Slaninka et al., 2015; Slaninka et al., running project).

### 2.2 Methods

Application of the EPMA analysis is oriented on chemical analysis of solid materials and is not intended for water or gas analysis. The EPMA microanalysis is designed for analysis of qualitative and quantitative content

of chemical elements. The EPMA analysis fails to analyse light elements with an atomic number less than lithium, making it impossible to analyse crystal-chemically bound -OH/H<sub>2</sub>O. Based on the analysed chemical composition of the solid phase, it is possible to identify a particular type of chemical phase or mineral and, in the case of a known crystallographic structure, to calculate the corresponding crystal-chemical formula.

Solid natural materials occur in several natural forms, such as solid compact rocks, minerals or glass. The solid phase is often present in the form of non-cohesive mixtures such as sludge, sands, dust aerosols or organic material.

The nature of the analysed material determines which preparation method is appropriate for the EPMA analysis. For compact materials, samples are treated directly into the form of a polished cut while bulk materials (soil, sludge) are cemented with epoxy resins to achieve compactness.

If needed, a 10 – 30 µm wide electron beam analysis can be used to address the distribution of chemical elements in the sample, resulting in an average analysis of some very fine objects. The use of a wide analytical beam is sometimes necessary due to the fineness of the analysed material.

The EPMA analysis is limited by electron beam parameters that can be focused on a circular space with a diameter of 1 µm. Analysed objects ranging in a nanoscale <1 µm can only be analysed as a mixture.

The samples were analysed at the SGIDŠ electron-optic methods workplace using BSE analysis of back-scattered electrons and EDXA energy dispersive X-ray spectroscopy microanalysis and chemical microanalysis using CAMECA SX100 electron microanalyser, hereinafter the EPMA “electron microprobe”.

Analytical conditions of measurement of chemical composition of sulphides are following: accelerating voltage 25 keV with electron beam current of 10 nA. The following chemical standards were used: S, Fe, Cu / CuFeS<sub>2</sub>, Pb / PbS, Zn / ZnS, As / GaS, Cd / Cd, Ag / Ag, Mn / Mn.

The analytical conditions for measuring the chemical composition of silicates and oxides were following: an accelerating voltage of 15 keV and electron beam current 20 nA.

The width of the analytical electron beam used was adapted to the analysed object, i.e. for phase analysis a beam with a diameter of 5 µm was used and for analysis of the area of fine-grained aggregates 15 – 30 µm.

The following chemical standards were used: F / LiF, Na / albite, Si, K / orthoclase, Al / Al<sub>2</sub>O<sub>3</sub>, Mg / forsterite, Cl / NaCl, Ca / wollastonite, Ti / TiO<sub>2</sub>, Fe / fayalite, Mn / rhodonite, Cr / Cr, Ni / Ni, As / GaAs, S, Ba / baryte, Pb / PbCO<sub>3</sub>, Cu / Cu, Zn / willemite, Sr / SrTiO<sub>3</sub>, P / apatite.

### 2.3 Overview of applications of the EPMA analysis in research and monitoring of EBs

The application of the EPMA microanalysis in dealing with the environmental burdens must necessarily be based on the initial field research of the site and the nature of the assumed or identified contamination. In case

of contamination with potentially toxic elements such as As, Pb, Zn, Cu, Sb, Co, Cr, Ni, Hg, it is important to target systematic sampling of suitable material, while the sampling itself must respect the concept of geochemistry of the landscape. The sample material should cover the source material of the contamination as well as the identified migration routes in and around the EB area. In the case of an unknown source of contamination or the location and extent of the contaminated area, sampling may be oriented as a survey.

A variety of natural or artificial synthetic materials can be encountered during sampling and subsequent EPMA studies. Each type of sample has its own specific pros and cons and can provide a variety of information about the distribution of contamination, migration or physico-chemical stability of the system. Therefore, the individual types of material are described separately systematically with a short overview obtained during our practice (Kordík & Slaninka et al., 2015; Demko, Šefčík & Luptáková, 2015; Šefčík & Demko, 2015; Demko, Luptáková & Šefčík, 2016; Demko & Šefčík, 2018; Šefčík & Demko, 2018; Šefčík & Demko, 2019).

**SAMPLING** for microchemical research to supplement full-mineral analysis of solid materials and waters must meet the principle of the geochemical relationships on the location or the concept of the landscape geochemistry (Darnley et al., 1995; Fortescue, 1992; Perefman, 1975). In a practice, it is always important to respect the real conditions of the area of interest with regard to natural or artificial characteristics of the environment. The identification of the assumed or identified source is the sampling focused on the primary source material, such as waste sludge (Fig. 2.1-A), macroscopically visible mineral products, which are exotic in the area of interest, or strange (Fig. 2.1-D). Sampling should be directed to a material that is characterized by suitable properties and acts as a natural geochemical barrier in the landscape geochemistry (Fig. 2.1-C).

Sampling should be directed towards zones that are direct migration routes of the analysed pollutants or act as communication transport zones between different geochemical entities in the country (Fig. 2.1-B). The sample material that can be analysed by the EPMA analysis can be solid and compact, or not solidified with varying degrees of disintegration.

Samples that are significantly non-solidified or disintegrate can be cemented prior to preparation of the analytical specimen in a manner that preserves primary texture and structural relationships. For samples that are primarily non-cohesive, loose (sands) or primarily plastic (clays, sludges), the specimen can also be cemented with epoxy resins. As a sample material we used even organic material – plant tissues, at a variable stage of decomposition. If there is a suspension in the water samples, it is possible by means of evaporation and filtration to separate the suspension, which can be adjusted for the EPMA analysis similarly to loose and plastic materials.

Examples of various materials sampled in the EBs monitoring are shown in Fig. 2.1.



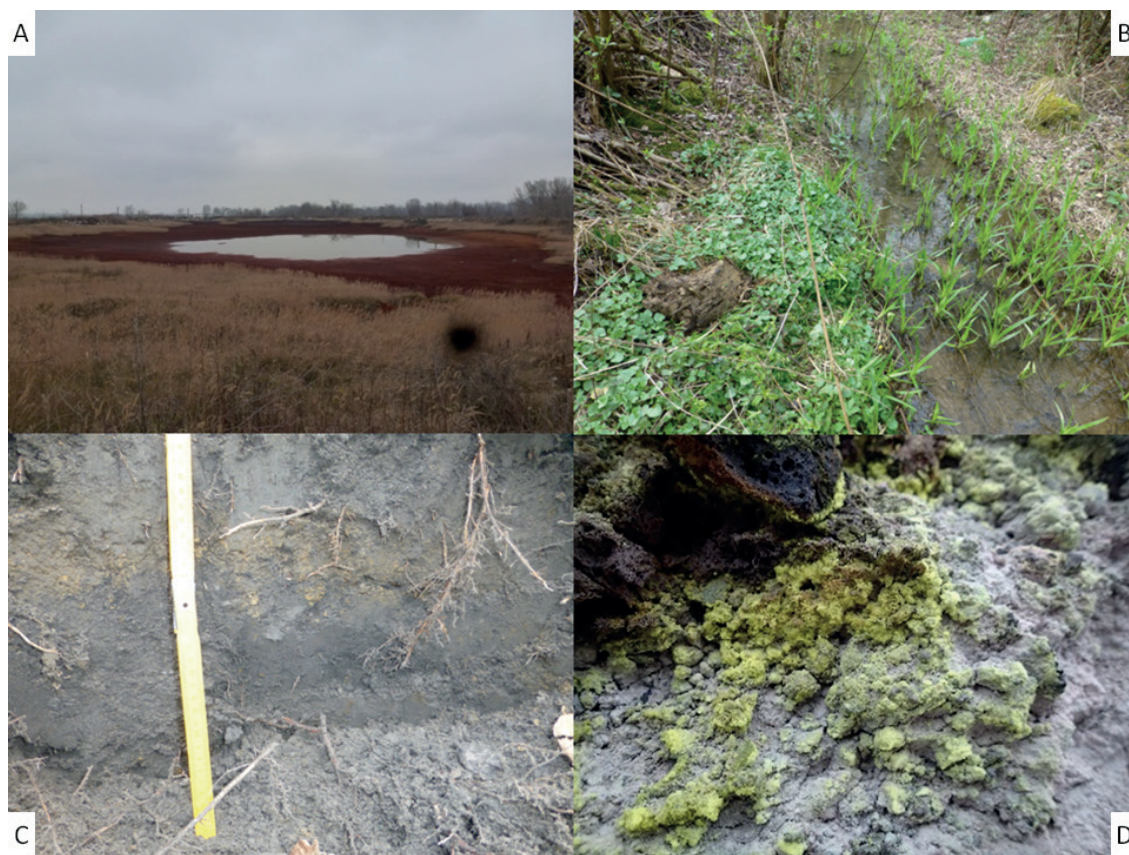


Fig. 2.1 Examples of various materials sampled within the EBs monitoring.

A) The Šulekovo tailings pond in Hlohovec as an example of the tailings pond for galvanic waste. The stored sludges containing Pb-Zn-Sn are in constant contact with atmospheric air and surface waters. The conditions in the tailings pond itself determine the physico-chemical properties of the environment influenced by surface water level fluctuations, sludge drying effect and wind erosion function. Fluctuations in pH/Eh properties of the environment directly determine the stability of the minerals that control the mobility of Pb-Zn-Sn within the vicinity of the tailings pond.

B) Artificial stream bed in close contact with the flotation ash dump in Trnové near Žilina. The brook line is the main migration path of leached arsenic from the landfill environment and ensures its contact with the final recipient of the Váh River. Stream sediment analysis can directly determine the potential migration and its intensity by the surface waters of the stream.

C) Detail of soil probe in landfill material of fly ash at the landfill in Trnové near Žilina. The soil probe shows the existence of a ferric horizon with the autogenous minerals FeOOH, which are good natural monitoring probes to identify the presence and migration of potentially toxic elements, e.g. such as As.

D) Efflorescence of chromium salts in the landfill of waste material after special metallurgical production in Istebné, Orava. The presence of chromium salts indicates an active reaction of the chromium-containing landfill material with the meteoric waters percolating through the landfill material. The reaction and migration of the metal is already identifiable during field inspections by means of strong colour contrast to the surrounding environment.

**INDUSTRIAL WASTE SLUDGE** is characterized by several principal properties.

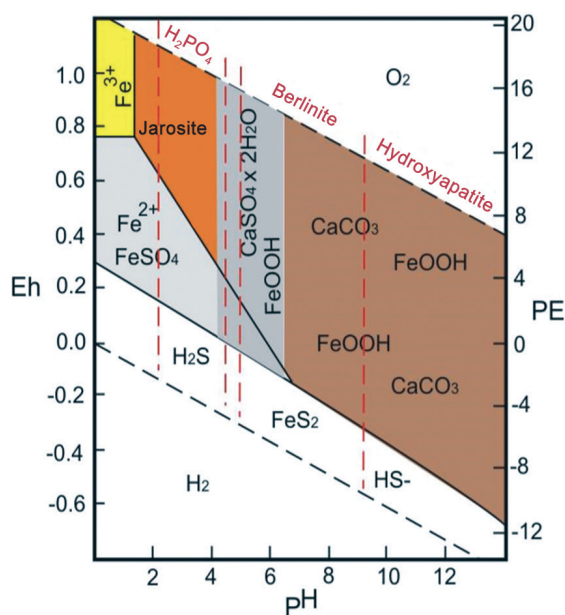
- The sludge material is very fine by granularity. It consists of mineral and amorphous phases, which reach often the size limits of microchemical EPMA measurement, namely fineness and lack of cohesiveness. In the case of a limiting size of suitable material for microchemical analysis, it is appropriate to use a wide diameter analytical electron beam. The results obtained will correspond to the mean volume analyses for the analysed space determined by the parameters of the analytical beam.
- The absence of sludge cohesiveness is due to the presence of porous water and the small size of the sludge particles. For the preparation of analytical specimens it is necessary to dry up the sludge material

and then cement it with epoxy resin. Impregnation with an epoxy resin results in the formation of a solid material suitable for the production of the analytical specimen (polished section), but on the other hand the impregnation itself may cause a fine resin overlap of the sample under study with a negative effect on the quantitative aspect of the analytical result.

- The sludge material itself is physically and chemically metastable, which is affected by H<sub>2</sub>O saturation controlling O<sub>2</sub> activity. Water level fluctuations in sludge ponds or marshes can change the Eh conditions and hence the sludge system stability. A similar process is encountered in the treatment of the sludge material sample, where increasing the drying temperature and subsequent



dehydration alter the physical character of the sample. However, the controlled treatment is naturally conservative against changes in the mass of the elements analysed.



An example of sludge material analysis is the EPMA microanalysis of the sludge waste from electrochemical production (galvanization) of the Šulekovo sludge pond near Hlohovec (Fig. 2.1-A and Fig. 2.2). Systematic EPMA analysis identified amorphous phosphates, gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{FeOOH}$  more closely identified by Raman spectroscopy as goethite in the samples (Demko, Luptáková & Šefčík, 2015). Significant contents with average  $\text{Pb}(0.76)\text{-Zn}(1.2)\text{-Cu}(0.7)$  wt% were identified in the mixture. The average goethite contents analysed reached  $\text{Pb}(0.4)\text{-Zn}(1.0)\text{-Cu}(0.2)$  wt%. Microchemical study, in addition to contamination composition and distribution, made it possible to reconstruct the phase system  $\text{Ca-Fe-SO}_4\text{-PO}_4\text{-CO}_3$ , which corresponds to the dynamic evolution from acidic oxidation conditions  $\text{Eh} > 0.4$  and  $\text{pH} < 4$  towards conditions  $\text{Eh} < 0.4$  and  $\text{pH} > 6.2$  (carbonate precipitation), Fig. 2.2. Reconstruction

Fig. 2.2 Reconstructed physicochemical Eh-pH conditions of the  $\text{Ca-Fe-SO}_4\text{-PO}_4\text{-CO}_3$  Fe-sludge phase system in the Šulekovo-Hlohovec tailings pond (Demko et al., 2016). EPMA identified Pb-Zn-Cu contamination is controlled by the stability of goethite  $\text{FeOOH}$  and amorphous phosphates.

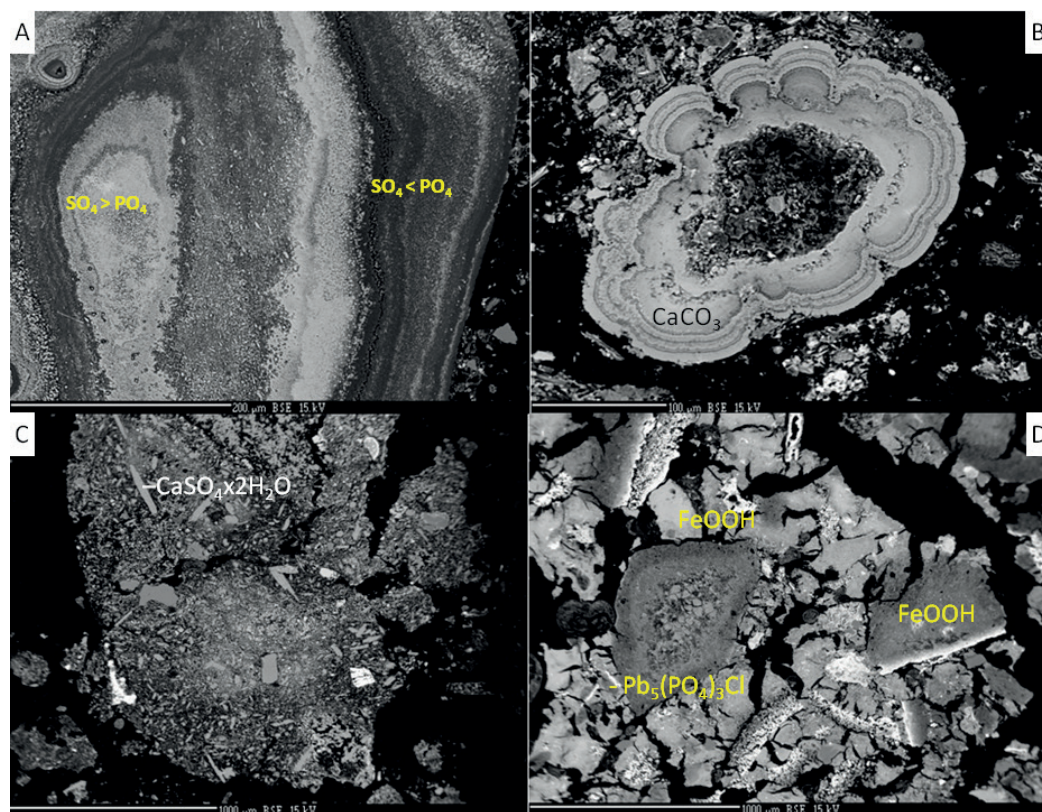


Fig. 2.3 BSE images of basic construction parts of sludge material from the sludge pond Šulekovo – Hlohovec (Demko et al., 2016). A) Oscillatory stratified concretion consisting of a mixture of amorphous phosphate ( $\text{P} = 13.14 - 11.02$  wt%) and sulphate ( $\text{S} = 0.7 - 0.4$  wt%). Light stripes are richer in sulphates. EPMA analysed Pb contents  $< 0.09$  wt%;  $\text{Cu} = 0.12 - 0.07$  wt%;  $\text{Zn} = 0.17 - 0.13$  wt%. B) Zonal geodes of autogenous  $\text{CaCO}_3$ , which are the product of the precipitation of carbonate from solutions percolating through the

drainage system of the sludge material.  $\text{CaCO}_3$  precipitation demonstrates the function of the dissolution – transport and  $\text{CaCO}_3$  precipitation in the respective Eh-pH physical conditions of Ca-carbonate stability. C) A mixture of detritic quartz sand and feldspars that are cemented with a sludge mixture containing autogenous  $\text{FeOOH}$  and sulphates. Thin needle-like crystals form gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  whose presence and morphology demonstrate physical Eh-pH conditions in the gypsum stability field. D) Goethite cementing mixture with  $\text{Pb}_3(\text{PO}_4)_3\text{Cl}$  phosphomimetite pale rims. EPMA contents analysed for Pb ( $0.54 - 0.09$ ), Cu ( $0.12 - 0.06$ ) and Zn ( $1.2 - 0.12$ ) wt% are representative Pb-Zn-Cu contents bound to the  $\text{FeOOH}$  phases. Phases of  $\text{FeOOH}$ , part of which is formed by goethite (identified by Raman spectroscopy), are the basic reservoir of Pb-Zn-Cu in sludge material in the tailings pond Šulekovo – Hlohovec. The identified fact shows that the stability of the source  $\text{FeOOH}$  is the basic factor determining the control of Pb-Zn-Cu migration in the tailings pond.



of natural physico-chemical conditions determines the simultaneous stabilization of sludge waste at the Šulekovo-Hlohovec tailings pond, which may be disrupted by external intervention into the system.

BSE images of the matrix parts of the sludge material from the Šulekovo – Hlohovec tailings pond are presented in Fig. 2.3 (Demko et al., 2016).

**METALLURGY WASTE MATERIAL** is surprisingly one of the most problematic wastes ever. Waste slag material is generally considered to be “clean” and “inert” and is therefore widely used as a “clean” and “inert” dump for roads or replacing building stone. It is likely and possible that most slag waste is “clean and inert”, but this assumption applies only to the ideal metallurgical treatment and high efficiency of metal extraction from the ore being processed. Systematic research of the slag material, which was legally exported as a heap material to the old tailings ponds sites, or just as a random part of landfills without identified origin, showed that metallurgical slag waste often reaches concentrations of Pb, Zn, Cu, Ni, Cr, Sb close to the those of deposits. In addition to the identified Cr-Fe or Ni-Fe alloys, the sulphides of Pb-Zn-Cu-As or

pure Sb, Cu, Sn are often identified. The slag material is loose-deposited in an environment where it interacts with meteoric waters. Hypergenic weathering of metastable synthetic material leads to the dissolution and release of potentially toxic elements into the natural ecosystem. The danger of metallurgical waste is compounded by the frequent presence of sulphides, which in the course of weathering produce  $\text{H}_2\text{SO}_4$ , which catalyses further dissolution. Under suitable conditions, an avalanche-like reaction can occur, which can result in extensive weathering and acidification of the environment. A few case-study examples are presented in Figs. 2.4-A, B, C, D.

**ORGANIC PLANT MATERIAL** is available in the natural environment virtually everywhere, where plants are available. Based on systematic EPMA research of soils, sludge material and stream sediments, in the scope of solving tasks related to organic monitoring, we developed an application based on EPMA analysis of decaying plant tissue. The plant tissues in soils or stream sediments are subject to natural decomposition. Decomposition of plant tissue leads to disruption of the plant's cell structure and degradation of highly organized carbon

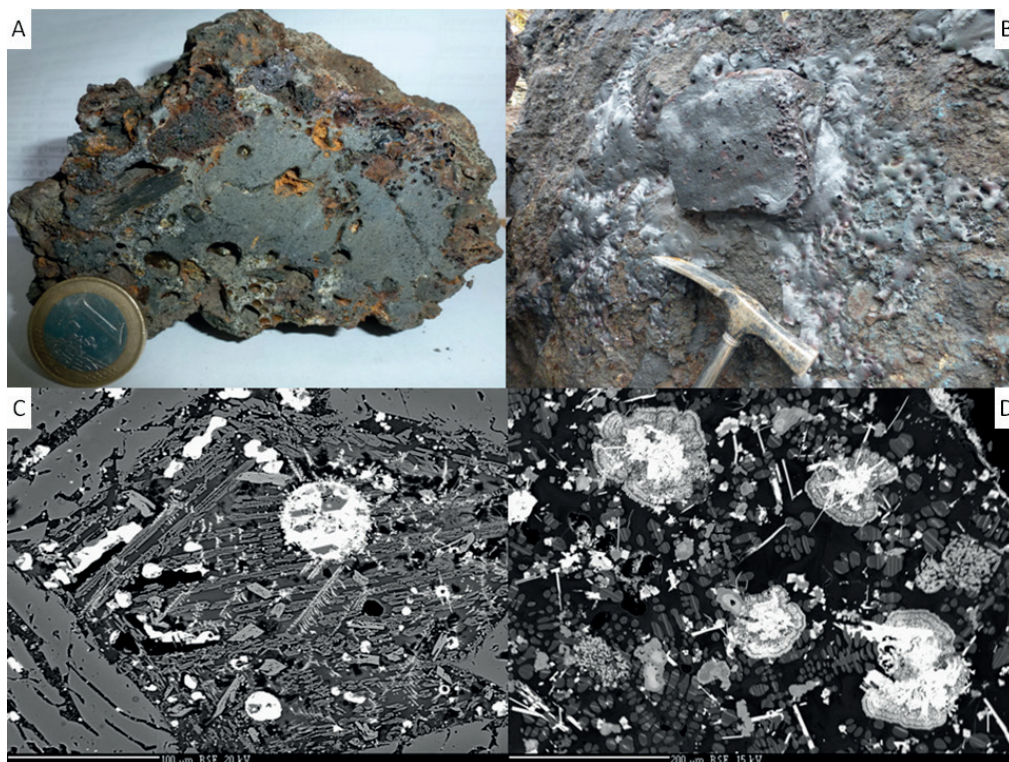


Fig. 2.4 Examples of investigated waste materials from metallurgy. A) Inside view of the split slag deposited in the Lintich tailings pond. Meteoric water, which infiltrated through the open pore space, caused the dissolution of Pb, Zn, Cu sulphides to form a solution of  $\text{H}_2\text{SO}_4$ , and consequently an overall alteration of the silicate slag. Decomposition of metastable silicate glass and sulphides releases Pb, Zn, Cu, As ions further into the environment (Demko et al., 2015). B) The metallurgical cast slag as a result of the sintering of molten waste material is a source of Cr, Ni, Pb, Zn, Cu, As, Sb

released from the waste in hypergenic weathering processes. Kovohuty – Krompachy. C) The BSE image of the metallurgical slag as a detail of the oxidized material in Fig. 2.4-A. The metallurgical slag contains skeletal crystals  $(\text{Zn-Fe-Mg})\text{SiO}_3$ , sulphosalts  $(\text{Pb-Zn-Cu-Fe})\text{S}$  (white) and silicate interstitial glass (dark grey). EPMA identified levels in sulphosalts reach values of Pb (67 – 0.17) wt% and Zn (55.4 – 0.6) wt%. Interstitial silicate glass achieves Pb (6.0 – 3.9) wt% and Zn (4.7 – 3.4) wt%. Pb + Zn interstitial glass as well as Pb-Zn-Fe sulphosalts are both markedly unstable phases under conditions of hypergenous weathering. Interaction with meteoric waters dissolves silicate glass and oxidizes sulphides with the concomitant production of an aggressive acidic solution capable of triggering the domino effect of altering and releasing Pb, Zn, Cu into the surrounding environment. D) Light crystals  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (chalcantite) with concentrically zonal rims as a product of dissolution of Pb-Zn-Cu sulphides in metallurgical slag in metal waste – Krompachy. The formation of secondary sulphates demonstrates the physico-chemical instability of metallurgical waste as a source of potentially toxic elements Cr, Ni, Pb, Zn, Cu, As, Sb (BSE image).



polymers containing naturally bound biogenic sulphur and phosphorus. The degradation of the organic system leads to an increase in active ion-exchange positions in the organic tissue. The release of phosphorus from the organic structure isolates the phosphate ions into separate amorphous phosphate aggregates. Degradation reactions of organic matter actively reduce the activity of  $O_2$  in the environment, thereby catalysing the precipitation of FeS and FeOOH compounds. The increase in active ion exchange centres produced by the mixture of phosphates and FeOOH phases results in the formation of a highly effective organic sorbent. Examples of analysed plant tissue at different stages of degradation are shown in Figs. 2.5-A, B, C, D.

Due to its high sorption capacity and sorption affinity for a wide range of elements, the decomposing material of plant tissues is a natural monitoring probe. A basic condition for the functioning of the plant tissue as a “monitoring probe” is a contact with a percolating aqueous solution which can serve as a transport medium. In the case of the presence of actively migrating elements in aqueous solution, sorption to the decaying organic material occurs. Positive identification directly indicates environ with

sorbed Pb, Zn, Cu, Cr, Ni, As, Sb as a migration path of contamination spreading or as an accumulation area.

The application of the EPMA analysis of plant tissues only works at the stage of tissue decomposition at a time when the primary structure of the tissue begins to lose its structure (Figs. 2.5-A, D). For freshly withered away plant tissues without signs of tissue morphology degradation, the analyses were not successful.

In case of negative identification of contamination on degraded plant tissue, the result is very successful as it shows that no water carrying contamination flows through the area with the analysed organic material. Decomposing plant tissues can be active in the natural environment as sorbent geochemical barriers for about 2 years. Negative analytical values may be interpreted in such a way that no contamination was present in the close vicinity, e.g. for 1 year back! The EPMA method for degraded plant tissues monitoring is very useful and very cheap compared to systematic sampling and water analysis. The absence of tissue contamination means no contamination, as opposed to zero analytical contamination values in waters, which can be interpreted as seasonal fluctuation in the style: “contamination leaked out yesterday”.

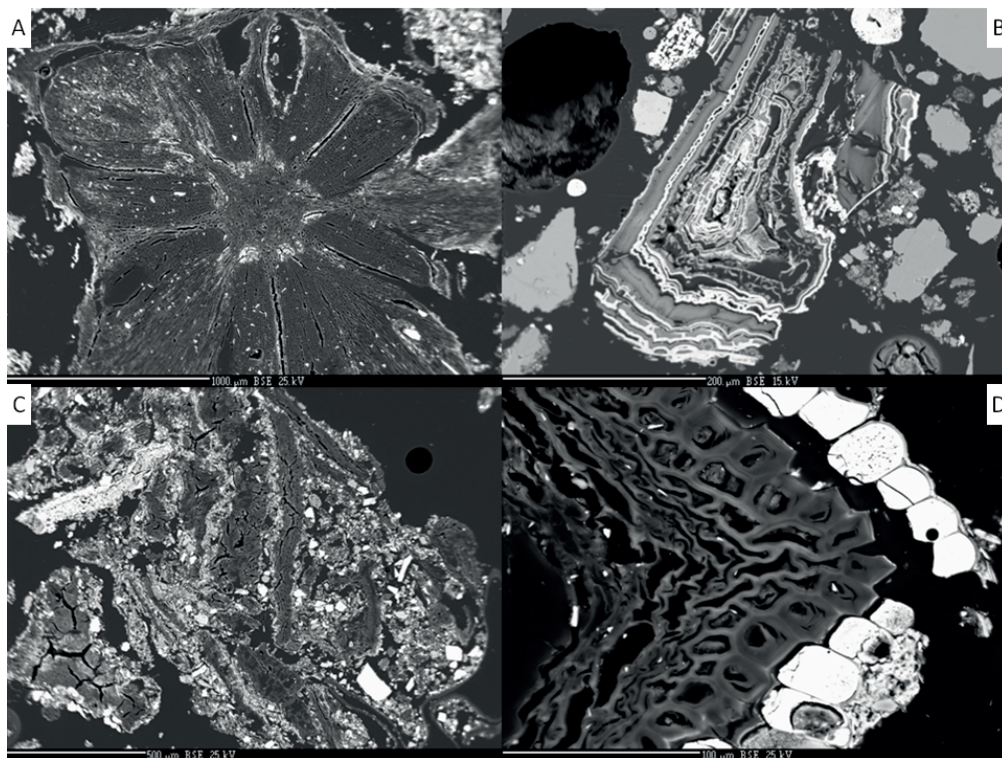


Fig. 2.5 Examples of analysed plant tissue at different stages of decomposition

A) Detail of flowering plant in middle stage of decomposition (decay). The surface of the plant tissue loses its morphology and the chemically identifiable organic material is transformed into complicated branched macromolecules with a large number of active ion centres suitable for bonding with the Pb, Zn, Cu, As, Co, Sb elements present in the environment. Originally organically bound sulphur and phosphorus form their own phases of the type  $-S-Fe-S-$ ,  $-(PO)_3-$ , which

contribute to the sorption potential of the decaying plant tissue (light streaks in the photograph). Location – Markušovský potok Brook, stream sediment, BSE image. B) Detail of decomposed plant tissue whose original structure is replicated by autogenously precipitated FeOOH or FeS (white bands). The organic material itself lost its original structure. Analysed contents of Cu (3.34 – 2.15), As (0.16 – 0.15), Sb (0.84 – 0.16) and Fe (43.1 – 14.6) wt%. Location Krompachy, BSE image. C) Rotten stems and tissues of decaying plants at an advanced stage of decay. The light flanges consist of the FeOOH and FeS phases, the precipitation of which was catalysed by the surface of the decaying plant tissue. Analytically identified contents of As (2.1 – 0.07), Cu (1.24 – 0.53), Sb (0.47 – 0.2), Fe (39.61 – 1.39) and S (3.0 – 0.23) wt% in organic material demonstrate effective sorption of migrating As, Cu, Sb on organic material and the role of decaying organic material as a temporary geochemical barrier. Location – Markušovce, BSE image (Demko & Šefčík, 2018). D) Detail of the plant tissue in the middle stage of decay, where the relict morphology of the cellular structure of the tissue structure still can be observed. The void cellular spaces at the edge of the decaying tissue (contact with the solutions) are filled with the autogenous phases FeOOH and FeS (white). The analysed contents are in the intervals of Fe (51.1 – 28.2), S (0.69 – 0.17), P (0.11 – 0.03), Co (0.05 – 0.04), As (0.66 – 0.44) and Sb (0.22 – 0.05) wt%. Location – Markušovce, BSE image.



## SANDS

As sands we understand a non-cohesive aggregate of rock and mineral detritus with a size corresponding to  $< 2$  mm. An important aspect is the absence of clay. Sand is a frequent natural sediment of stream sediments, or it can be produced as a product of geochemical heavy mineral prospecting with special targeted sediment sampling. Due to its non-cohesive and loose character, the EPMA analysis requires the preparation of a specimen that involves cementation with an epoxy resin. The chemical composition of the sand determines the modal representation of the detritic phases present. The EPMA analysis of sand is of fundamental importance when assessing the impact of mechanical migration of monitored elements or minerals when dealing with environmental geochemistry.

Despite the significant quantitative extent of mechanical transport and substance migration, systematic sampling of water for hydrochemical purposes is preferred in the EBs monitoring. It should be stressed that the absence of analysed elements in waters does not automatically mean a lack of element migration in the environment. The elements or their phases efficiently migrate also by mechanical transport and classical hydrochemistry is often blind to mechanical migration.

An example of the EPMA analysis for the needs of environmental burden survey is the analysis of wasted sand in the wider vicinity of a tailings pond in Markušovce, which is used for the storage of flotated waste after the treatment of sulphide ores. Images of the sand analysed are shown in Figs. 2.6-A, B, C, D. Qualitative and semi-quantitative composition of sand was evaluated by the EPMA analysis. The results showed that part of the stored flotation treated sand contained tetrahedrite, which served

as a source mineral for mercury extraction. The tetrahedrite is unstable as a sulphide under hypergenous conditions and is subject to oxidation and dissolution. It is a paradox that large volumes of flotation-treated sand are discarded outside the tailings pond (systematically monitored by hydrochemistry) and are ready for construction as an inert raw material.

Another example of the use of the presented EPMA qualitative analysis of sands is the identification of scattered baryte and siderite in agriculturally used soils in the vicinity of the Markušovce tailings pond. The presence of the identified baryte and siderite in the soil suggests aeolian transport of the flotation-stored material from the tailings pond to the surroundings by wind action. The flotated material is exposed at the tailings pond, thereby subjected to the direct wind erosion.

## FLY ASH

There are numerous ash dumps in Slovakia as a result of the massive use of fossil fuels in heating and power plants. Given the higher contents of sulphophilic elements in fossil fuels such as Pb, Zn, Cu, As, Cd, it is assumed that these increased concentrations are transformed into fly ash as residues.

In particular, carbon black and Si-Al glass beads, which are the product of melting the aluminosilicate minerals present in coal during high-temperature combustion, contribute to the ash composition (Figs. 2.7-A, B, C, D). The presence of sulphides, as primary minerals of fossil raw materials, is most unlikely because sulphides, like aluminosilicates, are incapable of existence during combustion. Systematic analysis of fly ashes from various fly ash dumps from Slovakia shows a negative answer:

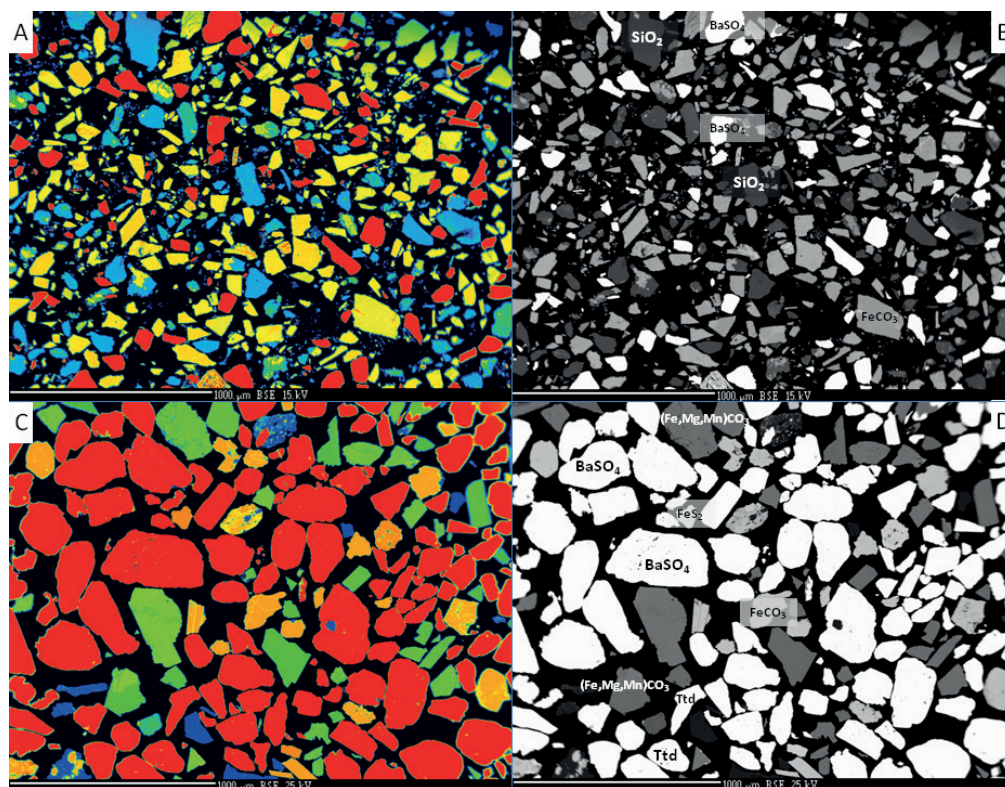


Fig. 2.6 BSE images of qualitatively analysed sand using EDXA analysis spectra interpretation (Demko & Šefčík, 2018). In the right part are the original BSE images and in the left part their artificially coloured equivalents.

A)  $\text{BaSO}_4$  – red,  $\text{SiO}_2$  quartz – light blue,  $\text{FeCO}_3$  siderite – yellow.  
B)  $\text{BaSO}_4$  + tetrahedrite ( $\text{Cu, Fe, Ag, Hg, Zn}$ ) ( $\text{Sb, As}$ ) $_4\text{S}_{13}$  – red,  $\text{FeCO}_3$  siderite – yellow,  $(\text{Fe, Mn})\text{CO}_3$  – green,  $\text{SiO}_2$  quartz – blue.



“In fly ashes the presence of presumed sulphophilic elements Pb, Zn, Cu, As, Cd is not identified by the EPMA analysis”. There are several explanations, and they are not mutually contradicting. The ashes analysed are pure to the extent that the detection limit of microanalysis permits. At the same time, the identified status indicates that the fly ash is pure and the contents of Pb, Zn, Cu, As, and Cd are lower than is expected intuitively from the fly ash. On the other hand, there is a natural technical explanation why the concentrations analysed are so low. This is a controlled migration of flue gases out of the combustion system in the form of smoke into the landscape around the boilers neighbourhood. There are results that systematically identify contamination with sulphophilic elements in the direction of the prevailing chimney flow. The effect of exhalants on the chemical composition of soils and plants is discussed in Hronec, 1996; Hronec et al., 1992; Čurlík & Šefčík, 1999. The above interpretation of the deficit of chalcophilic elements in fly ash after fossil fuel combustion is reliable, but it is no longer applicable to fly ash, which is a product of combustion using efficient filtering equipment after 1990 – 1995. In the flue gas escaping Pb, Zn, Cu, As, Cd are filtered and concentrated back to the fly ash in a concentrated form!

Another complication that affects the composition of the fly ash is the type of material to be burned, since oil has been added to the coal fuel. The black oil itself, as a heavy residual fraction of oil processing, is enriched with contaminants such as chalcophilic elements. The

ashes, which are a product of combustion of fuel enriched with black oil, should be enriched with chalcophilic contaminants.

Some metals such as Hg, Cd, Pb are principally concentrated into the fraction of airborne particles, while other non-volatile metals such as Fe, Cu, Cr and Ni are enriched in the heavy residual fly bottom ash fraction, which is typically present in high bulk spherical solids after melting aluminosilicates. The fractionation of elements such as As, Zn among the flying pollutants and the residual heavy fly ash fraction is intermediary. The results of Polc et al. (2016) show the preferential enrichment of Zn, Cu, Ba, Ni, Cr, As in the heavy residual ash fraction and the enrichment of Pb, Hg in the fly ash fraction as the product of “oily fuels” combustion. Examples of BSE images of the ashes are presented in Fig. 2.7.

**SOILS** are the product of the weathering of the rock substrate of the uppermost part of the continental crust in interaction with the hydrosphere, atmosphere and biosphere. The importance of soil's role in human nutrition and the existence of life itself is beyond question. Soils or pedosphere can be understood as a space where many processes of physico-chemical and biological nature take place. All processes taking place in soils have principally control over the distribution and mobility of the substance, including contamination by potentially toxic elements and their compounds.

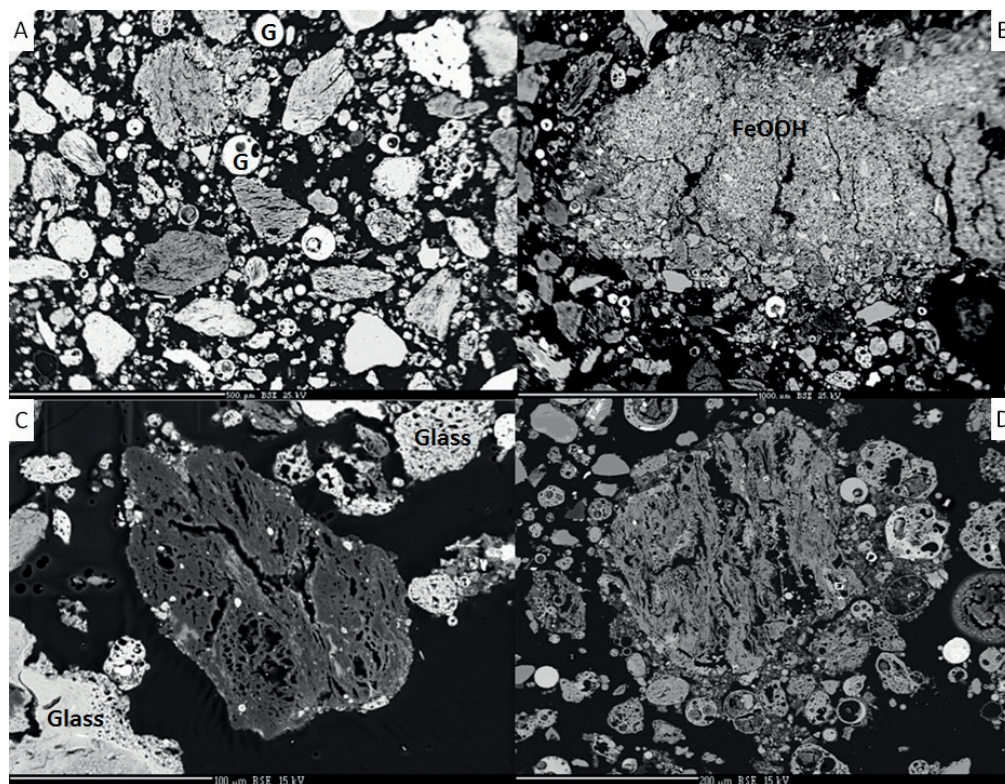


Fig. 2.7 Examples of BSE images of ashes.

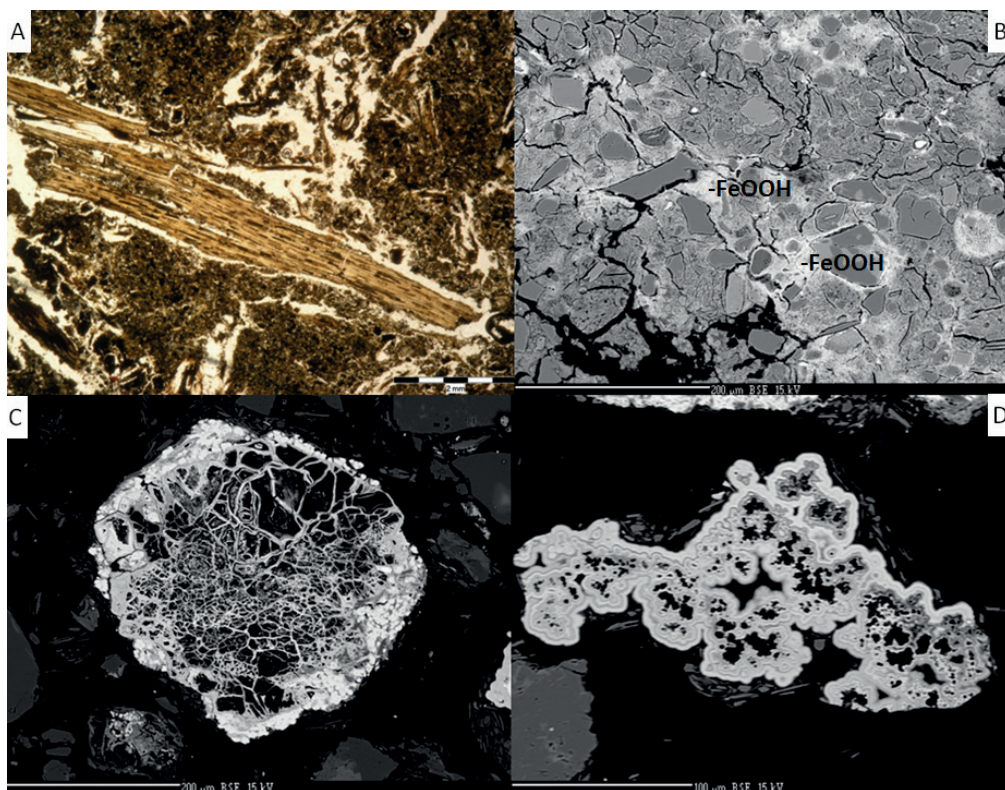
A) Fly ash composition view, BSE image. The spherical formations of silicate glass are mixed with the carbon blacks that form a porous organic carbon. Silicate glass spherical bodies are the product of aluminosilicate minerals melting in the original coal. B) A porous aggregate of autogenous FeOOH, which was formed by the dissolution and precipitation of migrating iron in a floated fly ash dump in Trnové, near Žilina. Autogenous FeOOH serves as an effective geochemical barrier in the environment of active migration of As, Pb, Zn,

Cu, Co, Sb. The analysed Fe contents are in the range (67.5 – 61.8) wt%. The identified As (0.15 – 0.09) wt% contents in porous FeOOH aggregates demonstrate the presence of arsenic in the environment of floated waste and its secondary remobilized binding to FeOOH (BSE image). C) Detail of carbon black particles (graphite) between porous silicate glass bodies. Analysed contents of As + Pb + Cu + Zn + Cr + Ni < DT limit (BSE image). D) Detail of the soot particle surrounded by porous silicate glass beads of spherical morphology. Analysed contents of Cr + Ni + Zn < DT limit (BSE image).



Fig. 2.8 Application of EPMA analysis for soils.

A) The fragments of stalks and plant tissue in the sample of fluvisol from the Markušovský potok Brook. The presence of organic material in soils increases the sorption potential of the soil as an effective geochemical barrier in the landscape. Photo from a polarizing microscope. B) BSE image of soil containing detritic quartz, plagioclase and K-feldspar. The light zones in the white fraction represent the autogenous FeOOH phases with a high sorption potential for retarding and accumulating actively migrating metals in the environment. Analysed contents



of Pb + Cu + Zn + Co + Cd + As + Ni + Cr < DT limit indicate the absence of accumulation of potentially toxic elements in the soil sample, as the FeOOH phases are effective sorbents and function as natural monitoring probes to assess active migration. Location Detva. C) Aggregate of autogenous FeOOH in the soil sample from Lubietová. The FeOOH aggregate was formed by the precipitation of migrating iron from percolating solutions by the catalytic effect of the surface of the decaying plant root system. Analysed contents: Fe (53.12 – 31.8), S (11.99 – 0.25), As (3.63 – 0.76), Sb (4.6 – 0.18) and Cu (2.25 – 0.23) wt%. D) Zonal geode (nodule) of autogenous FeOOH in the soil sample from Lubietová. Analyzed contents: Fe (49.58 – 48.02), S (1.87 – 1.8), As (0.76 – 0.64), Cu (0.32 – 0.21) wt%. BSE image.

Application of the EPMA analysis for soils results from soil composition: humus / organic substances, clay minerals, weathering rock substrate detritus, autogenous compounds (Mn,Fe)OOH, Figs. 2.8-A, B, C, D. An important role in dealing with migration and accumulation of elements in the soil complex is played by the analysis of organic material, especially the decaying residues of plant tissue. Another very successful objects for the identification of accumulation and migration flows are oxides and hydroxides of manganese and iron. All forms of (Mn,Fe)OOH are very potent and effective sorbents of the actively migrating elements Pb, Zn, Cu, Cr, Ni, As, Cd, Sb, Hg and can be successfully used as natural monitoring probes. For the EPMA analysis it is necessary to use cementation of the preparations with epoxy resins due to the non-cohesive decaying character of soil samples.

The use of the EPMA analysis of autogenous phases (Mn,Fe)OOH as natural monitoring probes is based on a simple logic. In the presence of free or actively migrating elements Pb, Zn, Cu, Cr, Ni, As, Cd, Sb, Hg, these elements are trapped on an effective sorption geochemical (Mn,Fe)OOH barrier. The identification of these elements by the EPMA analysis then shows that the area from which the (Mn,Fe)OOH sample was positively analysed is part of the migration contamination route or even belongs to the accumulation area. In the case of a negative result, we gain an important finding that during the existence of

the analysed (Mn,Fe)OOH phase through the investigated soil complex there was no contamination! The EPMA-analyses are more effective in dealing with the migration of potentially toxic elements than overall soil analyses alone, as overall soil analyses provide an analytical result including non-mobile forms of the elements under investigation. The currently applied standards for permissible and limit concentrations of Pb, Zn, Cu, Cr, Ni, As, Cd, Sb, Hg in soils deal with passive understanding of element distribution in soils (Act No. 220/2004).

The application of the EPMA analysis for soils in Fig. 2.8.

**STREAM SEDIMENTS** are the deposits that are formed during sedimentation in watercourse troughs in places with decreasing entrainment energy of the stream. Dynamic development of the watercourse depends on the total flow (precipitation) or local configuration of the river bank morphology and the placement of mechanical barriers continuously modeling the river flow. Due to the dynamics of the water system, it is possible to differentiate between sedimentary phenomena that develop in a higher current regime and those characterized by calm sedimentation behind mechanical obstacles or in the low-energy environment of passive edges of banks. The facies of the sediments in the high-energy flow regime are coarser-grained and practically free of fine silt and



clay fractions of sediment. Sediments formed in a quiet low-energy environment are finer-grained with a modal increase in silt and clay fractions.

The dynamics of stream sediment formation itself determines the potential of stream sediments as a tool for the investigation and monitoring of the spread of contamination in the aquatic environment. The coarse-grained sediments of the gravel to sand fraction are only useful for the identification of the mechanical form of migration. In addition to identifying mechanical migration of contamination, fine-grained sediments can also be used to assess the active transport of elements by an aqueous solution. It is important that the physical and chemical conditions allow precipitation of autogenous minerals such as  $(\text{Mn,Fe})\text{OOH}$  or longer accumulation and decomposition of organic matter in the sediment. For fine-grained stream sediments the same possibilities of using the EPMA analysis apply to soils and sands.

Given the time and energy dynamic development of stream sediments, complications resulting from re-sedimentation of sediments must be taken into account.

The application of the EPMA analysis for stream sediments is in Fig. 2.9.

## 2.4. Conclusion

The application of the EPMA analysis in environmental geochemistry is widespread, but with a predominant

focus on microchemical analysis as a complement to experimental research, e.g. Hiller et al. (2013; 2016), or as a solution to the stability of phases and their reactions under conditions of hypergenic weathering, e.g. Andráš et al. (2015), Radková et al. (2017), Majzlan et al. (2018).

The direct use of the EPMA analysis for the purposes of the environmental burdens monitoring stems from the fact that without knowledge of the primary distribution of potentially toxic elements in/around the source area, it is practically impossible to logically address the causes of the chemical elements migration in the landscape and to prognosticate the environmental emergencies.

The EPMA analysis provides the possibility of microchemical study of the elements to address the actual distribution of the elements among the phases or as the stability of the source phases under conditions of the hypergenic system, e.g. Fe-sludge at the tailings pond Šulekovo-Hlohovec, Fig. 2.3. The EPMA analysis is a direct tool for microchemistry of natural systems that cannot be replaced by whole-rock geochemistry of macro-samples. If a combination of classical geochemical analysis of rocks, soil, dust, ashes or stream sediments with microchemistry is possible, it is possible to reconstruct the geochemical dynamics of the system, such as in the case of various forms of As-Co and Hg-Sb-Cu migration (Fig. 2.10). Targeted application of a microchemical EPMA study for phase analysis such as  $(\text{Mn,Fe})\text{OH}$  or decaying

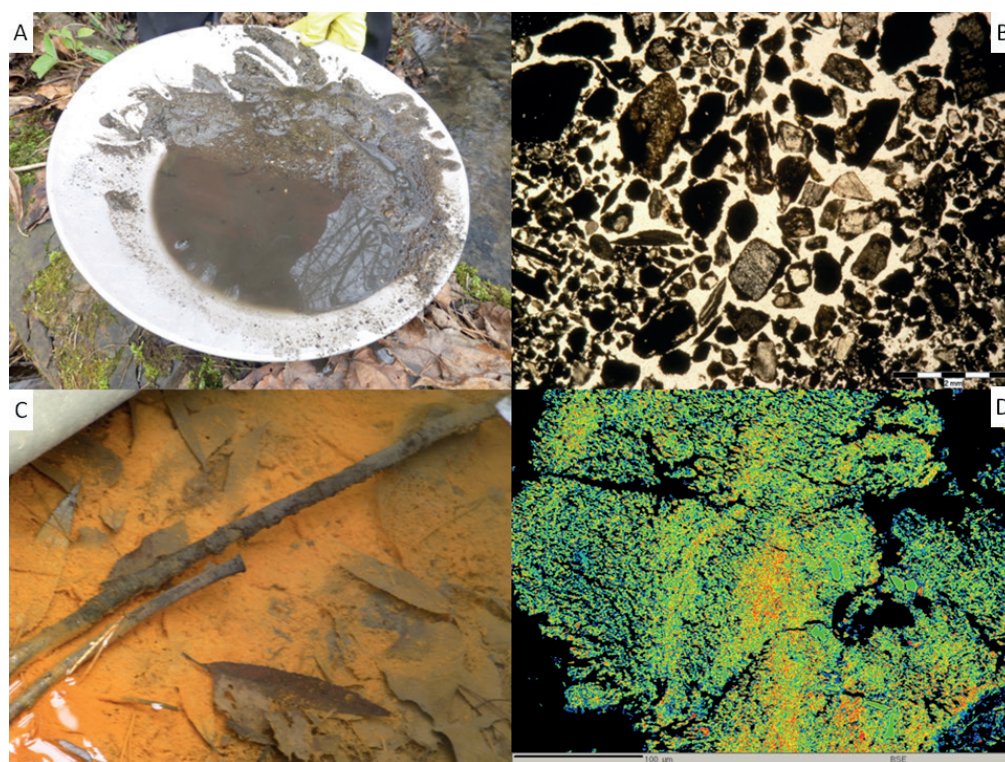


Fig. 2.9 Examples of application of microchemical survey for stream sediments.

A) A pan serving as sampling tool for heavy fraction of stream sediments. B) A view of the heavy fraction sized in the Markušovský potok Brook below the dam of a large tailings pond. The presence of baryte, siderite, and quartz residue after the dissolution of sulphide ore in the stream sediments indicates a compromised sealing function of the Markušovce sludge dam and passive “mechanical” migration of waste material in the surface stream below the tailings pond! C) Coagulation of iron in standing

marginal waters below the tailings pond in Markušovce. The resulting -Fe phases are an effective natural sorbent of actively migrating elements in the environment. Autogenous precipitates -Fe are natural monitoring probes to identify the migration of potentially toxic elements into the environment. D) Artificially stained BSE image of dendritic fractal texture of the  $\text{SiFeOOH}$  autogenous phase in a stream sediment sample. The high degree of branching determines the large active surface area of the strong sorbent with higher sorption efficiency. Analytically identified presence of Co 0.09 – 0.07% wt% and As 0.2 – 0.08 wt% demonstrates the function of active migration of Co + As in surface waters from the area of the Markušovce tailings pond (Demko & Šefčík, 2018).



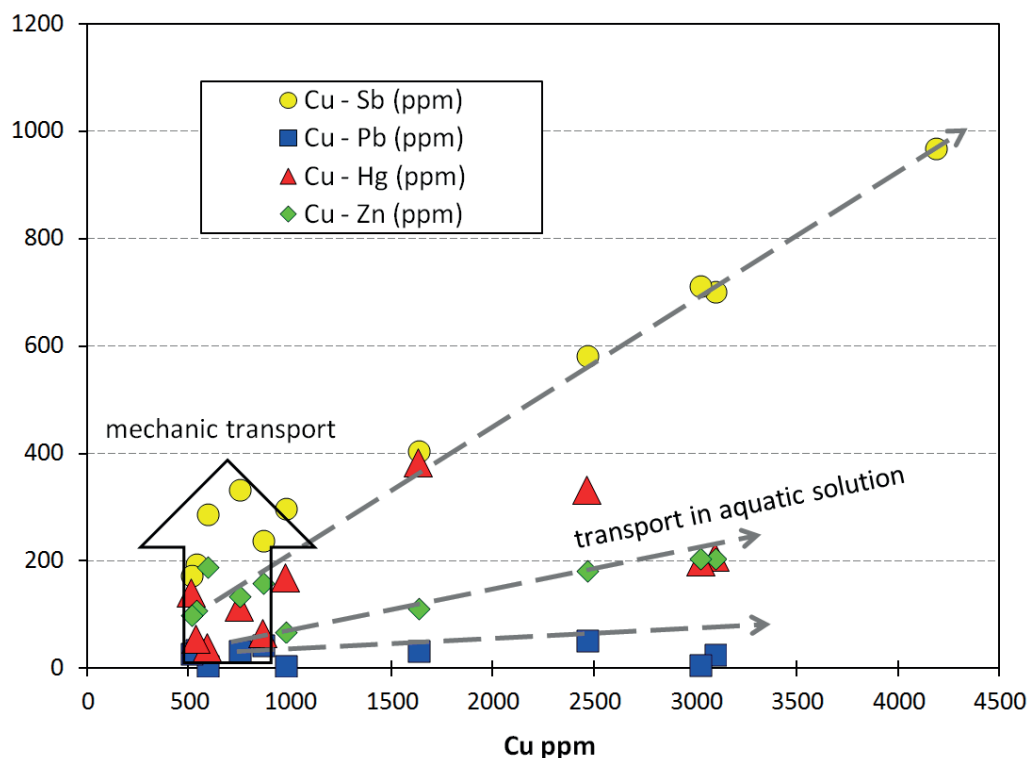


Fig. 2.10 Geochemical fractionation of Cu – Sb – Pb – Hg – Zn in samples of stream sediments of Markušovský potok Brook. Based on the application of EPMA microanalysis, which identified separate mechanical migration (transport of detritus) and independent active migration of Cu, Sb, Pb, Hg, Zn (sorption on plant tissues), it is possible to interpret movement and fractionation of contamination from tailings pond in Markušovce (Demko & Šefčík, 2018).

plant tissues uses the analysed objects as natural monitoring probes for their natural high sorption capacity. In the case of a positive microchemical identification of the elements of interest, it can be concluded that the analysed area is part of the source area or the pollutants migration route. In the case of a negative identification of the elements of interest by microchemical study of a natural monitoring probe, it is possible to draw an important conclusion that the studied area is not a source area or a migration route of the analysed pollutants. The advantage of application of the EPMA analysis is lower economic demands in comparison with classical hydrochemical monitoring. The cost of building a hydrogeological well is much higher than the production of an analytical preparation and EPMA analysis. A non-negligible factor in the use of natural materials as monitoring probes is that natural materials have been in direct long-term contact with water (transport medium), i.e. the analysed signal can be interpreted into the past of the existence of a natural probe. The analytical hydrochemical signal corresponds practically to the moment of sampling and is influenced by external climatic factors.

The presented overview of possible applications of the EPMA analysis as a research and monitoring method is not understood dogmatically as a solution for everything, but seeks to provide an idea and broader possibilities in the framework of the geochemical environmental research. It deserves special attention in the reconstruction of geochemical processes taking place on macrochemical and microchemical scales.

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### 3. Thematic Geological Information System for Environmental Burdens Monitoring

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**Abstract:** Specific geological information system for monitoring of environmental burdens (IS EBM) is a basic data platform for monitoring of environmental burdens carried out at SGIDŠ since 2012. The main objectives of the monitoring are to observe the release of pollutants into the environment and to assess trends in the development of contamination. IS EBM is basically divided into two parts: 1) text and general data part used for storing information of various formats, especially for storing various text and graphic files in the directories structure; 2) database and GIS part for managing database and GIS formats in a well-defined structured online form. The development of IS EBM has been necessary for solving tasks requiring effective and fast cooperation of a great number of employees involved in the monitoring process and at the same time when working with a large amount of various data. IS EBM is not publicly available and is part of the SGIDŠ internal network.

**Key words:** environmental burdens, geological information system, monitoring, database

#### 3.1 Introduction

The basic and official data platform ensuring the collection of data and the provision of general information on environmental burdens is the Information System of Environmental Burdens (abbreviated as IS EB, [www.enviportal.sk](http://www.enviportal.sk)) managed by the Slovak Environmental Agency (SEA) authorised by the Ministry of Environment of the Slovak Republic. The basis for its creation was the geological task “Systematic identification of environmental burdens of the Slovak Republic” carried out in 2006 – 2008 (Paluchová et al., 2008) and “Completion of the information system of environmental burdens” (Pacola, 2015).

Since 2012, the State Geological Institute of Dionýz Štúr has been gradually implementing tasks related to monitoring of 309 environmental burdens across Slovakia. The aim of the work is to monitor potential pollution/real pollution of the environment (mainly groundwater and surface waters) and assess trends of contamination development. The purpose of creating a thematic information system for environmental burdens monitoring (IS EBM) at SGIDŠ was to solve tasks requiring effective and fast cooperation of employees participating in the monitoring process, as well as processing a large amount of data of various types and quality. The primary basis for the creation of the IS EBM was the geological task “Monitoring of environmental burdens at selected localities in Slovakia”, which was carried out in 2012 –

2015 (Kordík & Slaninka et al., 2015). IS EBM is part of the SGIDŠ intranet and it is not publicly accessible.

The use of information technology in the field of research, monitoring and remediation of contaminated sites (environmental burdens) has been dealt with by many authors and institutions around the world (e.g. Tkacs, 1994; Krieger, 1995; Mattikall, 1994; Hiscock et al., 1995; Wilkinson, 1996; Chen et al., 2002). The paper discusses the thematic IS EBM developed at SGIDŠ. The purpose of the thematic information system is to provide information in such a way that it is accessible and easy to use by the team and that the results of the monitoring of environmental burdens are also usable for the needs to address the EBs in general.

#### 3.2 Information system for environmental burdens monitoring

As part of the planning and implementation of the environmental burdens monitoring, data and information from various types of geological work (geology, hydrogeology, geophysics, geochemistry, engineering geology, remote sensing, modeling, etc.) are developed, collected and analysed. Therefore, there has arisen a need in practice for a flexible and efficient evaluation of monitoring data, both temporally and spatially. The best solution was to create a dedicated information system for monitoring environmental burdens. The IS EBM is basically divided into two parts – 1) texts and general data, and 2) structured database and GIS. The text and data part of the system serves for storing general information of various formats obtained in the scope of the solution of the geological task, especially for storing various text and graphics files in the directory structure. The database and GIS part of the information system is used to manage database and GIS formats in a precisely defined structured form. In general, GIS in conjunction with the database tools is a highly effective means of solving a wide range of problems in any discipline (Demers, 1999).

##### 3.2.1 IS EBM – general data and text documents

The general data and text part of the IS EBM is used for central storage and archiving of various (final and temporary) documents/files. Access to this part of the information system is possible via FTP (File Transfer Protocol) connection. Access rights are defined at the

directory level, access is protected by a system that only allows users with appropriate access. Information stored in the general data and text part of the information system can be divided into main groups (directories), which are briefly commented below. The main directories are further subdivided as needed. Different access and editing rights are defined for directories and subdirectories according to the type of data and user needs.

The “*Sites*” directory contains essential files (information) that can be associated with a specific site. Subdirectory names are compiled by site names. For the sake of clarity, a subdirectory structure is proposed for each site to further unify storing the same types of information. For example, a separate location has storage of map layers, text files, primary geological documentation (sampling

protocols, audit records of monitoring objects, photo documentation, etc.), annual reports, and others. Such a structure serves for efficient orientation in the amount of stored data and at the same time it is easy to use.

The “*General*” directory serves as a repository of files/information that are not site-specific but important for the operation of EBM projects. The subdirectory structure is relatively flexible and depends on the type of information stored. The examples are, for instance, data files such as various information layers (mining works, geological map, hydrogeological zones, protected areas, buffer zones, groundwater bodies, etc.), legislation, archival reports, sample documents, and others.

The examples of photo documentation, or graphical, data and text information stored in the general data and

|                                                                                   |                                                               |                                          |                                                   |
|-----------------------------------------------------------------------------------|---------------------------------------------------------------|------------------------------------------|---------------------------------------------------|
|  | <b>ŠGÚDŠ</b><br>Geoanalytické laboratóriá<br>Spišská Nová Ves | <b>PROTOKOL O ODBERE<br/>VZORKY VODY</b> | č. dokumentu: 320.25.7.4                          |
|                                                                                   |                                                               |                                          | dátum vydania: 9/2005<br>dátum revízie: 16.3.2017 |

#### Plán odberu

|                                                                                              |                                                                                    |             |                    |            |
|----------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------|--------------------|------------|
| objednávateľ: ŠGÚDŠ Bratislava                                                               |                                                                                    |             |                    |            |
| názov úlohy: Zabezpečenie monitorovania environmentálnych záťaží Slovenska - 1. časť (ZMEZ1) |                                                                                    |             | číslo úlohy: 13 16 |            |
| názov lokality:<br>Pukanec - skládka kalov Hampoch                                           | zdroj: PV254-2                                                                     | č. lokality | označenie vzorky   | por. číslo |
|                                                                                              | <input type="checkbox"/> vzorka zlievaná<br><input type="checkbox"/> vzorka bodová | 254         |                    |            |
| koordinátor lokality:<br>Jozef Kordík                                                        | pôvodné označenie zdroja: —                                                        |             |                    |            |
| požadovaný druh rozboru: 17-BTEX; 18-PrChlArom; 19-PrChlAlif                                 |                                                                                    |             |                    |            |
| plánovaný dátum odberu [rrrr-mm-dd]: 2019-03-25                                              |                                                                                    |             |                    |            |
| postup odberu: IP 18.4 Odbery všetkých typov vôd                                             |                                                                                    |             |                    |            |

#### Odber vzorky

|                                            |                                                        |                |
|--------------------------------------------|--------------------------------------------------------|----------------|
| <b>dátum odberu:</b><br><b>hodina:</b>     | <b>dátum dodania do laboratória:</b><br><b>hodina:</b> |                |
| <b>vzorku odobral:</b><br>Kordík, Jankulár | <b>odovzdal:</b>                                       | <b>podpis:</b> |
|                                            | <b>prevzal:</b>                                        | <b>podpis:</b> |

#### Údaje zistené pri odbere

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                              |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| <b>teplota vody</b> [°C]:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | <b>teplota vzduchu</b> [°C]: |
| <b>pH:</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | <b>konduktivita</b> [mS/m]:  |
| <b>vzhľad vzorky:</b><br><b>zákal:</b> 0-bez, 1-nepatrný, 2-slabý, 3-viditeľný, 4-výrazný<br><b>farba:</b> 0-bez, 1-nažltlá, 2-hnedastá, 3-zelenkastá, 4-opalizujúca, 5-belavá, 6-sivastá, 7-hrdzavohnedá<br><b>sediment:</b> 0-bez, 1-nepatrný, 2-slabý, 3-mierny, 4-značný<br><b>pach (stupeň):</b> 0-bez, 1-nepatrný, 2-slabý, 3-znatelný, 4-výrazný<br><b>pach (druh):</b> 0-žiadny, 1-zemitý, 2-hnilobný, 3-chlórový, 4-plesňový, 5-zatuchlý, 6-organický, 7-po H <sub>2</sub> S, 8-po amoniaku, 9-TKO, 10-ropný, 11-dechtový, 12-chemický, 13-železitý |                              |
| <b>iné údaje:</b> O <sub>2</sub> [mg/l]:      O <sub>2</sub> [%]:      ORP (SenTix 900) [mV]:                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                              |

#### Vzorka konzervovaná v teréne: (nehodiace sa škrtnite)

| konzer.<br>číslo  | HNO <sub>3</sub> | H <sub>2</sub> SO <sub>4</sub> | NaOH   | HNO <sub>3</sub> +K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | CaCO <sub>3</sub>               | octan zinočnatý +<br>octan sodný   | octan sodný +<br>kyselina octová |
|-------------------|------------------|--------------------------------|--------|-----------------------------------------------------------------|---------------------------------|------------------------------------|----------------------------------|
| <b>stanovenie</b> | stopové prvky    | CHSK <sub>sn</sub>             | CN,FNI | Hg                                                              | agr.CO <sub>2</sub><br>p.Heyera | H <sub>2</sub> S + S <sup>2-</sup> | Fe <sup>2+</sup>                 |

#### Poznámka

|  |
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|  |
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|                                  |                       |
|----------------------------------|-----------------------|
| <b>laboratórne číslo vzorky:</b> | <b>číslo zákazky:</b> |
|----------------------------------|-----------------------|

Fig. 3.1 Water Sampling Protocol automatically generated directly from the IS EBM system. \*Note: As the IS is developed only in Slovak, the protocol is presented in its output form.



|                                                                                                                                                                                               |                                                    |                                                |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|------------------------------------------------|
| <b>Lokalita</b> (MEZ č. a názov): 90 Banská Štiavnica – odkalisko Lintich,                                                                                                                    |                                                    | <b>Koordinátor:</b> Kordík                     |
| <b>Vrt VN90-1</b>                                                                                                                                                                             |                                                    |                                                |
| <b>Dátum merania:</b>                                                                                                                                                                         | <b>Meranie vykonal:</b> Kordík – Jankulár          | <b>Fotodokumentácia:</b> áno / nie             |
| <b>Kontrola nadzemnej časti vrtu (nepoškodené – poškodené/opis):</b><br>(kovová chránička - uzáver, poklop chráničky - výtyčka s označením - zámok)<br>.....                                  |                                                    |                                                |
| <b>Meranie hĺbky vrtu - Odberný bod (o.b.)= vrchný okraj kovovej chráničky vrtu</b>                                                                                                           |                                                    |                                                |
| Hĺbka vrtu (m od o.b.) =                                                                                                                                                                      | pôvodná: ..... -                                   | aktuálna: .....                                |
| Kontrola priechodnosti vrtu:                                                                                                                                                                  | Výška vodného stĺpca:                              | Stav zanesenia vrtu:                           |
| <b>TERÉNNE MERANIA</b>                                                                                                                                                                        |                                                    |                                                |
| <b>HPV</b> (m od o.b.):                                                                                                                                                                       | Spôsob merania / odberu vzorky: odberák - čerpadlo |                                                |
| <b>pH</b> = .....                                                                                                                                                                             | <b>EC</b> = .....                                  | <b>T vody</b> = ..... <b>T vzduchu</b> = ..... |
| <b>O<sub>2</sub></b> (mg/l) = .....                                                                                                                                                           | <b>O<sub>2</sub> nasýtenie (%)</b> = .....         |                                                |
| <b>SENZORICKÉ VLASTNOSTI:</b>                                                                                                                                                                 |                                                    |                                                |
| <b>Ropné látky</b> = áno / nie, <b>Zákal</b> = 0-bez, 1-nepatrný, 2-slabý, 3-viditeľný, 4-výrazný                                                                                             |                                                    |                                                |
| <b>Farba</b> = 0-bez, 1-nažltlá, 2-hnedastá, 3-zelenkastá, 4- opalizujúca, 5-belavá, 6-sivastá, 7-hrdzavohnedá                                                                                |                                                    |                                                |
| <b>Sediment</b> = 0-bez, 1-nepatrný, 2-slabý, 3-mierny, 4-značný                                                                                                                              |                                                    |                                                |
| <b>Pach-stupeň</b> = 0-bez, 1-nepatrný, 2-slabý, 3-značný, 4-výrazný                                                                                                                          |                                                    |                                                |
| <b>Pach-druh</b> = 0-žiadny, 1-zemitý, 2-hnilobný, 3-chlórový, 4-plesňový, 5-zatuchlý, 6-organický,<br>7-po sírovodíku, 8-po amoniaku, 9-TKO, 10-ropný, 11-dechtový, 12-chemický, 13-železitý |                                                    |                                                |

Fig. 3.2 Monitoring Object (well) Revision Record form. \*Note: As the IS is developed only in Slovak, the protocol is presented in its output form.



Fig. 3.3 Field measurements (pH, conductivity, temperature, etc.) of surface water properties – (locality Istebné, slug heap)

text part of the IS EBM are shown in Figs. 3.1 to 3.4 (Water Sampling Protocol, Monitoring Object Review Record, Photo Documentation of Surface Sampling, Photo Documentation of Field Measurements).

### 3.2.2 IS EBM – structured database and GIS

Structured database of environmental burdens monitoring is built centrally on the SGIDŠ database server in Bratislava. The technical platform of the database is the object-relational database system PostgreSQL/PostGIS.

Access to the database is possible from different user interfaces, e.g. via web application, ODBC driver (e.g. from MS Access, MS Excel and MapInfo Professional), QGIS or pgAdmin. This flexibility of access and use is very important because of the wide diversity of users' needs of IS EB, while technical skills, conditions of use and users' demands are often significantly different.

### Internet interface and access to the database part of the IS EBM

The web application was created in the open-source PHP scripting language in combination with HTML, JavaScript and CSS. The application runs on the Apache web server (Linux) and is accessible online at the appropriate Internet address (Fig.

3.5). Internet communication between the browser and the server is encrypted using HTTPS, which enables secure communication between the client and the web server. Access to the application is protected by security features. For security reasons, the level of user access to information also varies depending on user rights. The database system in the web interface is divided according to the type of data into **general information** (e.g. list of monitored sites and objects, information about wells, information sources), **field characteristics** of monitored media (water, sediments, soils, rocks, soils), monitoring





Fig. 3.4 Photo documentation of field measurement and groundwater sampling from well in the shaft (locality Bratislava – Vrakuňa)

deleting, searching, and exporting records. In addition, it is possible to select individual records according to user requirements. Web interfaces for individual data areas have various functionalities that help with data processing. One of the most frequently used data areas are, for example, the results of chemical and isotopic analyses of water. In the web interface of this data area one can use specially created functions, e.g. function enabling automatic evaluation of analysed results of chemical composition of water compared to selected limit values (e.g. limit values of the Directive of the Ministry of Environment of the Slovak Republic No. 1 / 2015-7 on the analysis of risk analysis of contaminated area) highlighted

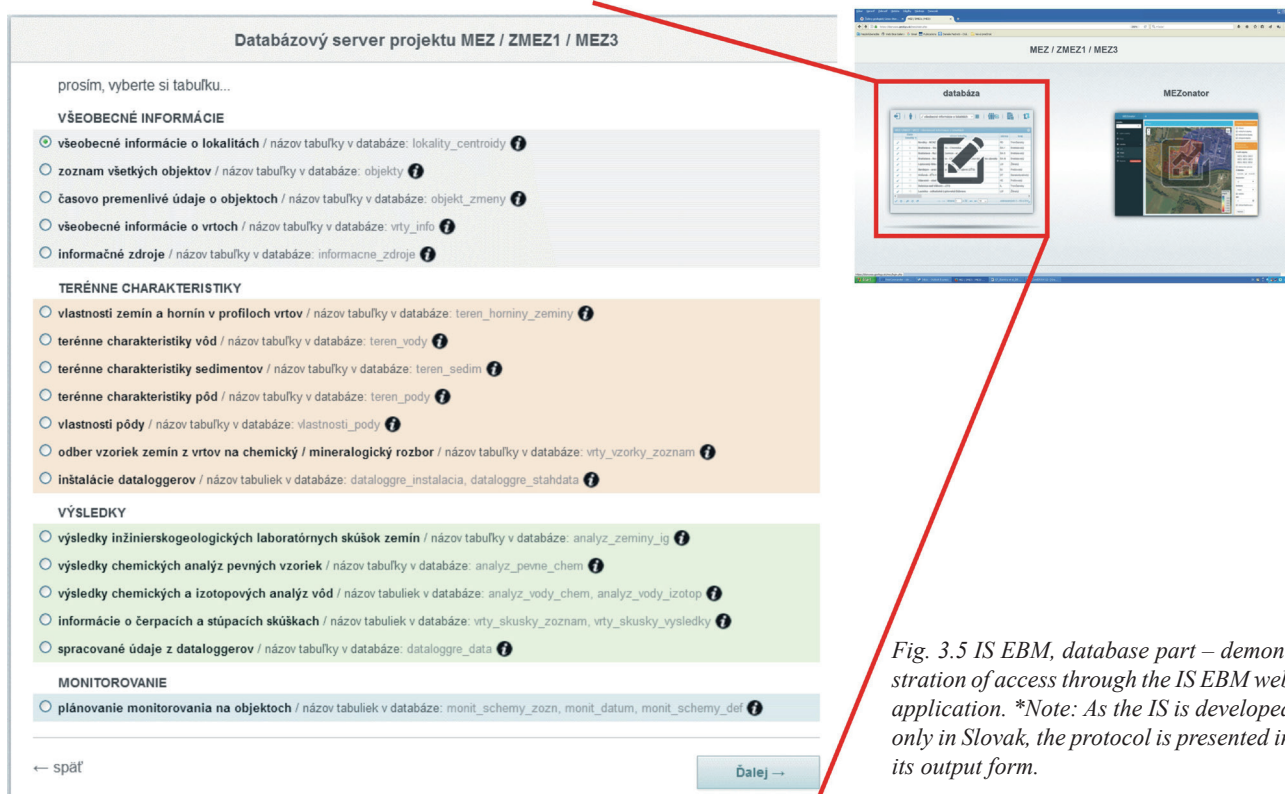


Fig. 3.5 IS EBM, database part – demonstration of access through the IS EBM web application. \*Note: As the IS is developed only in Slovak, the protocol is presented in its output form.

**results**, especially analytical (engineering-geological and laboratory soil tests, chemical analyses of water and solid samples, isotope analyses, pumping test results, data logger records) and **monitoring** (planning, management and archiving of the monitoring programme). Other user interfaces, such as MS Access or pgAdmin, can be used to access specific data areas of the IS EBM that are not available through a web application.

After log in to the web application and selecting the appropriate data area, the desired form will appear, along with the controls for inserting, editing, displaying,

in colour (black, green, orange, red) to distinguish the exceedance of the indication and intervention criteria within the meaning of the Directive (Fig. 3.6).

From the point of view of planning of field measurements and groundwater and surface water sampling, the data area “*monitoring design on objects*” is important, in which the respective site coordinator plans the date of field measurements and sampling for each year. In case of a change in the field work term, it is necessary to update the information in this table (Fig. 3.7). In the case of planning and implementation of such an extensive monitoring





programme, such as monitoring of environmental burdens at 309 sites, it was also necessary to create a control and alert system. The principle is to create functions (directly above the database), which signalise the deadlines of tasks, check the completeness of information, or implementation of planned tasks. For upcoming dates (especially field work), or to indicate delay in fulfilment of planned tasks (e.g. implementation and insertion of field measurements), they send an e-mail alert message.

Other specific results used by the investigators of the geological task of environmental burdens monitoring are stored, for example, in the data area of continuous measurements of groundwater heads in selected objects (table “*processed data from dataloggers*”). There is a function in the web application that allows graphical visualization of results (Fig. 3.8). The created graphic object can be transferred and used for interpretation in reports.

#### Access to the IS EBM via ODBC driver

The *ODBC (Open Database Connectivity)* driver is used to access and modify remote databases (insert, update and delete data) directly. It allows to load external data from the IS EBM database into selected user interface, e.g. to MS Office programmes (MS Access, MS Excel) or MapInfo Professional and work with them directly in this environment.

In **MS Access programme environment**, one can import source data into a new table in the current database via the ODBC driver or create a link to a data source by creating a linked table (changes to MS Access data are immediately applied to the source database and vice

versa). In the MS Access it is possible to create local user forms, functional elements or other support systems for work with data stored in the IS EBM. For example, in the IS EBM, a user interface is created in MS Access for online entry and modification of chemical analyses results of the EBM samples and other related data directly in the SGIDŠ GAL laboratory, which increases the reliability and efficiency of work.

In **MS Excel** it is possible to read data and work with them locally, but it is not possible to write directly back to the database, which is a disadvantage for work. MS Excel, on the other hand, offers wide possibilities for data processing, analysis and interpretation (creation of graphs, statistics, tables, etc.).

Editing database data stored in IS EBM via ODBC driver is also possible in the **MapInfo programme**, which is a GIS programme, but it also enables quite effective work with the structured IS EBM data.

#### Direct access to the IS EBM database on the intranet

##### Access from QGIS

The QGIS software is primarily a freeware GIS programme, but it also allows to work with structured spreadsheet data from connectable databases. The advantage is the ability to connect directly to the PostgreSQL database system, which forms the basis of the IS EBM and results in high reliability and link speed.

##### Management and editing data areas in pgAdmin

The pgAdmin graphical environment is accepted as the official graphical user interface of PostgreSQL.

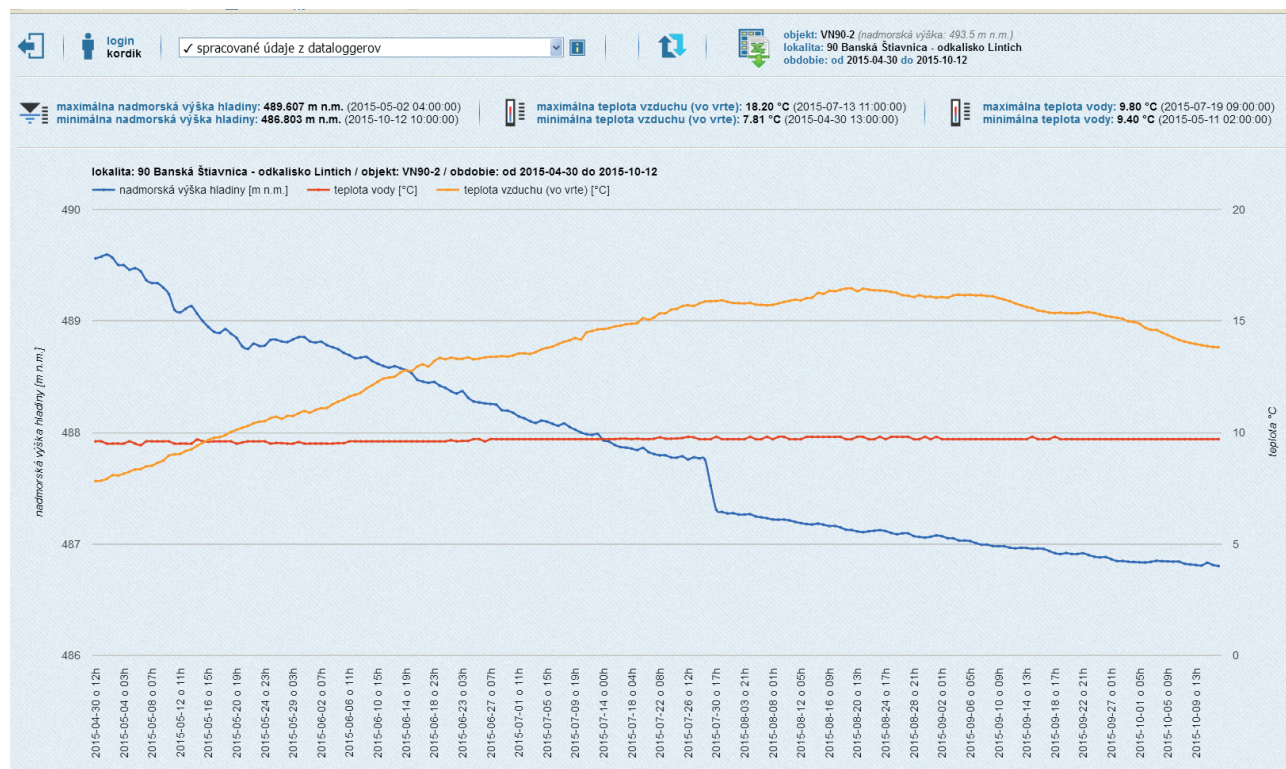


Fig. 3.8 Graphic object with groundwater levels, automatically processed on the basis of the table “*processed data from dataloggers*” – purpose functionality of the IS EBM web application. \*Note: As the IS is developed only in Slovak, the protocol is presented in its output form.



The pgAdmin programme is primarily used for Postgres database administrators. It is part of the open-source PostgreSQL project and the installation files can be freely downloaded from <http://www.pgadmin.org/download/>. It provides a set of tools not only for database administration (at the programming level), but also allows working with database tables – e.g. inserting data, updating data as well as deleting records and batch deleting (truncate). Very effective is a powerful SQL interpreter, which also incorporates the geographical functions associated with the spatial extension of Postgres (PostGIS).

### 3.2.3 Principle of compilation of database of environmental burdens monitoring

Structured relational database of results of environmental burdens monitoring is one of the key components of the IS EBM. Given the complex nature of the information provided, the database is divided into a number of data areas (tables) that create relations with each other. It is possible to combine the records listed in each database table through these relations in the database operations. An example of a relational link scheme of selected important data areas is shown in Fig.

3.9. An illustration is the interconnection of the data area that manages the data of monitored objects (table “*mez\_objekty*”) with the data about field measurements results (table “*mez\_teren\_vody*”) through the key system defined by the “*objekt\_oznacenie*” column, and/or consequently a field data field (“*mez\_teren\_vody*”) with a data area of chemical analyses results (table “*mez\_analyz\_vody\_chem*”) via the field “*id-teren*”. A similar system of relational links (system of primary or foreign keys) is created for the whole structure of the IS EBM.

### 3.2.4 Systematization of data areas – structure of database tables

Systematization of collected data from environmental burdens monitoring enables better storage, processing and analysis of data. One possibility is to define precisely structured database tables. Each database table consists of rows (records) and columns (fields). The names, number, and data types of each field determine the structure of each table. Some of the tables contain so-called spatial geometry (the ‘geom’ field), which allows spatial localization of stored information, in particular, that the information stored in a table is “mapable”; viewable and analysable

Table 3.1 Structure of the table “*lokalita\_centroidy*”

| Field           | Data type         | Metadata                                                                                                                                   |
|-----------------|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| row_id          | Serial            | Database record identifier, primary key                                                                                                    |
| cislo_lokalita  | Integer           | The sequence number of the site to which the object belongs                                                                                |
| lokalita        | Integer           | Official site name                                                                                                                         |
| centroid_x_jtsk | Float             | Centroid X coordinate in the S-JTSK03 coordinate system                                                                                    |
| centroid_y_jtsk | Float             | Centroid Y coordinate in the S-JTSK03 coordinate system                                                                                    |
| folder          | Text              | The name of the appropriate directory on the FTP file server                                                                               |
| okres           | Text              | District abbreviation                                                                                                                      |
| kraj            | Text              | Region Name                                                                                                                                |
| riesitel_meno   | Text              | Name and surname of the principal investigator                                                                                             |
| riesitel_id     | Integer           | ID of the principal investigator                                                                                                           |
| poznamka        | Text              | Miscellaneous remarks                                                                                                                      |
| geom            | Geometry          | PostGIS geometry (point topology) in binary WKB format                                                                                     |
| kraj_mez        | Text              | Integration to administrative units (counties)                                                                                             |
| barologger      | Logical data type | Barologger location at the site – yes / no                                                                                                 |
| kto             | Text              | The last user (login role) who edited the entry. It is automatically added based on the <i>current_user()</i> database function            |
| kedy            | Timestamp         | The date and time the record was last edited. Added automatically based on <i>now()</i> database function                                  |
| kde             | Inet              | The IP address from which the entry was last edited. Adds automatically based on the <i>inet_client_addr()</i> database function           |
| co              | Text              | Insert / Update statement. It is automatically added based on the <i>current_query()</i> database function                                 |
| bolo            | Text              | Old statement (query) – before the last change. It is automatically added based on a combination of database functions and <i>co</i> field |
| editor          | Text              | Name of current operator, or responsible solver of the authorized worker for entering data into the database for the given site            |

Table 3.2 Structure of table “mez.objekty”

| Field              | Data type | Metadata                                                                                                                                                                                                |
|--------------------|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| row_id             | Serial    | Database record identifier, primary key                                                                                                                                                                 |
| cislo_lokalita     | Integer   | The sequence number of the site to which the object belongs. It is generated automatically based on the object's designation                                                                            |
| objekt_oznacenie   | Text      | Object designation                                                                                                                                                                                      |
| kod_objekt_druh    | Integer   | Basic object type (category), generated automatically: adds one of the 10 options given by the code table                                                                                               |
| kod_objekt_typ     | Integer   | Basic type (category) of the object, one of the 33 options given by the coding table is selected                                                                                                        |
| objekt_nazov       | Text      | Existing, or the name of the object, if any                                                                                                                                                             |
| objekt_opis        | Text      | Brief description of the object                                                                                                                                                                         |
| x_jtsk             | Float     | Coordinate X in the S-JTSK03 coordinate system                                                                                                                                                          |
| y_jtsk             | Float     | Coordinate Y in the S-JTSK03 coordinate system                                                                                                                                                          |
| z_bpv              | Float     | Altitude – e.g. in the case of borehole its collar, for soil probes terrain surface, etc.                                                                                                               |
| funkcia_monit_bodu | Text      | Monitoring point function, choose from: “indication” – location in the indication area, “reference” – location in the reference area, “source” – location in the source area                            |
| pristup_monit_bodu | Text      | Indication of whether the proposed site is freely accessible or what the access conditions/on-site sampling options are                                                                                 |
| lokalita           | Text      | The official name of the site. To be populated automatically based on the site number and link to the mez.lokalita_centroidy table                                                                      |
| riesitel           | Text      | Name of the responsible investigator for the site. To be filled-in automatically based on the site number and link to the mez.lokalita_centroidy table                                                  |
| ku_nazov           | Text      | The name of the cadastral territory within which the object is located. To be filled in automatically based on the geographical position and link to the table mapove_podklady.svm50_katastralne_uzemia |
| cislo_lv           | Text      | The property sheet number of the relevant parcel                                                                                                                                                        |
| cislo_parcely_knc  | Text      | Registry number C (KNC)                                                                                                                                                                                 |
| cislo_parcely_kne  | Text      | Registry number E (KNE/UO)                                                                                                                                                                              |
| vlastnik_pozemku   | Text      | Name of the owner of the property concerned                                                                                                                                                             |
| najomca_uzivatel   | Text      | Name of the lessee / user or manager, if not the same as the owner and address                                                                                                                          |
| poznamka           | Text      | Miscellaneous remarks                                                                                                                                                                                   |
| geom               | Geometry  | PostGIS geometry (point topology). It is added automatically according to the entered object coordinates or by a direct click in the GIS programme                                                      |
| editor             | Text      | Name of current operator, or authorized worker to enter data into the database for the site. The name of the logged-in person is filled in automatically                                                |
| Kto                | Text      | The last user (login role) who edited the entry. It is automatically added based on the database function current_user()                                                                                |
| Kedy               | Timestamp | The date and time the record was last edited. It is automatically added based on the now() database function                                                                                            |
| kde                | Inet      | The IP address from which the entry was last edited. Adds automatically based on the inet_client_addr() database function                                                                               |
| Co                 | Text      | Insert / Update statement. It is automatically added based on the current_query() database function                                                                                                     |
| Bolo               | Text      | Old statement (query) – before the last change. It is automatically added based on a combination of database functions and field co                                                                     |
| mi_style           | Text      | How to display an entity in MapInfo. It is written automatically using the colour code in MapInfo                                                                                                       |



Table 3.3 Structure of table “teren\_vody”

| Field             | Data type                          | Metadata                                                                                                                                                                                                                                                          |
|-------------------|------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| row_id            | Serial                             | Database record identifier, primary key                                                                                                                                                                                                                           |
| cislo_lokality    | Integer                            | The sequence number of the site to which the object belongs. It is generated automatically based on the object's designation                                                                                                                                      |
| objekt_oznacenie  | Text                               | Indication of the object to which the record relates or from which the sample was taken                                                                                                                                                                           |
| id_teren          | Integer                            | Field documentation or sampling number (generated automatically and must be unique)                                                                                                                                                                               |
| vzorka_chem       | Logical data type                  | Indication of whether a sample for chemical analysis (yes/no) has been taken from a given horizon                                                                                                                                                                 |
| vzorka_izotop     | Logical data type                  | Indication of whether a sample for isotopic analysis (yes/no) was taken from the given horizon                                                                                                                                                                    |
| oznacenie_vzorky  | Text                               | Field designation of the sample. To be completed only if a sample has been taken (for chemical or isotopic analysis). An example of a typical designation: 14-VN66-4-20150422, i.e. fourteenth sample in the consignment taken from borehole VN66-4, on 22.4.2015 |
| datum_cas_merania | Datum form:<br>2014-10-10 00:00:00 | Date and time of field measurement/sampling                                                                                                                                                                                                                       |
| odobral           | Text                               | Name of the person taking the measurement/sampling                                                                                                                                                                                                                |
| ph_ter            | Float                              | Water reaction in situ                                                                                                                                                                                                                                            |
| t_vody            | Float                              | In-situ water temperature (°C)                                                                                                                                                                                                                                    |
| t_vzduchu         | Float                              | In-situ sampling air temperature (°C)                                                                                                                                                                                                                             |
| vodivost_25       | Float                              | Specific electrical conductivity at 25 °C (mS/m), in situ                                                                                                                                                                                                         |
| o2_mgl            | Float                              | Dissolved oxygen content (mg/l), in situ                                                                                                                                                                                                                          |
| o2_perc           | Float                              | Dissolved oxygen content (%), in situ                                                                                                                                                                                                                             |
| knk45_ter         | Float                              | Acid neutralization capacity 4.5 (mmol)                                                                                                                                                                                                                           |
| znk83_ter         | Float                              | Alkaline neutralization capacity 8.3 (mmol)                                                                                                                                                                                                                       |
| knk83_ter         | Float                              | Acid neutralization capacity 8.3 (mmol)                                                                                                                                                                                                                           |
| znk45_ter         | Float                              | Acid neutralization capacity 4.5 (mmol)                                                                                                                                                                                                                           |
| farba_senz        | Integer                            | Sensory determination of the colour of the water sample (list code)                                                                                                                                                                                               |
| zaka1_senz        | Integer                            | Sensory determination of turbidity in a water sample (list code)                                                                                                                                                                                                  |
| pach_stupen       | Integer                            | Sensory determination of the degree of odour strength of a water sample (list code)                                                                                                                                                                               |
| pach_druh         | Integer                            | Sensory determination of the type of odour of a water sample (list code)                                                                                                                                                                                          |
| eh_ter            | Float                              | The redox potential value (mV) converted to a hydrogen electrode                                                                                                                                                                                                  |
| ropne_latky_senz  | Logical data type                  | Presence of petroleum substances assessed visually (“free phase”): yes/no                                                                                                                                                                                         |
| vzhlad_vzorky     | Text                               | Sample appearance descriptively                                                                                                                                                                                                                                   |
| hlb_hlad_pv       | Float                              | Groundwater depth from casing/OB (m)                                                                                                                                                                                                                              |
| prietok           | Float                              | Surface flow rate (l/s)                                                                                                                                                                                                                                           |
| vydat_vyver       | Float                              | Groundwater output rate (l/s)                                                                                                                                                                                                                                     |
| poznamka          | Text                               | Miscellaneous remarks                                                                                                                                                                                                                                             |
| editor            | Text                               | Name of current operator, resp. responsible solver of the authorized worker for entering data into the database for the given site                                                                                                                                |
| kto               | Text                               | The last user (login role) who edited the entry. It is automatically added based on the current_user() database function                                                                                                                                          |
| kedy              | Timestamp                          | The date and time the record was last edited. Added automatically based on now() database function                                                                                                                                                                |
| kde               | Inet                               | The IP address from which the entry was last edited. Adds automatically based on the inet_client_addr() database function                                                                                                                                         |
| co                | Text                               | Insert/Update statement. It is automatically added based on the current_query() database function                                                                                                                                                                 |
| bolo              | Text                               | Old statement (query) – before the last change. It is automatically added based on a combination of database functions and field co                                                                                                                               |
| riesitel          | Text                               | Name of the responsible investigator for the site. To be populated automatically based on the site number and link to the mez.lokality_centroidy table                                                                                                            |
| lokalita          | Text                               | The official name of the site. To be populated automatically based on the site number and link to the mez.lokality_centroidy table                                                                                                                                |

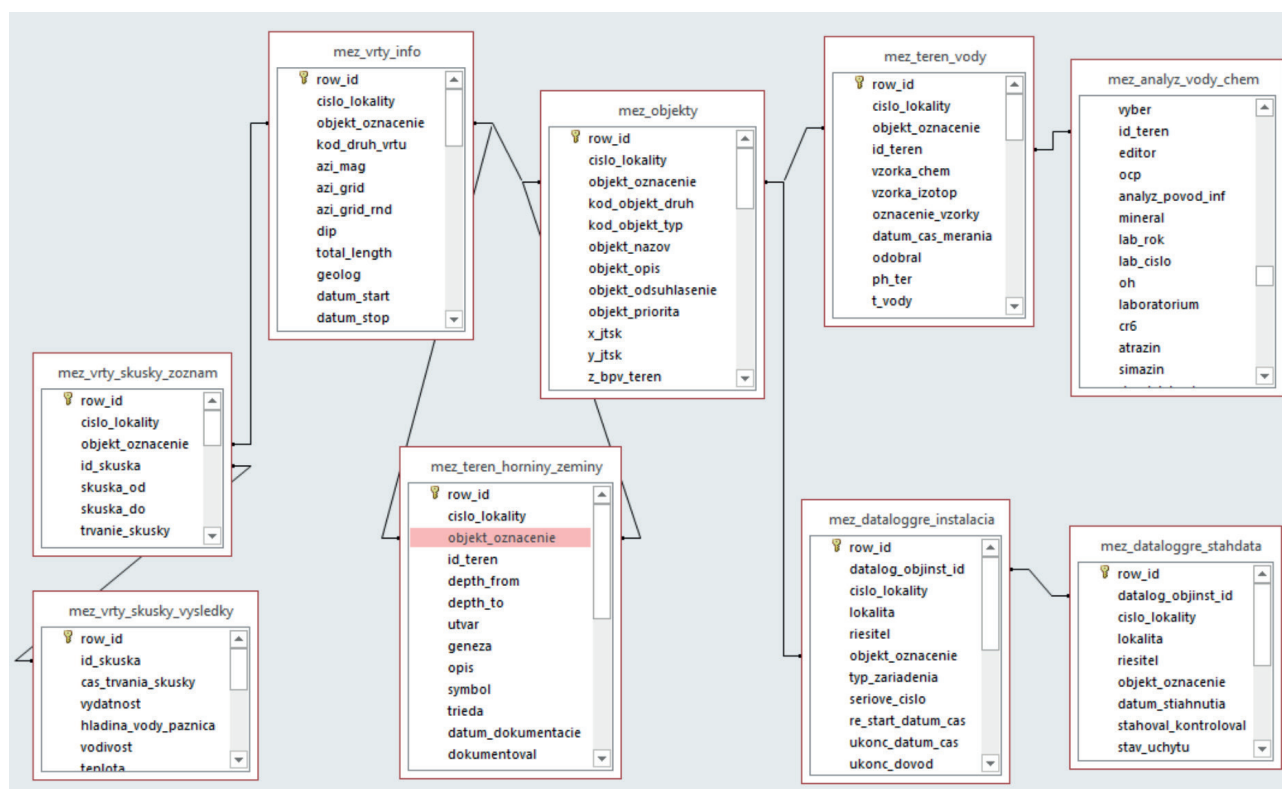


Fig. 3.9 Example of relation of selected tables

in any of the used GIS programmes/applications (e.g. MapInfo Professional, QGIS, thematic web application MEZonátor). Some of the table fields are filled in automatically based on defined criteria and requirements; while other fields must be filled in by the user (otherwise an error message will appear). The remaining fields are optional and may be left blank. At the same time, it is possible to introduce rules defining the required form, or the content of the data to be inserted. Several methods can be used for this purpose, e.g. defining the type of data for a given field when creating a database structure, using triggers (the trigger defines the action that takes place in the case of a certain event occurring above the database table, for example when data is entered), or the possibility of programming purpose-built functions linked to the database. The following text offers a brief description of selected relevant tables of the EBM database, whose simplified structures are shown in Tabs. 3.1 to 3.4.

#### Monitored data area – “lokalita\_centroidy” table

The table contains general information on environmental burdens sites, such as: name of the principal investigator, district, region, cadastral territory, launch and end of the monitoring network development, etc. (Tab. 3.1). The table is mapable, containing geometry with point topology – the point represents the geometric centroid of the polygon bounding the site.

#### Data area of monitored objects – table “mez\_objekty”

It contains a list of all EBM objects (boreholes, wells, springs, drainages, surface streams, soil probes, heaps,

etc.). Each object is given its own designation (field *objekt\_oznacenie*), which must be unique and unrepeatable. The table contains geometry (i.e., it is mapable) with point topology, i.e. each object in the map is represented by a point determined by its coordinates in S-JTSK03 (Tab. 3.2).

#### Data area including storage of results of field measurements of natural waters – table “teren\_vody”

This data area represents an important part of the results of natural water monitoring obtained directly during fieldwork. It contains the field characteristics of the waters at the time of documentation and/or sampling (Tab. 3.3). The table is not mapable and does not contain geometry. When entering a field measurement record, it shall be stated, inter alia, whether a sample has been taken for chemical and/or isotopic analysis. In the case of sampling, a record is automatically created in the appropriate analysis results table with all identification elements, which subsequently enables reliable insertion of the analysis results by laboratory staff.

#### Data area of chemical water analysis results – table “analyz\_vody\_chem”

It contains basic information about the results of chemical analyses of water samples or leakage liquids. The basic division of the structure of this table is shown in Tab. 3.4. There are many columns in this table due to the high number of indicators to be determined. The number of indicators varies depending on the addition of newly determined substances. Currently there are about 300 substances in the database. Similarly-structured are



Table 3.4 Structure of table “teren\_vody”

| Field                                                        | Data type              | Metadata                                                                                                                                                                                                                                                          |
|--------------------------------------------------------------|------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| id_teren                                                     | Integer                | Field documentation or sampling number (generated automatically and must be unique)                                                                                                                                                                               |
| objekt_oznacenie                                             | Text                   | Indication of the object to which the record relates or from which the sample was taken                                                                                                                                                                           |
| datum_odberu                                                 | Datum form: 2014-10-10 | Date of sampling                                                                                                                                                                                                                                                  |
| row_id                                                       | Serial                 | Database record identifier, primary key                                                                                                                                                                                                                           |
| cislo_lokality                                               | Integer                | Sequence number of the EBM site to which the object belongs. It is generated automatically based on the object's designation                                                                                                                                      |
| lokalita                                                     | Text                   | The official name of the site. To be populated automatically based on the site number and link to the mez.lokality_centroidy table                                                                                                                                |
| oznacenie_vzorky                                             | Text                   | Field designation of the sample. To be completed only if a sample has been taken (for chemical or isotopic analysis). An example of a typical designation: 14-VN66-4-20150422, i.e. fourteenth sample in the consignment taken from borehole VN66-4, on 22.4.2015 |
| labor_cislo                                                  | Text                   | Laboratory sample number                                                                                                                                                                                                                                          |
| ph_lab                                                       | Float                  | Water reaction in laboratory                                                                                                                                                                                                                                      |
| ek25_lab                                                     | Float                  | Specific electrical conductivity at 25 °C (mS/m) in the laboratory                                                                                                                                                                                                |
| knk45_lab                                                    | Float                  | Alkaline neutralization capacity 4.5 in mmol, in the laboratory                                                                                                                                                                                                   |
| znk83_lab                                                    | Float                  | Alkaline neutralization capacity 8.3, in mmol, in the laboratory                                                                                                                                                                                                  |
| knk83_lab                                                    | Float                  | Acid neutralization capacity 8.3 in mmol, in the laboratory                                                                                                                                                                                                       |
| znk45_lab                                                    | Float                  | Alkaline neutralization capacity 4.5 in mmol, in the laboratory                                                                                                                                                                                                   |
| poznamka                                                     | Text                   | Miscellaneous remarks                                                                                                                                                                                                                                             |
| Jednotlivé stanovované ukazovatele: (napr. nh4, ca, ....) *1 | Float                  | Values of each set of indicators*1                                                                                                                                                                                                                                |
| editor                                                       | Text                   | Name of current operator, or responsible solver of the authorized worker for entering data into the database for the given site                                                                                                                                   |
| kto                                                          | Text                   | The last user (login role) who edited the entry. Adds automatically based on the current_user() database function                                                                                                                                                 |
| kedy                                                         | Timestamp              | The date and time the record was last edited. Added automatically based on now() database function                                                                                                                                                                |
| kde                                                          | Inet                   | The IP address from which the entry was last edited. Adds automatically based on the inet_client_addr() database function                                                                                                                                         |
| co                                                           | Text                   | Insert/Update statement. It is automatically added based on the current_query() database function                                                                                                                                                                 |
| bolo                                                         | Text                   | Old statement (query) – before the last change. It is automatically added based on a combination of database functions and field co                                                                                                                               |
| riesitel                                                     | Text                   | Name of the responsible investigator for the site. To be filled in automatically based on the site number and link to the mez.lokality_centroidy table                                                                                                            |

Note. \* 1 – the row is only a symbolic representation of a large number, about 300 columns (indicators) in the respective database table representing the results of the chemical analysis

the tables of results of chemical analyses of solid materials (sediments, soils, rocks, earths) and isotope analyses of water. Data are entered in the IS EBM system directly in the laboratory, while the laboratory user interface in the MS Access environment has been developed for input. This environment also provides the initial check of completeness and correctness of analyses.

### 3.2.5 GIS applications in the IS EBM

An important feature of the IS EBM is the possibility of interconnection to standard and special-purpose GIS applications. This is important for efficient and flexible use of stored data for analysis, interpretation and presentation.

Multiple platforms and software applications are supported within the system. The purpose-built online web interface with GIS elements can include an application with an internal name MEZonátor (up to now publicly not accessible). It is possible to use several GIS applications that can be connected directly (e.g. QGIS) or via ODBC driver (e.g. MapInfo). Under certain conditions it is possible to use the currently used ESRI products (ArcGIS).

#### Special purpose web presentation GIS interface – MEZonátor

An interesting, particularly visualization and presentation platform is the web interface with the internal name

“MEZonátor” (Fig. 3.10), which enables GIS presentation of data from the IS EBM. The application was created in R, using the Shiny web framework. The main menu (Fig. 3.11) consists of sections: site selection, site list, info, meteo, map, Piper diagram, water quality, tables.

After selecting the site(s) it is possible to obtain basic information about the site (number of samples, records from continuous measurements, etc.) in the “Info” section

(Fig. 3.12), contamination data (frequency of exceedance of the standard, contamination intensity compared to the standard), site objects data.

The “Meteo” section (Fig. 3.13) shows the long-term average monthly precipitation amounts and the long-term average monthly air temperatures. The data are retrieved from WorldClim.org and represent the long-term averages for 1960 – 1990. For individual sites they are interpolated

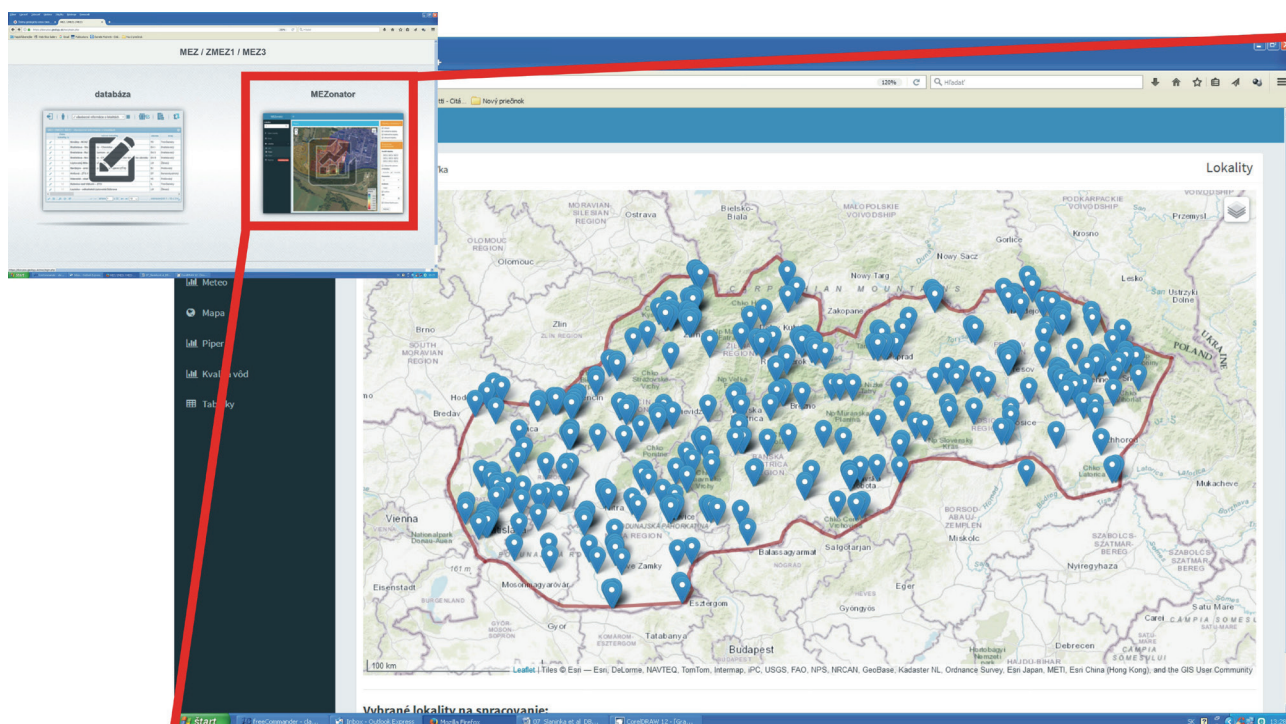


Fig. 3.10 Web application “MEZonator”

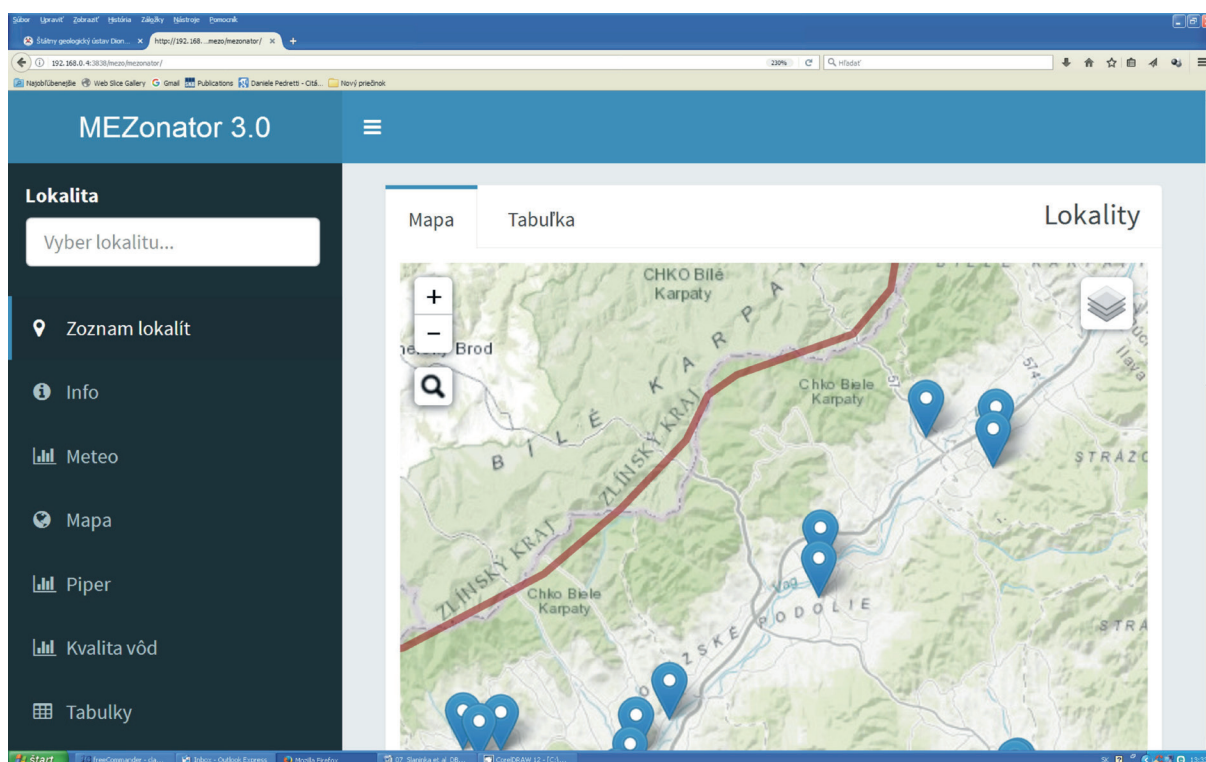


Fig. 3.11 Basic application menu “MEZonator”



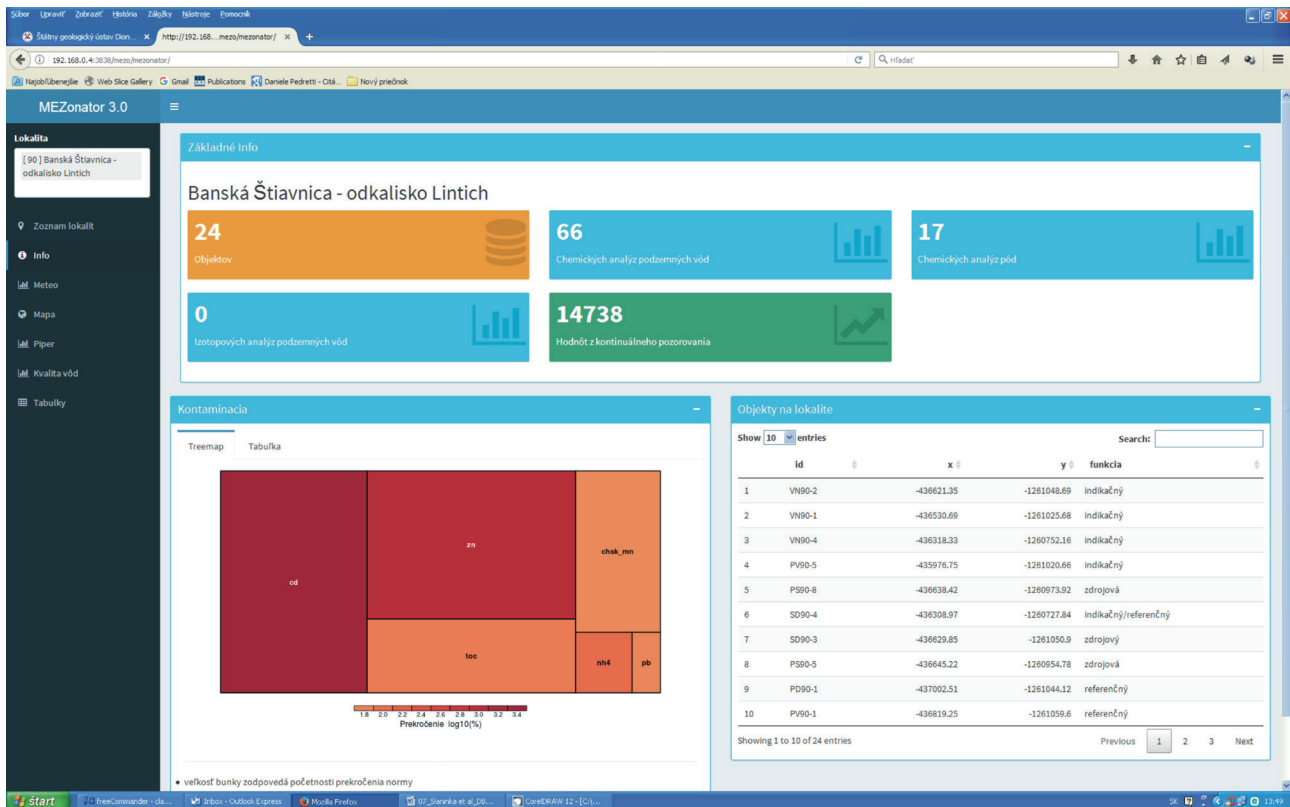


Fig. 3.12 Information under section “Info”

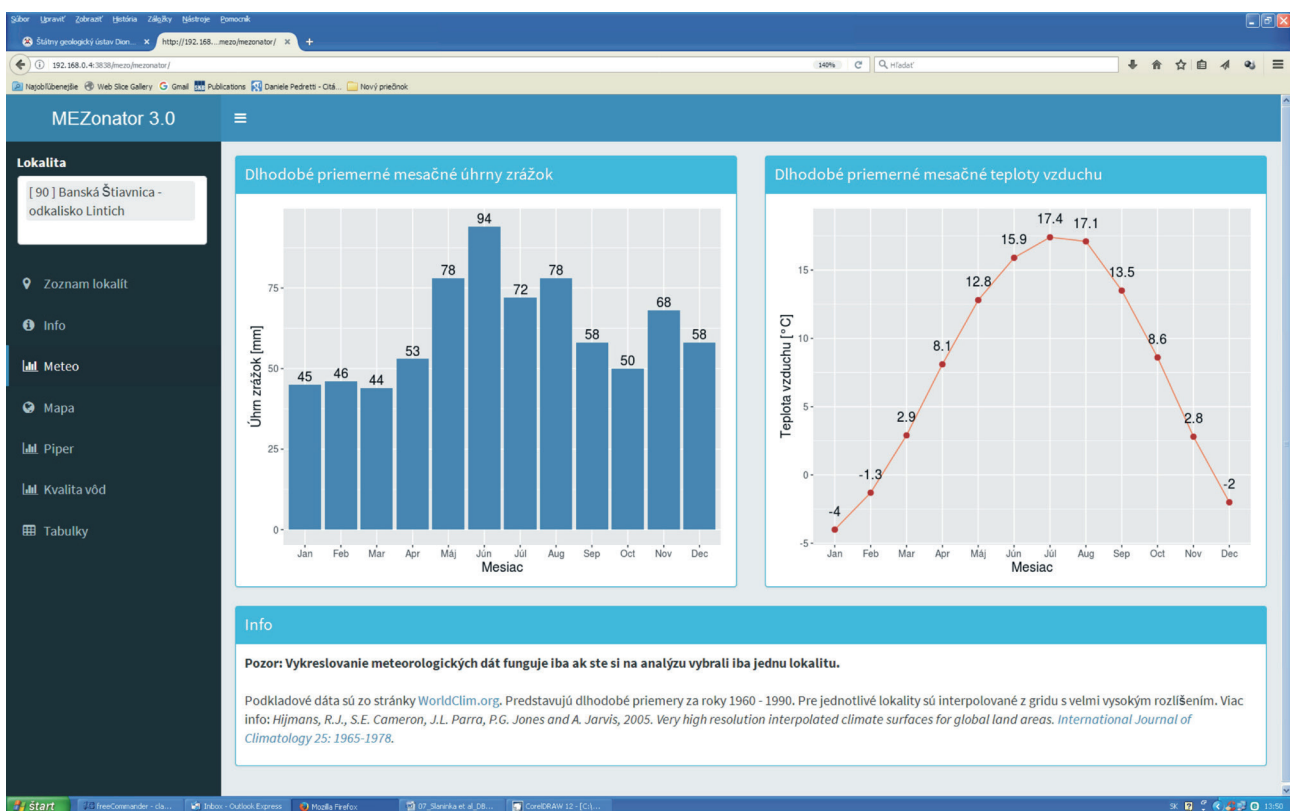


Fig. 3.13 Information provided in section “Meteo”

from a very high resolution grid (more info: Hijmans et al., 2005).

In the “Piper” section (Fig. 3.14) it is possible to plot the Piper systemization diagram for selected objects in the given locality. Piper diagrams represent one of the basic ways of presenting the chemical composition of groundwater.

In the section “Water quality” it is possible to obtain information from basic statistical processing, distribution, course of contents over time for selected objects and selected indicators (Fig. 3.15).

In the “Map” section (Fig. 3.16) it is possible to plot distribution maps of selected indicators for selected objects. The mapping of element concentrations can serve

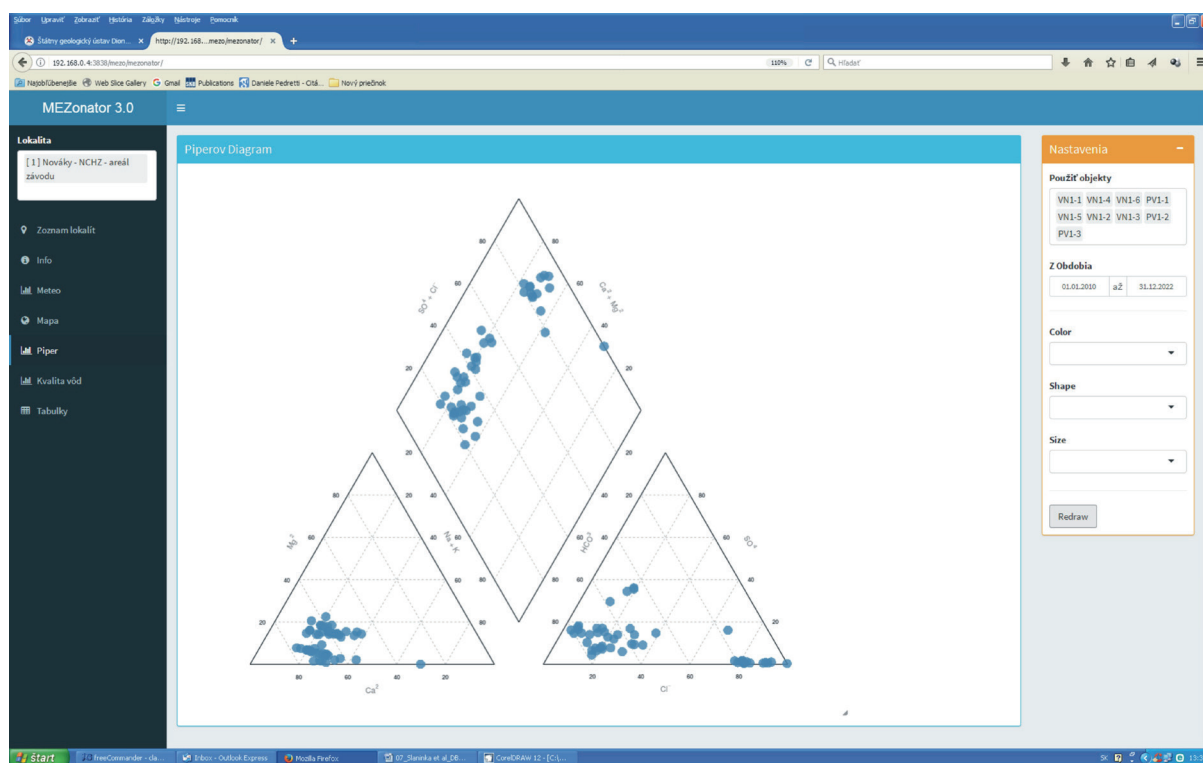


Fig. 3.14 Information provided in section “Piper”

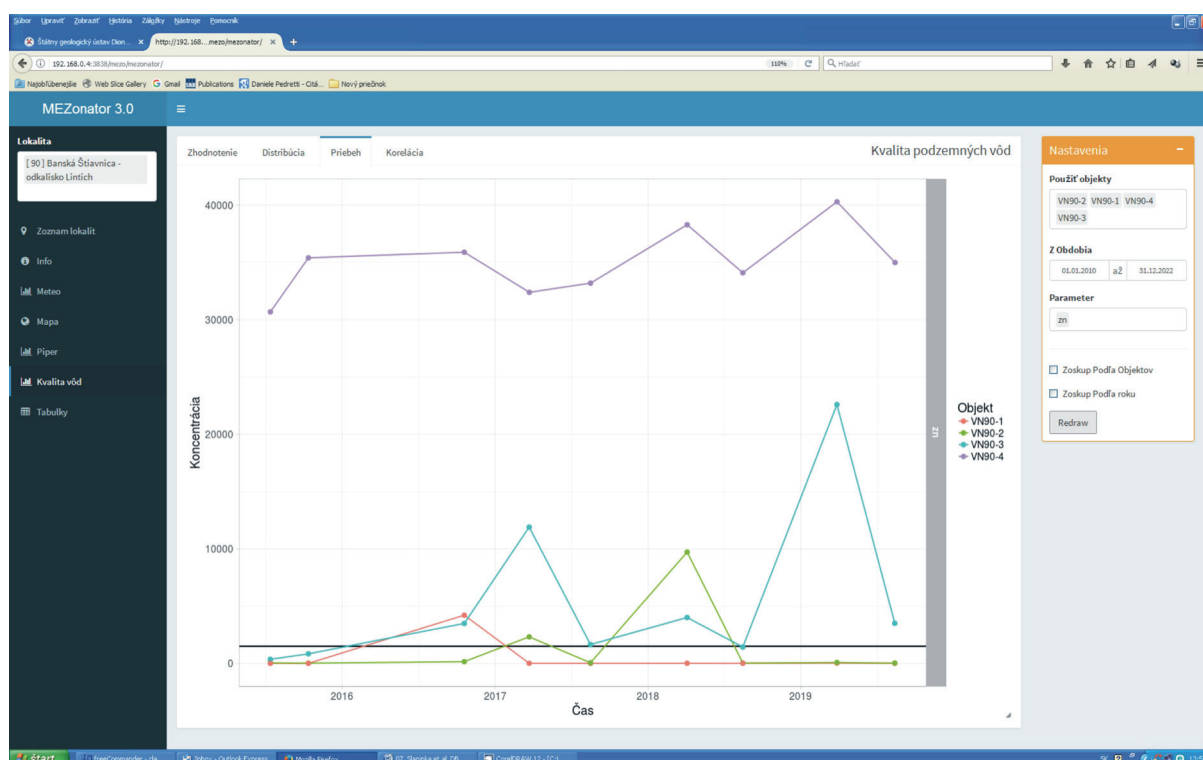


Fig. 3.15 Information provided in section “Water quality”



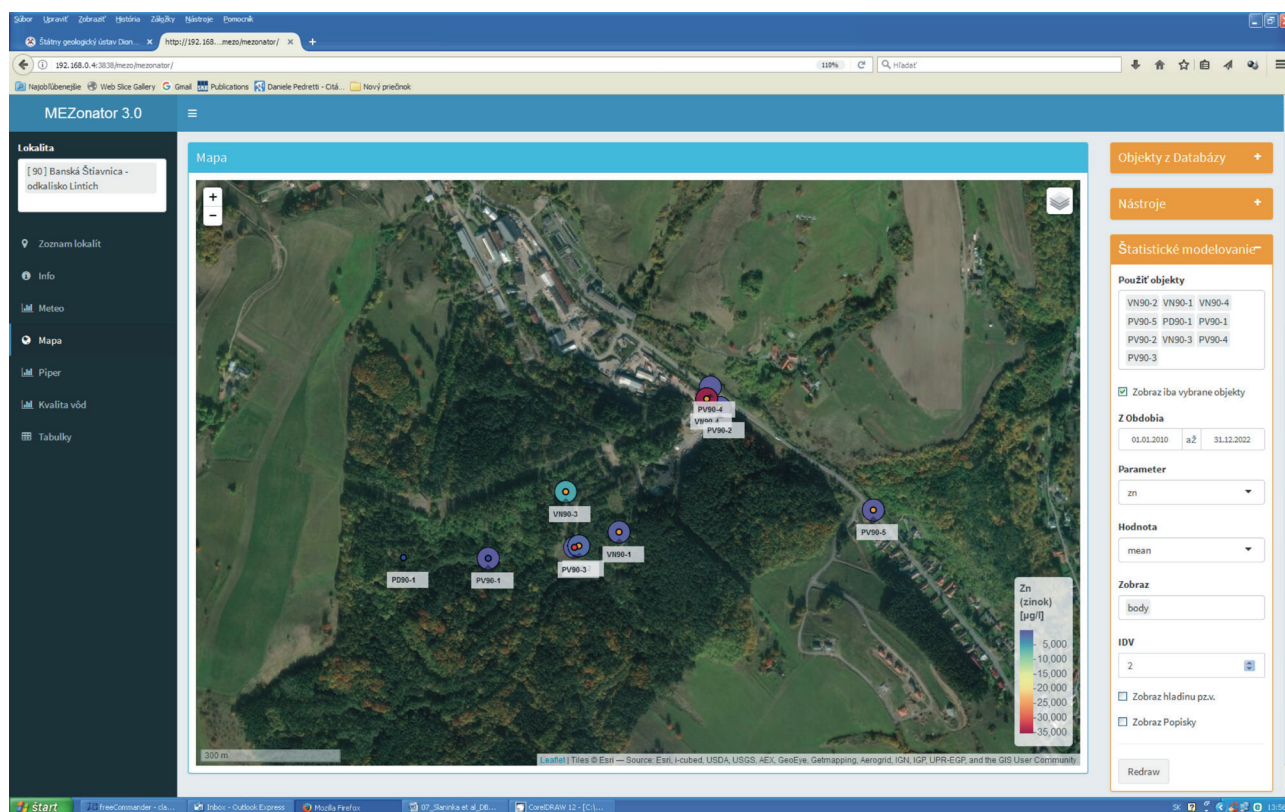


Fig. 3.16 Information provided in section “Map”

to quickly guide the user in the area-wide distribution of the values of the presented indicator. Created distribution maps can be transferred to another software environment, such as interim evaluation reports for sites.

### Standard GIS products usable for work with the IS EBM data

The **QGIS programme** is an open source (GPL) GIS programme distributed through the Internet (<http://www.qgis.org/>). Under the GPL License, the programme can be freely used, modified, and distributed, including for commercial purposes. The benefits of QGIS are also full support for multiple spatial databases (including PostGIS), full integration of GRASS GIS, SAGA GIS, R statistical software, and almost unlimited configurability (full programme source code available), as well as a number of optional external tools, so-called “plugins”. QGIS also allows to directly open files from other programmes (ESRI ArcGIS, MapInfo, Microstation, Autocad, etc.) and combine them in a map window.

### 3.3 Conclusions

The thematic information system for environmental burdens monitoring (IS EBM), created and developed in the SGIDŠ, is an essential tool for planning, storing and presenting the results of the environmental burdens monitoring in the Slovak Republic. Currently, it includes data on monitoring of selected 309 environmental burdens sites across Slovakia. The selection of sites was based on the requirements of the Operational Programmes “Environment” and “Quality of Environment”, as well as the requirements of the MoE SR.

The IS EBM is used for the implementation of projects aimed at the environmental burdens monitoring carried out by SGIDŠ. The system is interconnectable with the IS EB managed by the SEA for the needs of the MoE SR. In terms of content, the IS EBM stores various information resulting from the implementation of several types of geological work (in particular environmental monitoring, geochemistry, hydrogeology, geophysics, engineering geology, etc.). In terms of form, the IS EBM is divided into: 1) general data and text part and 2) structured database and GIS applications.

The information stored in the general data and text part of the IS is divided into a system of directories by type. The structured database of the EBs monitoring is built centrally; the technical platform of the database is the object-relational database system PostgreSQL/PostGIS. Access to the database is possible from various user interfaces, allowing great flexibility in data usage. This is very important because of the wide variety of users demands, whereas the technical skills, conditions of use and user demands are often significantly different.

Access to the IS EBM is possible under intranet and Internet conditions (including remote access via VPN – virtual private network) and through online web applications.

The IS EBM represents a significant help in ensuring the functioning of the monitoring of environmental burdens, and it is also highly economical due to the use of cost-effective “open-source” codes. At the same time, it is very flexible and allows flexible access to stored data, with the possibility of applying different levels of use as well as data security.

Despite the difficulty of creating a thematic IS EBM (the first such tool in the field of the EBs monitoring at SGIDŠ), the geological task of monitoring of 309 EBs with the involvement of nearly 100 experts from various specializations (hydrogeology, geochemistry, engineering geology, environmental geology, laboratory analyses, trend modeling, statistics, etc.) in a relatively short time it would not even be possible to realize it in the required professional level.

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## **4. Evaluation and Comparison of Results of Soil Permeability Determination by Hydrodynamic Tests, Laboratory Tests and Empirical Methods within the Project of Environmental Burdens Monitoring**

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**Abstract:** The study presents the results of the research from the geological task “Contaminated sites monitoring on selected localities in Slovak Republic” carried out at the State Geological Institute of Dionýz Štúr in the period of 2013 – 2015. The aim was to use the acquired knowledge on hydraulic parameters of the environment from hydrodynamic tests to evaluate the permeability of the environment. Within the construction of new wells, disturbed soil samples were also taken to determine the physical properties of the soils in the laboratory. Coefficients of hydraulic conductivity were determined in the laboratory on undisturbed samples. Another objective was to compare the values of the coefficients of hydraulic conductivity determined during pumping tests in boreholes, in laboratory conditions in a triaxial permeameter, in a constant head permeameter and a falling head permeameter and by empirical methods from grain-size distribution. In conclusion, the comparison of individual results of determination of the coefficient of hydraulic conductivity by different methods is presented. The resulting comparison shows that no significant correlations were found between the values obtained from pumping tests and laboratory methods. The pumping tests evaluate the permeability of the geological (or borehole-screened) environment in general, while the laboratory tests evaluate only the point value of the coefficient of hydraulic conductivity at a given sampling point. It is therefore necessary to evaluate the results on a case-by-case basis, taking into account the specificities of the method and the method of sampling for laboratory permeability tests. The coefficients of hydraulic conductivity determined in laboratory compared to results from empirical methods show good correlations, which confirms the dependence of permeability on the grain-size distribution of the soil.

**Key words:** permeability, coefficient of hydraulic conductivity, pumping tests, triaxial test, permeameter, grain size distribution, correlation

### **4.1 Introduction**

Permeability is a very important property of the geological environment when assessing the spread of contaminants. The permeability of a porous medium is its property of permeating liquid or gas. The geological environment has the ability to receive, store, and conduct groundwater (Mucha & Šestakov, 1987).

One of the main activities within the solution of the geological task “Monitoring of environmental burdens in selected localities of the Slovak Republic” carried out at the State Geological Institute of Dionýz Štúr (SGIDŠ) in the period from 2013 to 2015 was the realization of drilling

and related works for construction of the basic monitoring objects suitable for monitoring of groundwater quality and changes in groundwater chemical composition in areas of individual environmental burdens. The research sites are located throughout the Slovak Republic. Altogether there were 161 sites. 669 new monitoring boreholes were built at individual sites and another 156 boreholes were reconstructed. After the boreholes were cleaned, 6-hour orientation pumping tests were carried out in most boreholes in accordance with the Slovak technical standard STN 73 6614 (1984), which verified a borehole functionality. On the basis of pumping tests documentation, the hydraulic parameters of the rock environment around the active part of a borehole were determined. Upon completion of the pumping test, a recovery test was carried out, which lasted until the groundwater level had stabilized. During the pumping test, groundwater level, specific electrolytic conductivity and water temperature were monitored at regular intervals. In total, 638 hydrodynamic tests were carried out. One of the results of the hydrodynamic tests was also the determination of the coefficient of hydraulic conductivity of the environment around the well. Within the construction of new wells, disturbed soil samples were also taken to determine the physical properties of the soil in the laboratory. On undisturbed samples, the coefficients of hydraulic conductivity were determined in the laboratory in a constant head permeameter, falling head permeameter or triaxial. The coefficients of hydraulic conductivity were also calculated by empirical methods based on the results of the grain-size analysis.

The aim of this study is to compare the coefficients of hydraulic conductivity determined from the hydrodynamic field tests with the values of the laboratory coefficients of hydraulic conductivity (in the triaxial and constant and falling head permeameter) and the coefficients of hydraulic conductivity determined from grain-size analysis by empirical methods. We tried to find dependencies between methods, depending on the type of soil, their genesis, or grain composition.

The coefficient of hydraulic conductivity ( $k_p$ ) is the most important parameter in groundwater flow calculations. Its reliable evaluation is necessary for accurate calculation, modelling and evaluation of intergranular flow in porous environment. A number of methods are used to determine the coefficient of hydraulic conductivity. Hydrodynamic tests in wells or in situ permeability tests are conducted

in the field. Laboratory evaluation includes permeability tests in permeameters or triaxial devices. Empirical formulas serve to evaluate the value of the coefficient of hydraulic conductivity from the grain-size distribution of soils. In the case of in situ tests, the precise evaluation of the coefficient of hydraulic conductivity is limited by the uncertainties in the geometry of a soil layer under investigation and in the hydraulic boundary conditions. In laboratory tests, it is difficult to obtain representative samples; the size of the test samples is limited; therefore such samples do not fully represent the original layer in situ. The use of empirical equations is not suitable for low permeability soils such as clays and silts, but allows a quick and cost-effective estimation of the coefficient of hydraulic conductivity for soils such as sand and gravel. Comparison of the results of the determination of the coefficient of hydraulic conductivity by different methods was discussed by several authors.

The assumption that permeability is constant is not reasonable at shallow depths, in soils where porosity changes with depth, in normally consolidated soils or under heavy loads. Clarke et al. (1997) point out that laboratory measured permeability may not always correspond to in-situ permeability. Usually, a laboratory test of clay permeability lasts from two weeks to several months when using a low hydraulic gradient. It is possible to accelerate the test by increasing the hydraulic gradient, which causes seepage induced swelling creating a significant variation in effective stress and void ratio in a specimen. To avoid this using of back pressure is recommended.

Lee & Chang (2007) compared the results of laboratory falling head tests on soil samples from the borrow pits used as construction materials of Hwaong sea dike (7 tests) and in situ permeability tests performed directly at the Hwaong sea dike (27 constant hydraulic gradient tests). Silt sands and clays of low plasticity were sampled as disturbed and artificially compacted. The results confirmed significant differences between the laboratory coefficient of hydraulic conductivity and the in situ permeability. The differences between the results are caused due to the differences in the samples, the inhomogeneity of the soil in the embankment and the possibility of water flow in all directions in field tests, whereas in laboratory conditions the flow is only onedirectional.

Elarabi & Elfaki (2011) compared laboratory and field permeability tests on borehole samples at the new Khartoum International Airport (KNIA). The results showed a significant difference between the permeability measured in the laboratory and the permeability values in the field by one to four orders, attributing the unrepresentative nature of the laboratory sample to soil under natural conditions. Nevertheless, they found a very good correlation between the laboratory permeability and the relative coefficient between field and laboratory permeability. The authors stated that the ratio decreases at higher values of the coefficients of hydraulic conductivity determined in the laboratory.

Sobolewski (2005) presents an overview and classification of coefficients of hydraulic conductivity

determination methods and devices commonly used in Poland. In particular, he focuses on experimental methods and modern measuring instruments that serve to determine the coefficients of consolidation and filtration in cohesive soils. He also suggests introducing changes in methodology that would allow the values of coefficients of hydraulic conductivity determined in situ and from laboratory tests to be comparable. Determining the value of the coefficient of hydraulic conductivity is a complicated and complex engineering task. It is a property of soil, which is changing most significantly. The variations can be in the range of several orders, even in the case of relatively homogeneous layers. There is a huge number of laboratory and field tests to determine the coefficient of hydraulic conductivity. Each method has its advantages but also disadvantages, so the choice of the method depends on the actual situation.

Nagy et al. (2013) investigated various methods for determining the coefficient of hydraulic conductivity of silt sand and silt sand using Khafagi probe, Menard probe, water filtration method. They used a constant head and falling head permeability tests in laboratory. They also used an empirical method of calculating the coefficients of hydraulic conductivity from the grain-size distribution using the equation proposed by Hazen (1895). They accentuate the reliability of individual methods, the capability to sense the layer boundaries and their estimation accuracy. Based on the obtained results, the authors state that they cannot say, what the coefficient of permeability of the soil is, but only state the value obtained from a certain type of measurement. Even in this case one must take into account the disturbance of the sample, the method errors, etc.

The monitoring well screen and filter pack may cause significant head losses, which are not taken into account when interpreting the permeability test data performed in the monitoring wells. Baptiste & Chapuis (2014) have defined the equivalent coefficients of hydraulic conductivity of conventional PVC screens by hydraulic tests in a water tank. The tests have shown that gas microbubbles, which are a common problem in monitoring wells contribute to increasing parasitic head losses. They used closed-form equations and numerical models to explain by how much a field permeability tests in monitoring wells underestimate an aquifer coefficient of hydraulic conductivity due to parasitic head losses in the screen and the filter pack. The value of the local coefficients of hydraulic conductivity can only be correctly measured in the monitoring well only if it is significantly lower than the maximum value of the coefficient of hydraulic conductivity of the monitoring well obtained in the water tank. The measuring capacity of a monitoring well for large slots in perforation and de-aerated water could be two order higher in comparison to small slots in field conditions for poorly designed and installed monitoring well. When assessing groundwater flow conditions at any location, permeability data must be assessed with caution, as permeability tests could be performed in poorly designed and installed monitoring wells with limited measurement capacities. The result of such case is an underestimation of the coefficient of



hydraulic conductivity values and thus an underestimation of the seepage and contamination propagation rates.

## 4.2 Methods

The technical work included drilling, sampling and hydrodynamic testing. Soil samples were taken during drilling operations. A total of 1,979 disturbed soil samples, 299 undisturbed samples and 313 groundwater samples were collected. Sampling and transport of samples were performed in accordance with STN EN ISO 22475-1. Laboratory determination of geotechnical properties of soils and rocks was carried out at SGIDŠ in the laboratory of the Department of Engineering Geology (Kordík & Slaninka et al., 2015).

### Hydrodynamic tests

After the boreholes were cleaned, the pumping tests were carried out for 6 hours in accordance with STN 73 6614 (1984). Upon completion of the pumping test, a recovery test was carried out, which lasted until the groundwater level stabilized. During the pumping test, groundwater level, specific electrolytic conductivity and water temperature were monitored at fixed intervals. In total, 638 hydrodynamic tests were carried out. In the case of a high level of groundwater pollution, the pumping test was not carried out.

Transmissivity (T) and coefficient of hydraulic conductivity ( $k_f$ ) values were obtained by Jacob's modified

nonequilibrium method for adjusted drawdown curves method (Cooper & Jacob, 1946) or by type curve analysis (Moench, 1985).

An example of the pumping test record is shown in Fig. 4.1.

### Laboratory tests

Laboratory tests were carried out on the samples in the laboratory of engineering geology of SGIDŠ to determine the basic physical characteristics of soil samples and to determine the permeability.

### Grain-size analysis

The grain-size analysis (soil particle size analysis) is used to determine the distribution of soil particles and to express their percentage in the soil. The measured data are plotted in a semi-logarithmic graph. This graph expresses the relationship between the percentage (y-axis) and the average of the individual grain fractions (x-axis). The graphical representation, grain-size distribution curve, represents the weight or percentage grain content of the individual fractions from the dry total weight. The grain-size distribution is a basic parameter in the classification of soils and is also used for indirect determination of permeability (coefficient of hydraulic conductivity) using the empirical relationships. The size of the soil grains ranges from 0.001 to 200 mm (STN 72 1172, 1968). The grain-size was determined by two methods, the

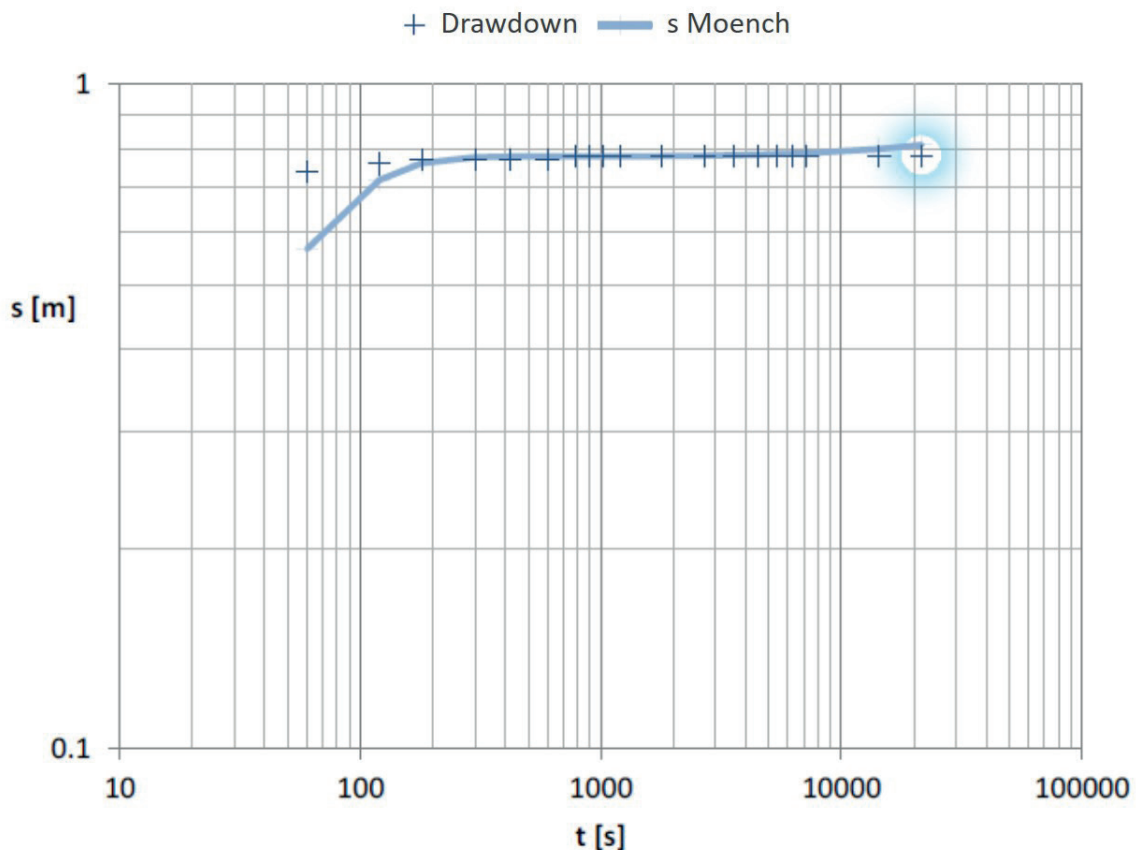


Fig. 4.1 Pumping test in well VN21-2 chart (locality Nové Mesto nad Váhom – landfill)

sieving method for particles larger than 63  $\mu\text{m}$  and the sedimentation method using a hydrometer for particles smaller than 63  $\mu\text{m}$ .

*Permeability – coefficient of hydraulic conductivity  $k_f$  ( $\text{m}\cdot\text{s}^{-1}$ ) determination*

Laboratory methods for the coefficients of hydraulic conductivity determining are based on the Darcy's filtration law, in which there is a direct proportion between the hydraulic gradient and the filtration rate in the laminar flow of fully saturated soil. The measurement is performed in apparatuses under constant or falling head. The head (hydraulic gradient) is considered to be constant if, during the test, the difference in pressure of the water flowing into the sample and flowing out does not change. We talk about the falling head, when the pressure levels on of the inflow and outflow levels decrease during the test.

On intact samples, the coefficients of hydraulic conductivity were determined in a triaxial chamber with pore pressure measurement and in a constant head and a falling head permeameter.

*Coefficient of hydraulic conductivity determination in triaxial chamber (STN 72 1020)*

The permeability was determined in a triaxial GDS (Geotechnical Digital System) with automatic control. The device permits constant hydraulic head permeability tests on 38 mm diameter samples and is equipped with hydraulic pumps to apply chamber, saturation and axial pressure. Test specimens with a diameter of 38 mm and heights from 19 mm to 50 mm were used. A weighed soil sample with a precisely measured volume was mounted

on a lower base fitted with a saturated filter plate. The base drainage system was filled with de-aerated distilled water and sealed. A saturated filter plate and an upper base with a drainage tube were mounted on the upper face of the test sample. A rubber sleeve (membrane) was mounted on the sample jacket, which was fastened to the jacket of both bases by flexible sealing rings. After the sample was prepared, the chamber was mounted and filled with de-aerated water. Sample prepared for triaxial test permeability is shown in Fig. 4.2.

Permeability was measured on totally saturated and consolidated samples. The saturation occurred simultaneously with the consolidation of the sample. The chamber pressure was always at least 20 kPa greater than the saturation and test pressure during both the saturation and consolidation and during the permeability measurement itself. The final saturation pressure was chosen according to the initial degree of saturation. The chamber and saturation pressures increased simultaneously until the final size of the chamber and saturation pressures was reached. The loading rate was not higher than 3 kPa per minute. At saturation, the amount of water received by the sample over time was automatically recorded. The final saturation pressure and chamber pressure were maintained until the volume of water received by the test sample was less than 0.2% of its initial volume in 24 hours. Upon completion of consolidation, as soon as water began to flow through the sample, permeability measurements were started while maintaining a constant value of the hydraulic inclination. The volume of flowed water  $V_w$  and its temperature were measured at least 5 times at suitably selected time intervals  $t$ . The length of the time interval was adapted to the permeability of the test soil. For more permeable soils the measurement intervals were usually from 2 to 10 minutes, for less permeable soils from 1 to 2 hours. The permeability measurements were carried out until the flow rate stabilized. The difference in pressure altitudes  $h$  was chosen so that the hydraulic gradient did not exceed 100 during the test.

At the end of the measurement, the water supply pressure sources were disconnected, the chamber pressure source was also disconnected, and the water was drained from the chamber. The samples were removed and, if possible due to the nature of the sample, the volume and weight of the sample after the test was determined.

Coefficient of hydraulic conductivity was calculated according to the formula:

$$k_f = \frac{Q \cdot L}{A \cdot h \cdot \Delta t} \cdot [\text{m} \cdot \text{s}^{-1}]$$

where  $Q$  is the volume of water in  $\text{m}^3$ ,  $L$  is the height of the sample before the test in m,  $A$  is the cross-section of the sample in  $\text{m}^2$ ,  $h$  is the difference of pressure levels in m, and  $t$  is the time interval of the measurement in s.

Coefficient of hydraulic conductivity measured at temperature  $\vartheta$  is marked as  $k_{\vartheta}$ . For comparative value  $k_{10}$  is calculated according:

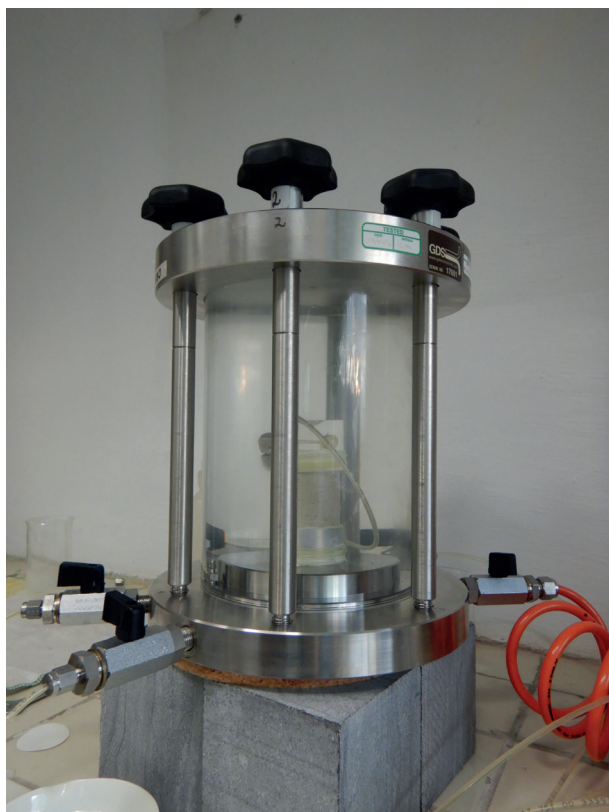


Fig. 4.2 Permeability in triaxial permeameter



$$k_{10} = \frac{1.359}{1 + 0.0337 \cdot \vartheta + 0.00022 \cdot \vartheta^2} \cdot k_{\vartheta} = \alpha \cdot k_{\vartheta} [m \cdot s^{-1}]$$

The values of the  $\alpha$  coefficient are set in the range of 5 to 25 °C, given in STN 72 1020 (1991). The temperature is determined as the average temperature to which it refers and at the end of the interval from which the coefficient of hydraulic conductivity was evaluated.

The resulting coefficient of hydraulic conductivity value is the average of all stabilized values. As stabilized values of coefficient of hydraulic conductivity those values are considered, which do not differ more than 20% of their average value. Physical parameters of the samples before and after the test were calculated according to the applicable relationships of soil mechanics.

#### Constant head permeability test

In the constant head permeability test water flows through a cylindrical-shaped soil sample with a constant differential pressure. The test is performed in a chamber whose dimensions were 116.5 mm high and 101.4 mm diameter. The permeameter is equipped with an adjustable water tank that allows a constant head flow during the test. For testing, deaerated water at a constant temperature is used. Before starting the flow measurement, the soil sample must be saturated. During the test, the amount of water flowing through the sample at given time intervals is measured.

Coefficient of hydraulic conductivity can be calculated as:

$$k_f = \frac{Q \cdot L}{A \cdot \Delta h \cdot \Delta t}$$

where  $L$  is the height of the sample,  $A$  is the cross-section of the sample,  $\Delta h$  is the pressure level difference,  $Q$  is the volume of flow-through water,  $\Delta t$  is the time interval.

#### Falling head permeability test

A falling head permeability test means water flow through a soil sample in a chamber with a height of 116.5 mm and a diameter of 101.4 mm attached to a burette that provides a hydraulic height and also allows measurement of the volume of water passing through the sample.

Before starting the flow measurement, the soil sample is saturated with de-aerated water. The burette is filled to the specified height. The test is then started and the water flows through the sample until the water in the burette reaches the lower limit. The time taken to fall from the upper level to the lower level is recorded. The procedure is repeated several times until the recorded time varies by less than 10% (Head, 1981).

Coefficient of hydraulic conductivity is calculated as:

$$k_f = \frac{a \cdot L}{A \cdot \Delta t} \cdot \log \left( \frac{h_0}{h_1} \right)$$

where  $L$  is the height of the soil sample,  $A$  is the cross-sectional area of the sample,  $a$  is the cross-sectional area of the burette,  $\Delta t$  is recorded time,  $h_0$  and  $h_1$  are upper and lower water levels in the burette.

The resulting values of the coefficient of hydraulic conductivity, which were determined at a given temperature in the laboratory  $k_{\vartheta}$ , were calculated to a comparative value of 10 °C  $k_{10}$ . Permeameter for constant and falling head tests is shown in Fig. 4.3.



Fig. 4.3 Permeameter for constant and falling head test

#### Empirical methods

Since the permeability of the porous rock depends on the relative grain content of the various sizes, the granularity of the rock is also reflected in its coefficient of hydraulic conductivity. Different ways of deriving the coefficient of hydraulic conductivity from the grain-size distribution curves were developed. These are used for noncohesive sedimentary rocks, especially for sandy and gravel soils (Dananaj, 2004).

These methods are indirect, based on the size and shape of the particles, so it is necessary to establish a grain-size distribution curve that captures the amounts of the individual grain fractions. Several equations are used to relate the permeability of soils (especially sands) to their granular composition and other classification values. The best known are the Hazen equation, which is simple and based on the grain-size distribution curve and the Kozeny equation and its Carman modification. Other methods are, for example, Jaky, Terzaghi, Orechova, American formula, Seelheim, Zieschang, Beyer, Zauerbrej, Zamarin,

Schlichter, Krüger, Palagin. These methods are particularly suitable for sands and their use is not suitable for fine-grained soils. Coefficients of hydraulic conductivity were determined from the grain curves using the GeoFil computer program, which uses the above mentioned methods.

Carman – Kozeny method puts permeability into a relationship with grain-size, porosity, particle shape, specific surface and water viscosity. The formula is valid only for sands, but sometimes is extrapolated for fine-grained soils to approximately determinate their permeability (Head, 1981):

$$k_f = \frac{\rho_w \cdot g}{C \cdot \eta_w \cdot S^2} \cdot \frac{e^3}{1+e}; C = 5 \cdot f$$

or (simplified for spherical grain shape)

$$k_f = \frac{1}{5} \cdot \frac{g \cdot n^3}{\gamma \cdot (1-n)^2} \cdot \frac{d_e}{\alpha},$$

where  $e$  is porosity index,  $\rho_w$  is water density,  $\gamma$  is volumetric gravity,  $g$  is gravity acceleration,  $\eta_w$  is water viscosity,  $S$  is surface area,  $C$  is shape coefficient (= 5 for spherical shape),  $f$  is angularity coefficient (1.1 – 1.4),  $n$  is porosity,  $d_e$  is effective grain diameter and  $\alpha$  is pore shape coefficient.

Seelheim, American formula and Orechova put coefficient of hydraulic conductivity into relationship with grain-size expressed by diameters  $d_{30}$ ,  $d_{20}$  and  $d_{17}$ .

Seelheim is valid for soils with fraction less than 0.063 mm content < 35%

$$k_f = \frac{0.357 \cdot (d_{50})^2}{100}$$

American formula is valid for soils with effective grain diameter ( $0.01 < d_{20} < 2.0$ )

$$k_f = \frac{0.36 \cdot (d_{50})^{2.3}}{100}$$

Orechova formula is valid for soils with fraction less than 0.063 mm content < 35%.

$$k_f = \frac{640 \cdot (d_{17})^2}{86,400}$$

### 4.3 Results

Rocks of different ages and origin were found in the areas of monitored localities. Most of the sites were Quaternary and Neogene rocks. Palaeogene, Mesozoic and Palaeozoic rocks were also found in some localities.

Only the Quaternary and Neogene sediments were processed in the Laboratory of engineering geology.

The Quaternary is represented by anthropogenic, fluvial, deluvial, eluvial, proluvial, aeolian, polygenetic, organogenic and glaciuvial sediments. The counts of soil samples by their genetic origin are shown in Tab. 4.1.

Tab. 4.1 Genetic classification

| Genesis       | Formation  | Count |
|---------------|------------|-------|
| Anthropogenic | Quaternary | 80    |
| Deluvial      | Quaternary | 295   |
| Eluvial       | Quaternary | 58    |
| Aeolian       | Quaternary | 23    |
| Fluvial       | Quaternary | 1,170 |
| Glaciuvial    | Quaternary | 4     |
| Proluvial     | Quaternary | 48    |
| Polygenetic   | Quaternary | 65    |
| Organogenic   | Quaternary | 1     |
| Sedimentary   | Neogene    | 416   |
| Volcanic      | Neogene    | 1     |
| Effusive      | Neogene    | 6     |
| Sedimentary   | Palaeogene | 80    |
| Sedimentary   | Mesozoic   | 29    |
| Sedimentary   | Permian    | 2     |
| Metamorphic   | Palaeozoic | 2     |

A total of 2,315 disturbed and undisturbed soil samples were processed. Moisture content was determined on all of them and granulometric analysis for soil classification according to STN 72 1001 on 2,313 samples. Consistency limits were determined on 56 samples.

A total of 3 samples of boulder fraction (200 – 60 mm), 722 gravelly, 368 sandy and 1,220 fine-grained soils were tested. The numbers of soils according to the classification based on STN 72 1001 are given for gravelly soils in Tab. 4.2, for sandy soils in Tab. 4.3 and for fine-grained soils in Tab. 4.4.

Tab. 4.2 Classification of gravelly soils

| Class   | Symbol | Classification (STN 72 1001)                | Count |
|---------|--------|---------------------------------------------|-------|
| G1      | GW     | Well graded gravel                          | 29    |
| G2      | GP     | Poorly graded gravel                        | 56    |
| G3      | G-F    | Gravels with admixture of fine-grained soil | 363   |
| G4      | GM     | Silty gravel                                | 21    |
| G5      | GC     | Clayey gravel                               | 253   |
| Overall |        | Gravelly soils                              | 722   |

Tab. 4.3 Classification of sandy soils

| Class   | Symbol | Classification (STN 72 1001)             | Count |
|---------|--------|------------------------------------------|-------|
| S1      | SW     | Well graded sand                         | 1     |
| S2      | SP     | Poorly graded sand                       | 57    |
| S3      | S-F    | Sand with admixture of fine-grained soil | 84    |
| S4      | SM     | Silty sand                               | 18    |
| S5      | SC     | Clayey sand                              | 208   |
| Overall |        | Sandy soils                              | 368   |



Tab. 4.4 Classification of fine-grained soils

| Class   | Symbol | Classification (STN 72 1001)      | Count |
|---------|--------|-----------------------------------|-------|
| F1      | MG     | Gravelly silt                     | 2     |
| F2      | CG     | Gravelly clay                     | 66    |
| F3      | MS     | Sandy silt                        | 28    |
| F4      | CS     | Sandy clay                        | 313   |
| F5      | ML     | Silt of low plasticity            | 42    |
|         | MI     | Silt of intermediate plasticity   |       |
| F6      | CL     | Clay of low plasticity            | 513   |
|         | CI     | Clay of intermediate plasticity   |       |
| F7      | MH     | Silt of high plasticity           | 3     |
|         | MV     | Silt of very high plasticity      |       |
|         | ME     | Silt of extremely high plasticity |       |
| F8      | CH     | Clay of high plasticity           | 253   |
|         | CV     | Clay of very high plasticity      |       |
|         | CE     | Clay of extremely high plasticity |       |
| Overall |        | Fine-grained soil                 | 1,220 |

Based on the results of granulometric analyses, the computer programme GeoFil was used to determine the coefficients of hydraulic conductivity values by empirical methods from grain curves. The program uses the methods Hazen1, Hazen2, Orechova, American formula, Seelheim, Zieschang, Beyer, Zaubrebj, Kozeny1, Kozeny2, Zamarin1, Zamarin2, Zamarin3, Zamarin4, Schlichter1, Schlichter2, Schlichter3, Kruger, Palagin, Carman – Kozeny. The programme automatically selected the appropriate methods for the soil type. The criteria are defined by the program itself and cannot be influenced except for the approximate porosity setting. The total number of coefficients of hydraulic conductivity for each method is shown in Tab. 4.5.

Permeability and bulk density were determined on intact and reconstituted samples. The permeability in the

triaxial permeameter was determined on 218 samples. The permeability in the constant head permeameter was determined on 58 samples. The permeability in the falling head permeameter was determined on 19 samples. In statistical processing, the results of the coefficient of hydraulic conductivity determination in the constant head permeameter and falling head permeameter were evaluated together with the result from triaxial permeameter.

The results of engineering geological properties determinations and values of coefficients of hydraulic conductivity determined by various methods were summarized in the database of all project data. The evaluation was based on a total dataset of 2,281 samples, which included the physical properties of soils together with the results of the determination of the coefficient of hydraulic conductivity by empirical methods and laboratory determination of the coefficient of hydraulic conductivity. From hydrodynamic tests in boreholes it was possible to determine coefficients of hydraulic conductivity in 254 cases. Based on the determination of the main collector, the results from the laboratory determination for the soil type were subsequently assigned to the well.

In this dataset, the results of determined coefficients of hydraulic conductivity were compared directly with each other, as well as depending on the grain-size, soil type or genesis.

By direct comparison between the values of the coefficients of hydraulic conductivity determined by hydrodynamic and laboratory tests, only twelve data could be compared, since only in these cases data from both tests were available. This was due to the fact that for the laboratory determination of the coefficient of hydraulic conductivity the impermeable soils were preferably taken. The results of this comparison are shown in Fig. 4.4. It is clear that the differences are considerable, in the order of several orders, which is also confirmed by the weak exponential relationship with the correlation coefficient  $R = 0.36455$ . The results from hydrodynamic tests generally give a higher  $k_f$  value than laboratory tests.

Tab. 4.5 Number of coefficients of hydraulic conductivity calculated by empirical methods (in  $m \cdot s^{-1}$ )

| Method | Hazen1                 | Hazen2                 | Orechova               | American               | Seelheim               | Zieschang              | Beyer                  |
|--------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Min    | $2.13 \times 10^{-08}$ | $8.49 \times 10^{-09}$ | $1.40 \times 10^{-08}$ | $8.94 \times 10^{-10}$ | $7.32 \times 10^{-09}$ | $3.95 \times 10^{-09}$ | $4.30 \times 10^{-09}$ |
| Max    | $2.45 \times 10^{-01}$ | $1.96 \times 10^{-01}$ | $2.77 \times 10^{-01}$ | $3.88 \times 10^{-01}$ | $9.36 \times 10^{-01}$ | $2.57 \times 10^{-01}$ | $2.08 \times 10^{-01}$ |
| Count  | 854                    | 860                    | 1,416                  | 1,531                  | 1,516                  | 861                    | 866                    |
| Method | Zaubrebj               | Kozeny1                | Kozeny2                | Zamarin1               | Zamarin2               | Zamarin3               | Zamarin4               |
| Min    | $1.86 \times 10^{-09}$ | $5.23 \times 10^{-08}$ | $1.63 \times 10^{-07}$ | $4.58 \times 10^{-09}$ | $1.16 \times 10^{-10}$ | $7.27 \times 10^{-11}$ | $1.13 \times 10^{-09}$ |
| Max    | $9.05 \times 10^{-02}$ | $6.98 \times 10^{-02}$ | $5.27 \times 10^{-03}$ | $2.20 \times 10^{-01}$ | $3.29 \times 10^{-02}$ | $1.48 \times 10^{-02}$ | $5.46 \times 10^{-03}$ |
| Count  | 909                    | 941                    | 943                    | 868                    | 864                    | 855                    | 858                    |
| Method | Schlichter1            | Schlichter2            | Schlichter3            | Kruger                 | Palagin                | Carman – Kozeny        | Average                |
| Min    | $6.52 \times 10^{-09}$ | $2.34 \times 10^{-08}$ | $6.07 \times 10^{-10}$ | $6.59 \times 10^{-09}$ | $1.69 \times 10^{-10}$ | $2.25 \times 10^{-09}$ | $2.30 \times 10^{-09}$ |
| Max    | $5.40 \times 10^{-02}$ | $2.99 \times 10^{-02}$ | $2.90 \times 10^{-02}$ | $8.19 \times 10^{-02}$ | $1.11 \times 10^{-01}$ | $5.74 \times 10^{-02}$ | $2.22 \times 10^{-01}$ |
| Count  | 869                    | 869                    | 867                    | 872                    | 945                    | 2,240                  | 2,246                  |

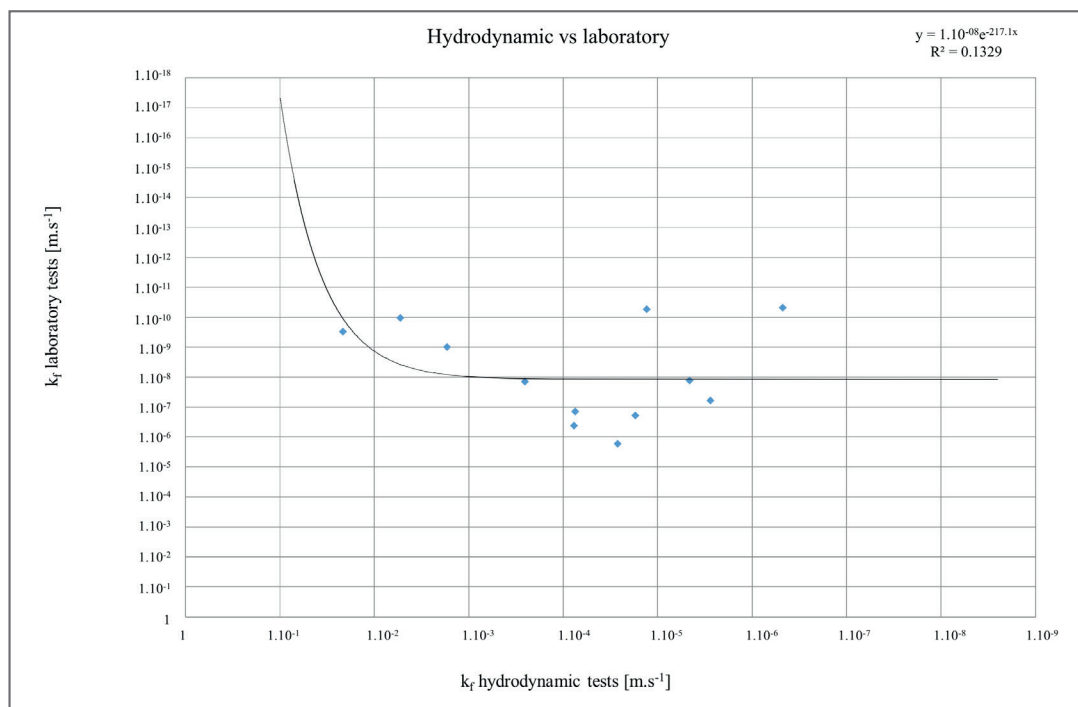


Fig. 4.4 Comparison between values of coefficients of hydraulic conductivity determined by hydrodynamic and laboratory tests

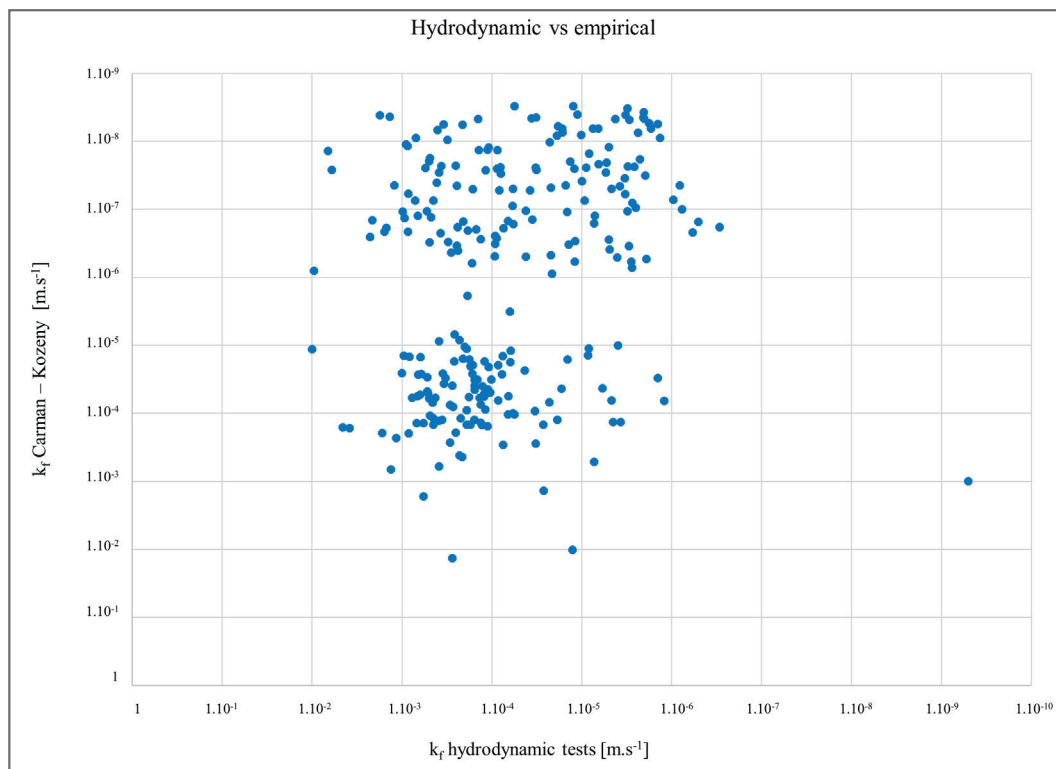


Fig. 4.5 Comparison between values of coefficients of hydraulic conductivity determined by hydrodynamic tests and Carman – Kozeny empirical method

To compare the coefficients of hydraulic conductivity from hydrodynamic tests and from empirical relationships, the average values per well were calculated from the determined values of the coefficients of hydraulic conductivity obtained from empirical formulas to increase the impact of heterogeneity of the whole environment and “simulate” the cross-section of the well geological profile. The Carman – Kozeny method, which was calculated

for almost all samples, was used for the evaluation. The resulting graph is shown in Fig. 4.5. No correlation is seen, as well.

The values of coefficients of hydraulic conductivity determined by hydrodynamic tests and mean values calculated from all empirical methods were also compared. The samples were divided into 4 groups according to the percentage of clay particles (< 0.002 mm). The first group



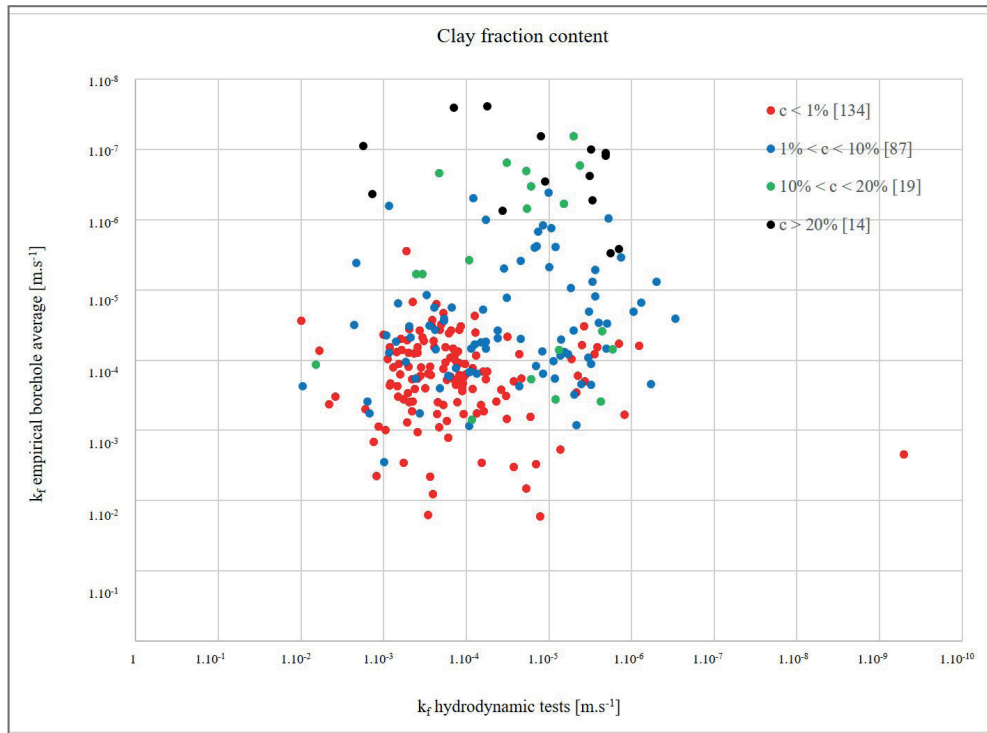


Fig. 4.6 Comparison between the values of coefficients of hydraulic conductivity determined by hydrodynamic tests and from grain-size distribution curves in dependence to clay fraction content

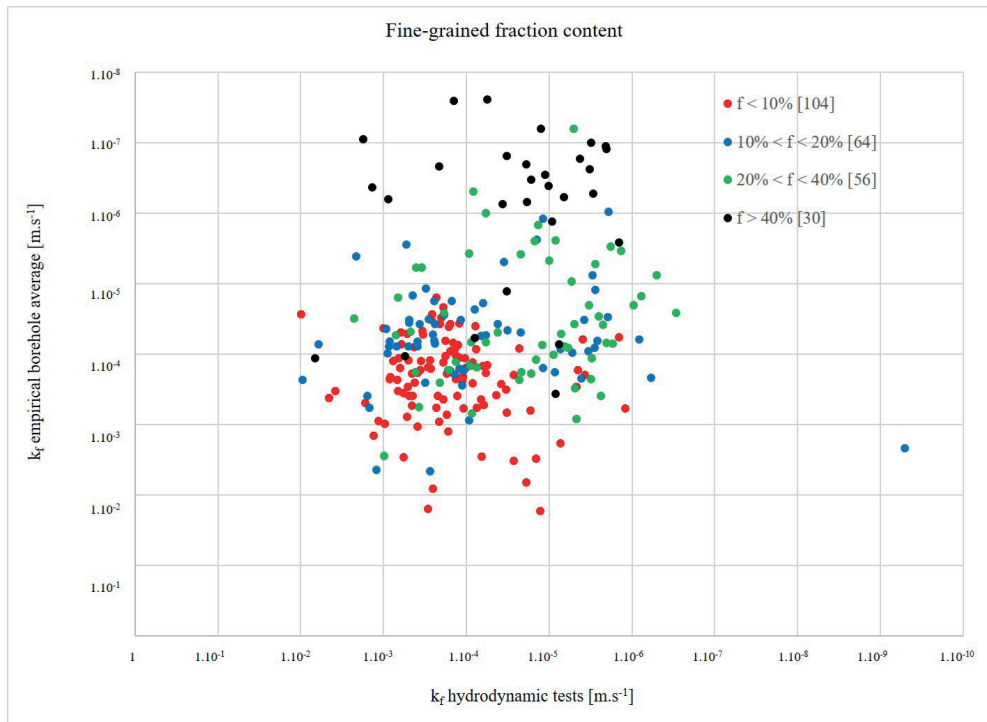


Fig. 4.7 Comparison between the values of coefficients of hydraulic conductivity determined by hydrodynamic tests and from the grain-size distribution curves in dependence to the content of fine-grained fraction

represented the samples with clay content less than 1%, the second from 1% to 10%, the third from 10% to 20% and the fourth above 20%. This comparison is shown in Fig. 4.6. Again, there was no apparent correlation for any of the four groups.

A similar comparison was also made with a fine grain fraction ( $< 0.063$  mm). The samples were divided

into 4 groups according to the percentage of fine-grained particles. The first group represented the samples with a fine particle content of less than 10%, the second group from 10% to 20%, the third group from 20% to 40% and the fourth group above 40%. This comparison is shown in Fig. 4.7. Even this comparison did not bring any significant correlations.

Comparison with respect to soil type is shown in Fig. 4.8. It is clear from the figure that, there is no significant correlation.

Another comparison was made for samples divided by genetic origin (Fig. 4.9). Again, no significant correlations can be seen based on genetic types.

Fig. 4.10 shows a comparison of the coefficients of hydraulic conductivity from hydrodynamic tests and the difference between the coefficient of hydraulic conductivity of hydrodynamic tests and the coefficient of hydraulic conductivity of empirical methods depending on the clay fraction content. With such a distribution it can be

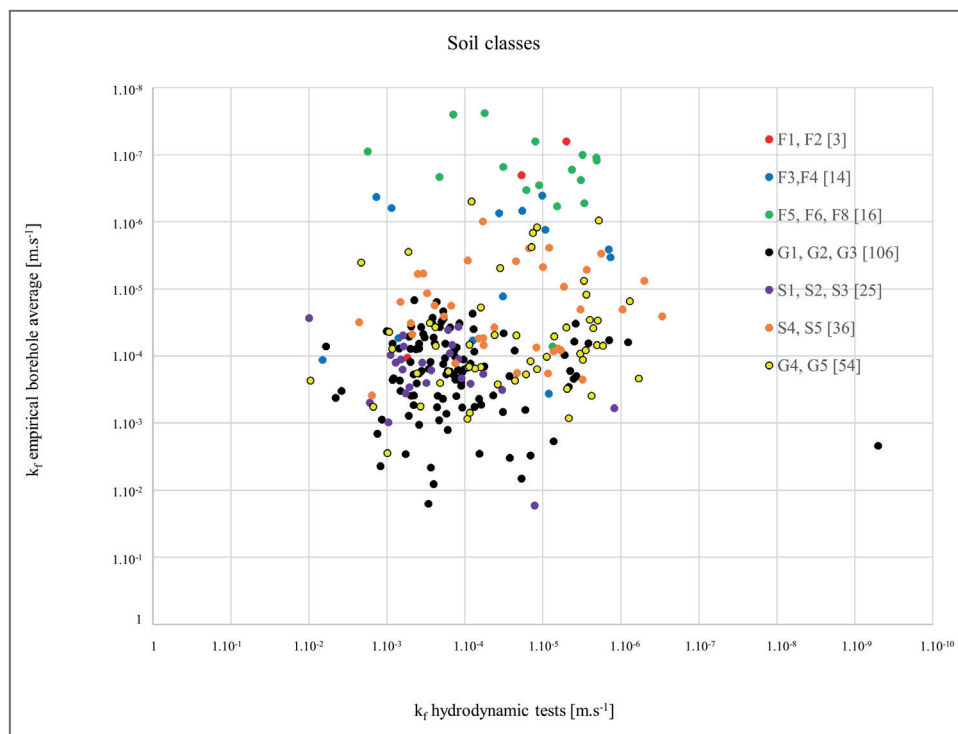


Fig. 4.8 Comparison between the values of the coefficients of hydraulic conductivity determined by hydrodynamic and from the grain-size distribution categorized by soil type

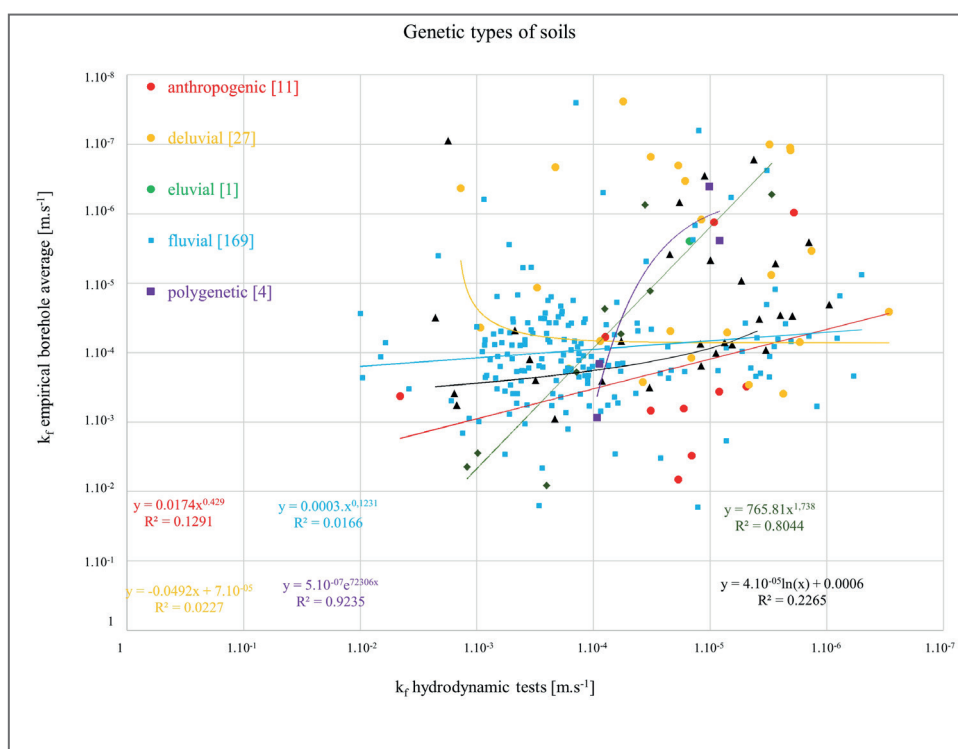


Fig. 4.9 Comparison between the values of coefficients of hydraulic conductivity determined by hydrodynamic tests and from the grain-size distribution based on genetic origin



seen that the greatest differences are with soils having the lowest clay content.

In Fig. 4.11, there is a comparison of the values of the coefficients of hydraulic conductivity determined in the triaxial permeameter with the average values obtained by empirical methods. The values are significantly different,

since the minimum values from the grain-size distribution curves reach values of the order of  $10^{-9}$  m.s<sup>-1</sup>. The values determined in the triaxial permeameter reach the order values up to  $10^{-11}$  m.s<sup>-1</sup>. The value of the correlation coefficient R for the given statistical set of 215 samples for the power trend line is 0.452769, with the determination

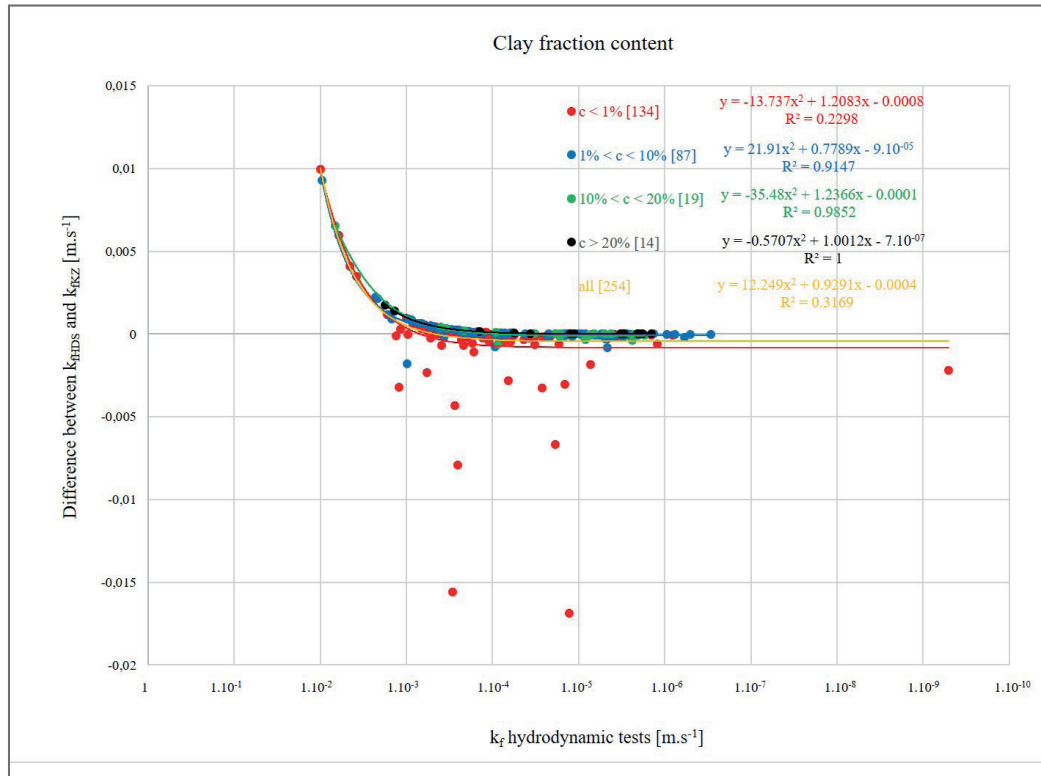


Fig. 4.10 Comparison of the coefficients of hydraulic conductivity from hydrodynamic tests and the difference between the coefficients of hydraulic conductivity from hydrodynamic tests and from empirical methods depending on the clay fraction content

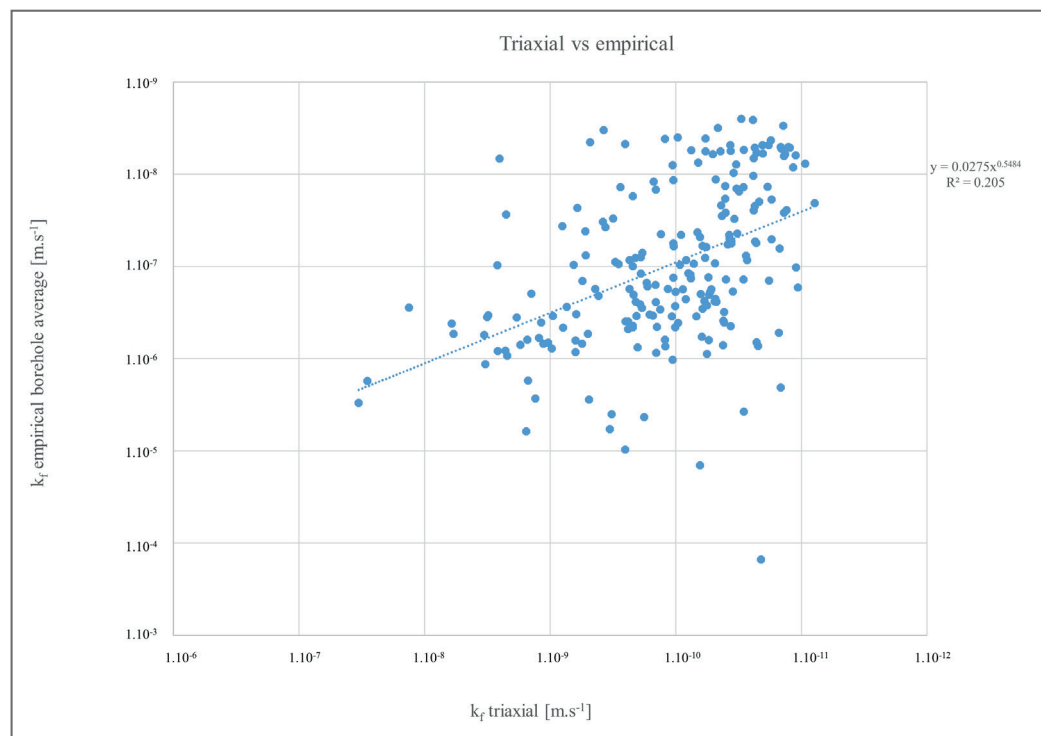


Fig. 4.11 Comparison of the coefficients of hydraulic conductivity determined in a triaxial permeameter with the average values obtained from empirical methods

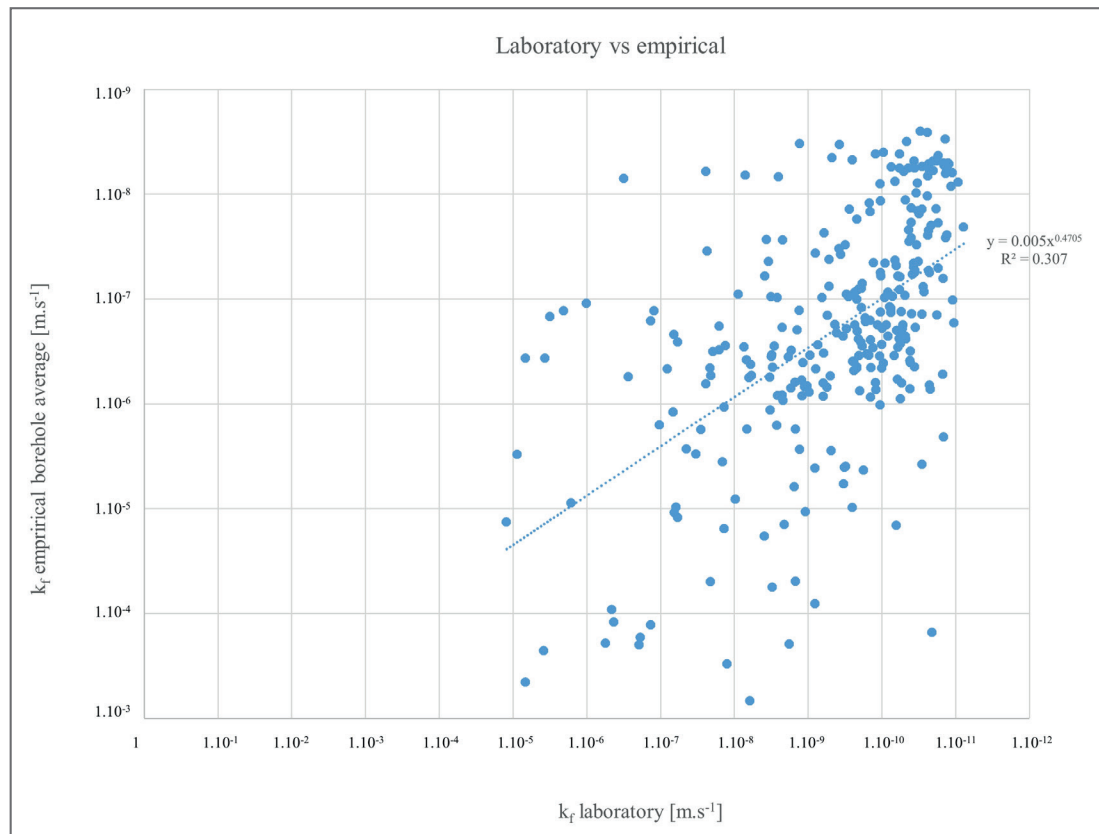


Fig. 4.12 Comparison of the coefficients of hydraulic conductivity in all permeameters with the average values obtained from empirical methods

coefficient  $R^2 = 0.205$  and confirms mutual correlation.

Similar comparison is shown in Fig. 4.12, but in addition to the results in the triaxial permeameter, the results from the constant head and falling head permeameters are included. This set of laboratory determinations is compared with the average values obtained from empirical methods. The value of the correlation coefficient  $R$  for the statistical set of 289 samples for the power trend line is 0.554076, which corresponds to the determination coefficient  $R^2 = 0.307$ . Again, a good correlation is shown.

The laboratory determination of the coefficients of hydraulic conductivity in a triaxial permeameter and constant head and falling head permeameters compared to the average value obtained from all valid empirical methods gives a good correlation due to the high number of samples in the statistical set, confirming the permeability dependence on the grain-size of the soil. Therefore, the values of the coefficient of filtration from the grain-size distribution curves, especially for coarse-grained soils, give at least an approximate idea of the value of the coefficients of hydraulic conductivity that can be expected from permeability tests in laboratory instruments.

The results of this research showed no correlation between the coefficient of hydraulic conductivity values from the hydrodynamic tests, the laboratory tests and the empirical methods. The differences between the tests were in the magnitude of orders and no trends of interdependence or functional relationships were found.

Similar results were obtained in research of Elarabi & Elfaki (2011), who observed a difference between

the permeability measured in the laboratory and the permeability values in the field by one to four orders. Author also attributed the difference to the unrepresentative nature of the laboratory sample to soil under natural conditions. They also found a very good correlation between the laboratory permeability and the relative coefficient between field and laboratory permeability.

Lee & Chang (2007) also found significant differences between the laboratory coefficient of hydraulic conductivity and the in situ permeability. According to them the differences between the results are caused due to the differences in the samples are caused by the inhomogeneity of the soil in the environment and the possibility of water flow in all directions in field tests, whereas in laboratory conditions the flow is only one-directional.

On the contrary Rapp (1965) found a very good correlation between field and laboratory tests. His research was focused specifically on the comparison of field and laboratory methods with sampling adjusted to the research objective.

The reason for our finding is that the geological task “Monitoring of environmental burdens in selected localities of the Slovak Republic” was not focused specifically on the comparison of individual methods of determination of coefficients of hydraulic conductivity. Therefore, sampling of undisturbed samples was not targeted specifically for this purpose, but laboratory samples were taken mostly to determine coefficients of hydraulic conductivity of the fine-grained soils to verify their sealing function. At the same time, the irregular sampling of the soil from



the drill core itself is influenced by an error based on the subjectivity of the sampling selection.

The ratio of fine and coarse fraction samples for drill core sampling was predominantly 3/1, which is why the average values of the coefficient of hydraulic conductivity calculated by laboratory methods and empirical methods are burdened by subjective sampling error or error between proportions of fractions with different hydrogeological function.

On the contrary, hydrodynamic tests characterize the environment around well overall and were carried out in order to determine the water-permeability of the environment, which mainly concerns sandy and gravel soils. The disadvantage of these tests, however, was their short duration, which was a 6-hour test, and therefore can only be considered as indicative, because their results affect only the vicinity of the well, which was in many cases affected by drilling technology. Also the permeability tests in well could be performed in poorly designed and installed monitoring wells with limited measurement capacities as was also claimed by Baptiste & Chapuis (2014).

Although a large number of coefficients of hydraulic conductivity values were obtained to compare them, there were not enough relevant data. The numbers of determination of the coefficients of hydraulic conductivity values by the various methods alone do not guarantee comparable results. For laboratory tests, only very small samples with a diameter of 38 mm and a height of 20 to 50 mm in a triaxial instrument or with a diameter of 100 mm and a height of 90 mm in a constant head and falling head permeameters were used. The results of such tests therefore cover only a very small part of the environment and do not take into account the possible occurrence of disturbances in the natural environment of much larger dimensions that alter the sealing properties of soils or, conversely, their ability to permeate water. It can therefore be stated that laboratory methods for determining the coefficient of hydraulic conductivity are useful in the oriented research of specific horizons at which their sealing function is assumed or verified. Conversely, properly performed hydrodynamic tests can be used specifically to characterize the permeability of the geological environment within a perforated well section. At the same time, the methodological differentiation of both values can also influence the economic aspects of environmental burdens monitoring so that there is no unnecessary duplication.

Based on the results obtained, the statement published by Nagy et al. (2013) that they are not able to express what the coefficient of permeability (coefficient of hydraulic conductivity) of soils is, but only state the value obtained from a certain type of measurement was confirmed. They also accentuated the reliability of individual methods, the capability to sense the layer boundaries and their estimation accuracy.

#### 4.4 Conclusions

The main objective was to evaluate the results of the determination of coefficients of hydraulic conductivity

using hydrodynamic tests, laboratory tests and empirical methods, to compare them and possibly to find correlations between individual methods. The results of 254 hydrodynamic tests were used to calculate the coefficient of hydraulic conductivity, 218 laboratory permeability tests in a triaxial permeameter, 58 tests in a constant head permeameter and 19 tests in a falling head permeameter were performed and laboratory test results of 2,246 samples were used for coefficient of hydraulic conductivity calculation by using empirical methods.

Comparison of the laboratory determination of the coefficients of hydraulic conductivity in the laboratory apparatus compared to the values obtained from empirical methods gives good correlation due to the high number of samples in the statistical set, confirming the dependence of the permeability on the grain-size distribution of the soil.

The results of the comparison of the coefficients of hydraulic conductivity determined by the hydrodynamic tests and the laboratory methods show that no correlations were found either in comparison of the individual methods, nor in relation to the clay fraction, fine-grained fraction, soil type or its genesis. The reason for this is that the selection of individual samples for laboratory tests focuses primarily on less permeable soils, while hydrodynamic tests characterize the overall environment of a well.

In the future, in the case of further research aimed at comparing the coefficients of hydraulic conductivity from hydrodynamic tests with the values of coefficients of hydraulic conductivity from laboratory tests or empirical methods, more attention should be paid to the correct design of the sampling, in order the selected samples would represent the rock environment of the main collector or more collectors. It is also necessary to focus on the correct performance of hydrodynamic tests, especially in terms of pumping time, and avoid to perform just indicative short-term tests.

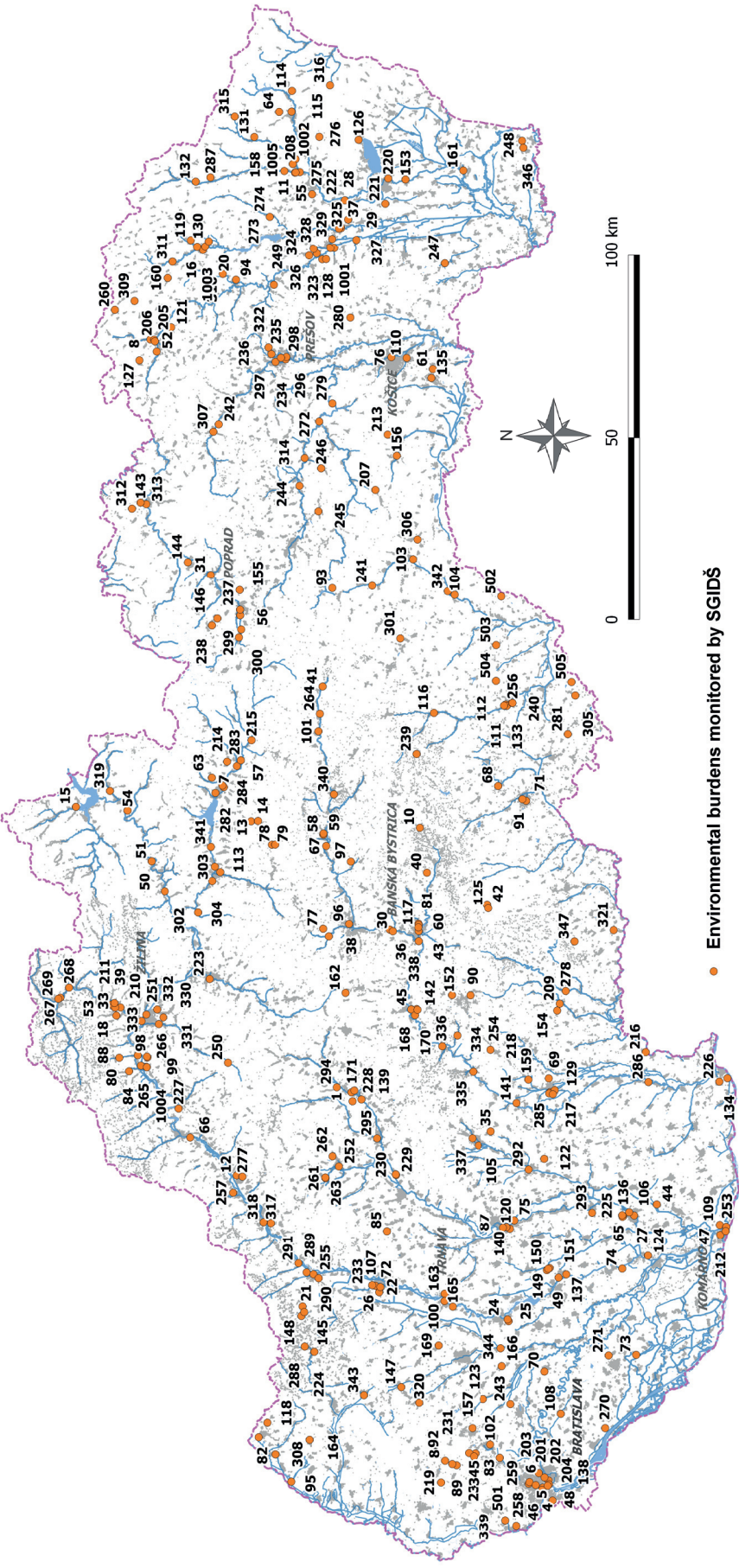
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Map of monitored environmental burdens (at SGIDS)



**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID | Environmental burden                                                | Coord x_jtsk | Coord y_jtsk | ID Slovak Environmental Agency |
|----|---------------------------------------------------------------------|--------------|--------------|--------------------------------|
| 1  | Nováky – Chemical plants (2)                                        | -463209      | -1228520     | SK/EZ/PD/626                   |
| 4  | Bratislava – Chemika (2)                                            | -572101      | -1280930     | SK/EZ/B1/116                   |
| 5  | Bratislava – Gumon (2)                                              | -571942      | -1281047     | SK/EZ/B2/122                   |
| 6  | Bratislava – Juraj Dimitrov chemical plants (2)                     | -570457      | -1277293     | SK/EZ/B3/138                   |
| 7  | Liptovský Mikuláš – Leather plants (2)                              | -379688      | -1193613     | SK/EZ/LM/406                   |
| 8  | Bardejov – Heavy engineering factory (2)                            | -256943      | -1173508     | SK/EZ/BJ/22                    |
| 10 | Hriňová – Heavy engineering factory (2)                             | -390812      | -1247203     | SK/EZ/DT/209                   |
| 11 | Udavské – Coating of bitumen blends (7)                             | -211218      | -1213290     | SK/EZ/HE/261                   |
| 12 | Dubnica nad Váhom – Heavy engineering factory (2)                   | -485976      | -1197183     | SK/EZ/IL/271                   |
| 13 | Lazisko – tailings of Liptovská Dúbrava (6)                         | -389017      | -1201131     | SK/EZ/LM/397                   |
| 14 | Dúbrava – galleries and heaps of Liptovská Dúbrava (6)              | -388923      | -1202967     | SK/EZ/LM/390                   |
| 15 | Zubrohlava – sludge field – Heavy engineering factory Námestovo (2) | -385085      | -1153122     | SK/EZ/NO/541                   |
| 16 | Stropkov – Coating (7)                                              | -232387      | -1187919     | SK/EZ/SP/917                   |
| 18 | Nesluša – landfill (1)                                              | -442288      | -1163974     | SK/EZ/KM/321                   |
| 20 | Stropkov – TESLA (2)                                                | -231488      | -1188491     | SK/EZ/SP/915                   |
| 21 | Nové Mesto nad Váhom – landfill Mnešice – Tušková (1)               | -512735      | -1216258     | SK/EZ/NM/533                   |
| 22 | Piešťany – Chirana (2)                                              | -516851      | -1236436     | SK/EZ/PN/676                   |
| 24 | Sereď – Nickel plant – landfill dump (2)                            | -525645      | -1271459     | SK/EZ/GA/222                   |
| 25 | Sereď – Nickel plant – former factory area (2)                      | -526082      | -1271801     | SK/EZ/GA/221                   |
| 26 | Piešťany – Tesla – contamination plume under the housing estate (2) | -518189      | -1236114     | SK/EZ/PN/675                   |
| 27 | Nové Zámky – Real H.M. – terminal (4)                               | -497372      | -1302917     | SK/EZ/NZ/588                   |
| 28 | Nižný Hrabovec – tailings Bukocel (2)                               | -226076      | -1225790     | SK/EZ/VT/1026                  |
| 29 | Poša – tailings of Chemko Strážske (2)                              | -224087      | -1227840     | SK/EZ/VT/103                   |
| 30 | Sliač – airport – south (4)                                         | -419167      | -1239838     | SK/EZ/ZV/1128                  |
| 31 | Kežmarok – OKTAN (3)                                                | -321490      | -1190097     | SK/EZ/KK/295                   |
| 33 | Kysucké Nové Mesto – NN Slovakia (2)                                | -440059      | -1163866,4   | SK/EZ/KM/315                   |
| 35 | Zlaté Moravce – Calx (2)                                            | -475816      | -1261651     | SK/EZ/ZM/111                   |
| 36 | Zvolen – Bučina – black impregnation (2)                            | -417966      | -1246810     | SK/EZ/ZV/1132                  |
| 37 | Nižný Hrabovec – landfill (1)                                       | -226429      | -1225920     | SK/EZ/VT/1027                  |
| 38 | Banská Bystrica – Chemika (2)                                       | -420550      | -1222360     | SK/EZ/BB/6                     |
| 39 | Kysucké Nové Mesto – KINEX-KLF (2)                                  | -439621      | -1163443     | SK/EZ/KM/312                   |
| 40 | Detva – PPS Group (2)                                               | -403084      | -1249160     | SK/EZ/DT/207                   |
| 41 | Pohorelá – Strojsmalt Holding (2)                                   | -352179      | -1220658     | SK/EZ/BR/69                    |
| 42 | Lešť (military district) – garage yards (5)                         | -411828      | -1265912     | SK/EZ/ZV/1123                  |
| 43 | Zvolen – Bučina – white impregnation (2)                            | -417437      | -1246916,8   | SK/EZ/ZV/1131                  |
| 44 | Bajč – landfill (1)                                                 | -493881      | -1312319     | SK/EZ/KN/324                   |
| 45 | Žiar nad Hronom – ZSNP – former factory area (2)                    | -440551      | -1244825     | SK/EZ/ZH/1102                  |
| 46 | Bratislava – Slovak Gas Company – Votrubova street (3)              | -571557      | -1281119,9   | SK/EZ/B2/131                   |



**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID | Environmental burden                                                                  | Coord x_jtsk | Coord y_jtsk | ID Slovak Environmental Agency |
|----|---------------------------------------------------------------------------------------|--------------|--------------|--------------------------------|
| 47 | Komárno – Slovak Gas Company (3)                                                      | -502019      | -1329909     | SK/EZ/KN/337                   |
| 48 | Bratislava – Matador – former factory area (2)                                        | -575067      | -1283587     | SK/EZ/B5/161                   |
| 49 | Trnovec nad Váhom – RSTO landfill (1)                                                 | -514165      | -1285472     | SK/EZ/SA/804                   |
| 50 | Istebné – OFZ – slag piles (1)                                                        | -408170      | -1177459     | SK/EZ/DK/178                   |
| 51 | Medzibrodie nad Oravou – landfill Široká (1)                                          | -399976      | -1173867     | SK/EZ/DK/180                   |
| 52 | Bardejov – electric station (2)                                                       | -260273      | -1175202     | SK/EZ/BJ/26                    |
| 53 | Kysucké Nové Mesto – KLF – Energetics (2)                                             | -439176      | -1162934     | SK/EZ/KM/313                   |
| 54 | Nižná – OTF – sludge field Malá Orava (2)                                             | -385880      | -1167131     | SK/EZ/TS/969                   |
| 55 | Myslína – old landfill (1)                                                            | -217156      | -1218009     | SK/EZ/HE/254                   |
| 56 | Svit – Chemosvit landfill (1)                                                         | -336559      | -1198390     | SK/EZ/PP/710                   |
| 57 | Podtureň – Žadovica landfill (1)                                                      | -373938      | -1197231     | SK/EZ/LM/417                   |
| 58 | Predajná – industrial landfill Predajná II. (1)                                       | -392716      | -1220871     | SK/EZ/BR/74                    |
| 59 | Predajná – industrial landfill Predajná I. (1)                                        | -392377      | -1220881     | SK/EZ/BR/73                    |
| 60 | Zvolen – Railway repair shops and machinery (4)                                       | -418816      | -1246965     | SK/EZ/ZV/1135                  |
| 61 | Haniska – Slovak Gas Company (3)                                                      | -265049      | -1250782     | SK/EZ/KS/346                   |
| 63 | Veterná Poruba – landfill I. (1)                                                      | -377193      | -1190354     | SK/EZ/LM/424                   |
| 64 | Snina – old landfill (1)                                                              | -194572      | -1208987     | SK/EZ/SV/929                   |
| 65 | Nové Zámky – locomotive depo – diagnostic centre (4)                                  | -496277      | -1304462     | SK/EZ/NZ/1789                  |
| 66 | Lednické Rovne – Podstránie landfill (1)                                              | -475597      | -1184428     | SK/EZ/PU/727                   |
| 67 | Nemecká – Petrochema (2)                                                              | -395786      | -1221633     | SK/EZ/BR/67                    |
| 68 | Kalinovo – phenol pit (Žiaromat) (2)                                                  | -379412      | -1268957     | SK/EZ/PT/720                   |
| 69 | Levice – mall Benzínol (3)                                                            | -463502      | -1282909     | SK/EZ/LV/433                   |
| 70 | Veľké Úľany – landfill (1)                                                            | -539881      | -1281637     | SK/EZ/GA/230                   |
| 71 | Lučenec – Laundry and dry cleaning (7)                                                | -383419      | -1276561     | SK/EZ/LC/371                   |
| 72 | Piešťany – former tractor station (7)                                                 | -517234      | -1236230     | SK/EZ/PN/674                   |
| 73 | Mad – landfill (1)                                                                    | -535273      | -1306724     | SK/EZ/DS/194                   |
| 74 | Neded – former farm (QUEEN) (7)                                                       | -511712      | -1302914     | SK/EZ/SA/795                   |
| 75 | Nitra - illegal release of oil substances at the sewage treatment (Horné Krškany) (3) | -498320      | -1273381     | SK/EZ/NR/557                   |
| 76 | Košice – old gasworks (3)                                                             | -261808      | -1239439     | SK/EZ/K4/364                   |
| 77 | Špania Dolina – flotation treatment plant (6)                                         | -418465      | -1220789     | SK/EZ/BB/17                    |
| 78 | Partizánska Ľupča – galleries and heaps Magurka (6)                                   | -395402      | -1207683     | SK/EZ/LM/416                   |
| 79 | Partizánska Ľupča – tailings Magurka (6)                                              | -395413      | -1206794     | SK/EZ/LM/414                   |
| 80 | Veľké Rovné – landfill I (1)                                                          | -453800      | -1165018     | SK/EZ/BY/113                   |
| 81 | Zvolen – Bučina – old depot (2)                                                       | -417080      | -1246871     | SK/EZ/ZV/1133                  |
| 82 | Skalica – former roller bearing plant (2)                                             | -557783      | -1203171     | SK/EZ/SI/857                   |
| 83 | Svätý Jur – Brestová – landfill (1)                                                   | -563431      | -1269360     | SK/EZ/PK/665                   |
| 84 | Petrovice – Pšurnovice – playground (1)                                               | -459565      | -1168626     | SK/EZ/BY/104                   |
| 85 | Bojná – landfill – part A (1)                                                         | -501153      | -1238308     | SK/EZ/TO/961                   |

**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID  | Environmental burden                                              | Coord x <sub>jtsk</sub> | Coord y <sub>jtsk</sub> | ID Slovak Environmental Agency |
|-----|-------------------------------------------------------------------|-------------------------|-------------------------|--------------------------------|
| 86  | Pernek – old mining works (6)                                     | -564233                 | -1254939                | SK/EZ/MA/467                   |
| 87  | Nitra – locomotive depo (Cargo) (4)                               | -500278                 | -1270600                | SK/EZ/NR/559                   |
| 88  | Hlboké nad Váhom – landfill II (1)                                | -453692                 | -1172674                | SK/EZ/BY/98                    |
| 89  | Pernek – Dolná Karol adit and heap (6)                            | -565534                 | -1257410                | SK/EZ/MA/466                   |
| 90  | Banská Štiavnica – Lintich tailings (6)                           | -436679                 | -1261109                | SK/EZ/BS/85                    |
| 91  | Lučenec – Marián Šustek – M Fruit (3)                             | -383003                 | -1275550                | SK/EZ/LC/370                   |
| 92  | Pernek – Pavol adit and heap (6)                                  | -564910                 | -1256585                | SK/EZ/MA/468                   |
| 93  | Dobšiná – Bingarten landfill (1)                                  | -325221                 | -1223290                | SK/EZ/RV/779                   |
| 94  | Giraltovce – landfill (1)                                         | -240595                 | -1196972                | SK/EZ/SK/866                   |
| 95  | Unín – oil collection centre Cunín (3)                            | -569888                 | -1212086                | SK/EZ/SI/863                   |
| 96  | Banská Bystrica – former galvanizing shop LOBB (2)                | -417238                 | -1227977                | SK/EZ/BB/1                     |
| 97  | Lubietová – Podlipa (6)                                           | -400245                 | -1228733                | SK/EZ/BB/12                    |
| 98  | Kotešová – landfill (1)                                           | -452408                 | -1169950                | SK/EZ/BY/101                   |
| 99  | Hlboké nad Váhom – landfill V (under the birch) (1)               | -453439                 | -1172571                | SK/EZ/BY/97                    |
| 100 | Hlohovec – Šulekovo – landfill (1)                                | -520667                 | -1253880                | SK/EZ/HC/243                   |
| 101 | Polomka – wood plant (2)                                          | -364407                 | -1219524                | SK/EZ/BR/71                    |
| 102 | Pezinok – stream Mahulianka (3)                                   | -559765                 | -1266747                | SK/EZ/PK/663                   |
| 103 | Rožňava – plume of chlorinated hydrocarbons at barracks (2)       | -317114                 | -1245099                | SK/EZ/RV/786                   |
| 104 | Plešivec – retention ponds (2)                                    | -327072                 | -1256755                | SK/EZ/RV/785                   |
| 105 | Čierne Kľačany – landfill (under the apple orchard) (1)           | -473930                 | -1266908                | SK/EZ/ZM/110                   |
| 106 | Nové Zámky – Former Barracks of the Soviet Army – Novocentrum (5) | -496923                 | -1306096                | SK/EZ/NZ/585                   |
| 107 | Piešťany – oil refuelling station (3)                             | -516445                 | -1235095                | SK/EZ/PN/678                   |
| 108 | Zlaté Klasy – landfill (1)                                        | -551380                 | -1286106                | SK/EZ/DS/206                   |
| 109 | Komárno – Madzagoš landfill (1)                                   | -499605                 | -1329581                | SK/EZ/KN/336                   |
| 110 | Košice – Eastern Slovakia Engineering Works (2)                   | -262042                 | -1243627                | SK/EZ/K4/365                   |
| 111 | Rimavská Sobota – Slovak Sugar Factory (3)                        | -357466                 | -1271274                | SK/EZ/RS/768                   |
| 112 | Rimavská Sobota – Gemer nákup (3)                                 | -357128                 | -1271009                | SK/EZ/RS/767                   |
| 113 | Ružomberok – brick factory (2)                                    | -402964                 | -1192633                | SK/EZ/RK/753                   |
| 114 | Stakčín – landfill (1)                                            | -188832                 | -1212473                | SK/EZ/SV/934                   |
| 115 | Belá nad Cirochou – landfill (1)                                  | -198738                 | -1215177                | SK/EZ/SV/922                   |
| 116 | Hnúšťa – former SLZ factory (2)                                   | -359394                 | -1251072                | SK/EZ/RS/756                   |
| 117 | Sliač – airport – pipeline (3)                                    | -418771                 | -1239025                | SK/EZ/ZV/1129                  |
| 118 | Skalica – landfill Zlatnícka dolina Valley (1)                    | -553827                 | -1205583                | SK/EZ/SI/860                   |
| 119 | Chotča – landfill (1)                                             | -229758                 | -1184529                | SK/EZ/SP/912                   |
| 120 | Nitra – former fuel depots on the Novozámocká Road (3)            | -500162                 | -1271223                | SK/EZ/NR/553                   |
| 121 | Komárov – Lukavica landfill (1)                                   | -253644                 | -1179249                | SK/EZ/BJ/36                    |
| 122 | Vráble – landfill (part Židová) (1)                               | -481406                 | -1281569                | SK/EZ/NR/567                   |
| 123 | Báhoň – landfill (1)                                              | -547367                 | -1264735                | SK/EZ/PK/640                   |



**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID  | Environmental burden                                       | Coord x_jtsk | Coord y_jtsk | ID Slovak Environmental Agency |
|-----|------------------------------------------------------------|--------------|--------------|--------------------------------|
| 124 | Kolárovo – landfill Pačérok (1)                            | -508142      | -1309915     | SK/EZ/KN/333                   |
| 125 | Lešť (military district) – main camp (5)                   | -412765      | -1266218     | SK/EZ/ZV/1124                  |
| 126 | Jovsa – landfill (1)                                       | -202233      | -1230702     | SK/EZ/MI/485                   |
| 127 | Zlaté – landfill (1)                                       | -262725      | -1170369     | SK/EZ/BJ/54                    |
| 128 | Čaklov – landfill (1)                                      | -234915      | -1221598     | SK/EZ/VT/101                   |
| 129 | Levice – Levitex (2)                                       | -462533      | -1284520     | SK/EZ/LV/432                   |
| 130 | Stropkov – poison cemetery Vojtovce (2)                    | -230063      | -1189420     | SK/EZ/SP/916                   |
| 131 | Papín – landfill (1)                                       | -201424      | -1202207     | SK/EZ/HE/256                   |
| 132 | Krásny Brod – Monastýr landfill (1)                        | -213557      | -1185619     | SK/EZ/ML/503                   |
| 133 | Rimavská Sobota – Heavy engineering factory (2)            | -357386      | -1270577     | SK/EZ/RS/766                   |
| 134 | Štúrovo – former JCP, asphalt and oil storage facility (2) | -459362      | -1331690     | SK/EZ/NZ/595                   |
| 135 | Košice – U.S. Steel (2)                                    | -267680      | -1250596     | SK/EZ/K2/362                   |
| 136 | Nové Zámky – landfill (1)                                  | -497055      | -1303194     | SK/EZ/NZ/587                   |
| 137 | Trnovec nad Váhom – tailings Amerika I (2)                 | -513322      | -1287571     | SK/EZ/SA/803                   |
| 138 | Bratislava – Malý Dunaj – influx object (2)                | -570618      | -1282824     | SK/EZ/B2/123                   |
| 139 | Bystričany – ENO – temporary tailings (2)                  | -465166      | -1231271     | SK/EZ/PD/623                   |
| 140 | Nitra – Katruša landfill (1)                               | -500586      | -1272164     | SK/EZ/NR/560                   |
| 141 | Tlmače – SES (2)                                           | -466212      | -1273955     | SK/EZ/LV/449                   |
| 142 | Žiar nad Hronom – ZSNP sludge field (2)                    | -442201      | -1245889     | SK/EZ/ZH/1097                  |
| 143 | Stará Ľubovňa – Skalka landfill (1)                        | -301601      | -1170798     | SK/EZ/SL/890                   |
| 144 | Spišská Belá – landfill (1)                                | -317951      | -1183812     | SK/EZ/KK/300                   |
| 145 | Stará Turá – Chirana (2)                                   | -523608      | -1215630     | SK/EZ/NM/534                   |
| 146 | Veľký Slavkov – landfill Under the farm (1)                | -333532      | -1191871     | SK/EZ/PP/716                   |
| 147 | Smolenice – Chemolak (2)                                   | -544186      | -1241935     | SK/EZ/TT/981                   |
| 148 | Lubina – Palčekové landfill (1)                            | -522054      | -1215173     | SK/EZ/NM/526                   |
| 149 | Šaľa – Duslo – production of LAD and ammonium nitrate (2)  | -511816      | -1282606     | SK/EZ/SA/798                   |
| 150 | Šaľa – Duslo – nitric acid production (2)                  | -511795      | -1282628     | SK/EZ/SA/797                   |
| 151 | Šaľa – Duslo – production of rubber chemicals (2)          | -511805      | -1282597     | SK/EZ/SA/796                   |
| 152 | Banská Belá – Sedem žien tailings (6)                      | -436630      | -1256014     | SK/EZ/BS/79                    |
| 153 | Lastomír – landfill (1)                                    | -213130      | -1243545     | SK/EZ/MI/486                   |
| 154 | Hontianske Tesáre – landfill (1)                           | -440933      | -1285025     | SK/EZ/KA/289                   |
| 155 | Žakovce – Úsvit landfill (1)                               | -325731      | -1197977     | SK/EZ/KK/310                   |
| 156 | Medzev – Strojsmalt (2)                                    | -296955      | -1239329     | SK/EZ/KS/349                   |
| 157 | Modra – Hliny – landfill (1)                               | -555205      | -1261599     | SK/EZ/PK/645                   |
| 158 | Udavské – Janov dol landfill (1)                           | -208867      | -1212736     | SK/EZ/HE/262                   |
| 159 | Levice – landfill Levitex – Nixbrod (1)                    | -459394      | -1282797     | SK/EZ/LV/436                   |
| 160 | Hrabovčik – landfill (1)                                   | -240102      | -1178318     | SK/EZ/SK/867                   |
| 161 | Vojany – EVO tailings (2)                                  | -210611      | -1259356     | SK/EZ/MI/498                   |

**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID  | Environmental burden                                          | Coord x_jtsk | Coord y_jtsk | ID Slovak Environmental Agency |
|-----|---------------------------------------------------------------|--------------|--------------|--------------------------------|
| 162 | Kremnické Bane – sheepfold (7)                                | -436017      | -1226911     | SK/EZ/ZH/1092                  |
| 163 | Hlohovec – industrial park (2)                                | -518594      | -1254000     | SK/EZ/HC/241                   |
| 164 | Unín – landfill (1)                                           | -558302      | -1217074     | SK/EZ/SI/862                   |
| 165 | Hlohovec – Šulekovo – Fe-sludge (2)                           | -522099      | -1256223     | SK/EZ/HC/242                   |
| 166 | Majcichov – landfill (1)                                      | -533491      | -1269579     | SK/EZ/TT/979                   |
| 168 | Žiar nad Hronom – ZSNP old industrial landfill (1)            | -440436      | -1246428     | SK/EZ/ZH/1101                  |
| 169 | Špačince – landfill (1)                                       | -532746      | -1252365     | SK/EZ/TT/982                   |
| 170 | Žiar nad Hronom – Horné Opatovce landfill (1)                 | -440582      | -1246537     | SK/EZ/ZH/1100                  |
| 171 | Zemianske Kostolany – Xella (2)                               | -456973      | -1229023     | SK/EZ/PD/634                   |
| 201 | Bratislava – Ružinov – Čierny les (2)                         | -569573      | -1282711     | SK/EZ/B2/120                   |
| 202 | Bratislava – Ružinov – Central freight station (4)            | -568721      | -1281604     | SK/EZ/B2/133                   |
| 203 | Bratislava – Vrakuňa – CHZJD landfill (1)                     | -567560      | -1280050     | SK/EZ/B2/136                   |
| 204 | Bratislava – Ružinov – Harbor (4)                             | -571007      | -1282494     | SK/EZ/B2/1904                  |
| 205 | Bardejov – JAS (2)                                            | -257028      | -1174540     | SK/EZ/BJ/23                    |
| 206 | Bardejov – SNAHA (2)                                          | -257452      | -1174748     | SK/EZ/BJ/24                    |
| 207 | Smolník – pyrite ores (6)                                     | -298127      | -1235055     | SK/EZ/GL/237                   |
| 208 | Rovné – farm area (7)                                         | -207513      | -1213456     | SK/EZ/HE/260                   |
| 209 | Hontianske Tesáre – agrochemical warehouse, poultry house (1) | -438981      | -1285777     | SK/EZ/KA/1742                  |
| 210 | Kysucké Nové Mesto – city landfill (1)                        | -440014      | -1165330     | SK/EZ/KM/314                   |
| 211 | Kysucké Nové Mesto – landfill at Secondary school (1)         | -438796      | -1163664     | SK/EZ/KM/318                   |
| 212 | Komárno – Harčáš (1)                                          | -500080      | -1331330     | SK/EZ/KN/335                   |
| 213 | Poproč – Petrova dolina Valley (6)                            | -282993      | -1238424     | SK/EZ/KS/353                   |
| 214 | Jamník – barracks and Mokrad' airport (5)                     | -372730      | -1194516     | SK/EZ/LM/1909                  |
| 215 | Kráľova Lehota – landfill III (1)                             | -366863      | -1201219     | SK/EZ/LM/395                   |
| 216 | Bielovce – pesticide storage (1)                              | -452235      | -1309306     | SK/EZ/LV/428                   |
| 217 | Levice – laundry and dry cleaning (7)                         | -463753      | -1283881     | SK/EZ/LV/434                   |
| 218 | Nová Dedina – pesticide storage (1)                           | -459758      | -1277179     | SK/EZ/LV/438                   |
| 219 | Kuchyňa – airport (5)                                         | -570133      | -1253016     | SK/EZ/MA/459                   |
| 220 | Michalovce – city barracks – autopark (5)                     | -212816      | -1238783     | SK/EZ/MI/1905                  |
| 221 | Pozdišovce – objects of former state material reserves (7)    | -219751      | -1238007     | SK/EZ/MI/1913                  |
| 222 | Strážske – Chemko – waste channel (2)                         | -218806      | -1226945     | SK/EZ/MI/494                   |
| 223 | Martin – SNP barracks (5)                                     | -432215      | -1189765     | SK/EZ/MT/512                   |
| 224 | Myjava – dump of galvanic sludge – Holíčov vrch (1)           | -534450      | -1218380     | SK/EZ/MY/521                   |
| 225 | Nové Zámky – traction power station (2)                       | -496879      | -1302870     | SK/EZ/NZ/1911                  |
| 226 | Štúrovo – main railway station (4)                            | -460313      | -1329431     | SK/EZ/NZ/598                   |
| 227 | Považská Bystrica – former Považské Engineering Works (2)     | -467678      | -1181284     | SK/EZ/PB/1894                  |
| 228 | Zemianske Kostolany – army area (5)                           | -465686      | -1228829     | SK/EZ/PD/636                   |
| 229 | Bošany – tannery dump I (2)                                   | -485863      | -1240740     | SK/EZ/PE/1874                  |



**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID  | Environmental burden                                           | Coord x_jtsk | Coord y_jtsk | ID Slovak Environmental Agency |
|-----|----------------------------------------------------------------|--------------|--------------|--------------------------------|
| 230 | Bošany – tannery dump II (2)                                   | -485689      | -1240633     | SK/EZ/PE/637                   |
| 231 | Pezinok – ore mines and old mines (6)                          | -562068      | -1260702     | SK/EZ/PK/654                   |
| 232 | Pezinok – Rudné bane – tailings (6)                            | -562177      | -1262448     | SK/EZ/PK/656                   |
| 233 | Piešťany – barracks (5)                                        | -516250      | -1234200     | SK/EZ/PN/677                   |
| 234 | Prešov – Sokolovské barracks (5)                               | -263085      | -1207752     | SK/EZ/PO/1898                  |
| 235 | Prešov – Duklianske barracks (5)                               | -261949      | -1209260     | SK/EZ/PO/1899                  |
| 236 | Prešov – airport (4)                                           | -259116      | -1205859     | SK/EZ/PO/1907                  |
| 237 | Poprad – Railway station (4)                                   | -331146      | -1198085     | SK/EZ/PP/1447                  |
| 238 | Vysoké Tatry – landfill Pod lesom (1)                          | -335471      | -1190394     | SK/EZ/PP/718                   |
| 239 | Utekáč – former Clara glassworks (2)                           | -370642      | -1246340     | SK/EZ/PT/1786                  |
| 240 | Rimavská Sobota – area after Soviet Army – Industrial park (5) | -356630      | -1272708     | SK/EZ/RS/1980                  |
| 241 | Nižná Slaná – mining plant and surroundings (6)                | -324549      | -1234194     | SK/EZ/RV/784                   |
| 242 | Rožkovany – plume of chlorinated hydrocarbons (2)              | -280162      | -1192249     | SK/EZ/SB/811                   |
| 243 | Boldog – pesticide storage (1)                                 | -548730      | -1272280     | SK/EZ/SC/813                   |
| 244 | Markušovce – ore mining (6)                                    | -297009      | -1214298     | SK/EZ/SN/898                   |
| 245 | Rudňany – ore mining and processing (6)                        | -303984      | -1219510     | SK/EZ/SN/899                   |
| 246 | Slovinky – ore mining and processing (6)                       | -292219      | -1220252     | SK/EZ/SN/900                   |
| 247 | Čel'ovce – pesticide storage (1)                               | -236062      | -1254059     | SK/EZ/TV/989                   |
| 248 | Čierna nad Tisou – transshipment station (4)                   | -202487      | -1275412     | SK/EZ/TV/990                   |
| 249 | Merník – mercury mines (6)                                     | -233904      | -1216960     | SK/EZ/VT/1024                  |
| 250 | Fačkov – landfill (1)                                          | -455139      | -1194777     | SK/EZ/ZA/1053                  |
| 251 | Žilina – eastern industrial zone (2)                           | -441957      | -1172400     | SK/EZ/ZA/1070                  |
| 252 | Bánovce nad Bebravou – Railway station (4)                     | -483512      | -1225084     | SK/EZ/BN/57                    |
| 253 | Komárno – area abandoned by the Soviet Army (5)                | -501240      | -1331180     | SK/EZ/KN/334                   |
| 254 | Pukanec – sludge dump Hampoch (1)                              | -451591      | -1266828     | SK/EZ/LV/441                   |
| 255 | Nové Mesto nad Váhom – area of military unit (5)               | -514369      | -1219550     | SK/EZ/NM/530                   |
| 256 | Rimavská Sobota – area abandoned by the Soviet Army (5)        | -356675      | -1272870     | SK/EZ/RS/1979                  |
| 257 | Nemšová – military unit (5)                                    | -490718      | -1196176     | SK/EZ/TN/945                   |
| 258 | Bratislava – Ružinov – chemical dry cleaner (2)                | -570830      | -1279200     | SK/EZ/B2/124                   |
| 259 | Bratislava – Nové Mesto – Heating plant II (2)                 | -570000      | -1277500     | SK/EZ/B3/140                   |
| 260 | Nižná Polianka – stock of agrochemicals (1)                    | -248833      | -1163777     | SK/EZ/BJ/44                    |
| 261 | Dežerice – VAB tailings (2)                                    | -486730      | -1221445     | SK/EZ/BN/1926                  |
| 262 | Horné Naštice – fly ash dump (1)                               | -480740      | -1223337     | SK/EZ/BN/55                    |
| 263 | Dežerice – Veronika tailings (1)                               | -486542      | -1221373     | SK/EZ/BN/58                    |
| 264 | Závadka nad Hronom – Poľnospol Plus area (7)                   | -359640      | -1219912     | SK/EZ/BR/78                    |
| 265 | Bytča – former Slovak bus transportation (4)                   | -455928      | -1170902     | SK/EZ/BY/89                    |
| 266 | Bytča – KK NEFT (2)                                            | -456278      | -1172377     | SK/EZ/BY/93                    |
| 267 | Čadca – Slovak bus transportation (4)                          | -437334      | -1148853     | SK/EZ/CA/168                   |

**List of 309 monitored environmental burdens (at SGIDŠ)**

| ID  | Environmental burden                                                  | Coord x <sub>jtsk</sub> | Coord y <sub>jtsk</sub> | ID Slovak Environmental Agency |
|-----|-----------------------------------------------------------------------|-------------------------|-------------------------|--------------------------------|
| 268 | Oščadnica – FRACHO (2)                                                | -434584                 | -1151254                | SK/EZ/CA/173                   |
| 269 | Čadca – AVC – supermarket (2)                                         | -437635                 | -1148298                | SK/EZ/CA/1959                  |
| 270 | Báč – former STS (4)                                                  | -555278                 | -1298205                | SK/EZ/DS/182                   |
| 271 | Malé Dvorníky – pesticide storage (1)                                 | -535449                 | -1299144                | SK/EZ/DS/195                   |
| 272 | Margecany – Locomotive depo, Cargo (4)                                | -279405                 | -1219708                | SK/EZ/GL/1879                  |
| 273 | Košarovce – Pastovník – fuel storage (3)                              | -223352                 | -1206421                | SK/EZ/HE/249                   |
| 274 | Lubiša – farm area (7)                                                | -210781                 | -1210384                | SK/EZ/HE/251                   |
| 275 | Udavské – railway station (4)                                         | -211094                 | -1214637                | SK/EZ/HE/264                   |
| 276 | Valaškovce (military area) – washbasin (4)                            | -201425                 | -1219965                | SK/EZ/HE/265                   |
| 277 | Dubnica nad Váhom – ZVS (2)                                           | -486313                 | -1198723                | SK/EZ/IL/272                   |
| 278 | Rykynčice – stock of old agrochemicals (1)                            | -435510                 | -1287415                | SK/EZ/KA/291                   |
| 279 | Malá Lodina – dam Ružín (7)                                           | -274456                 | -1223311                | SK/EZ/KS/1998                  |
| 280 | Kecеровce – landfill Kecеровské Pekľany II (1)                        | -250949                 | -1228231                | SK/EZ/KS/347                   |
| 281 | Šurice – former farm – pesticide storage (1)                          | -365207                 | -1287990                | SK/EZ/LC/373                   |
| 282 | Liptovský Mikuláš – Locomotive depo, Cargo (4)                        | -381276                 | -1191351                | SK/EZ/LM/1884                  |
| 283 | Liptovský Hrádok – Rettenmeier Tatra Timber (2)                       | -372362                 | -1198282                | SK/EZ/LM/403                   |
| 284 | Liptovský Mikuláš – Velvetex (2)                                      | -379246                 | -1193240                | SK/EZ/LM/410                   |
| 285 | Levice – Slovak Railways – surroundings of aboveground reservoirs (2) | -463168                 | -1283167                | SK/EZ/LV/437                   |
| 286 | Pohronský Ruskov – black oil industry of former sugar refinery (4)    | -460424                 | -1310037                | SK/EZ/LV/440                   |
| 287 | Čabiny – farm area (7)                                                | -212529                 | -1189893                | SK/EZ/ML/500                   |
| 288 | Myjava – former SAM (2)                                               | -533013                 | -1215748                | SK/EZ/MY/519                   |
| 289 | Nové Mesto nad Váhom – locomotive depo (4)                            | -513288                 | -1218158                | SK/EZ/NM/532                   |
| 290 | Stará Turá – Drahý vrch landfill (1)                                  | -524678                 | -1214826                | SK/EZ/NM/535                   |
| 291 | Trenčianske Bohuslavice – Hydrostav (2)                               | -510241                 | -1214040                | SK/EZ/NM/536                   |
| 292 | Vráble – Tesla (TESGAL) (2)                                           | -484365                 | -1277245                | SK/EZ/NR/566                   |
| 293 | Šurany – former ELITEX and STS (2)                                    | -496222                 | -1294619                | SK/EZ/NZ/605                   |
| 294 | Nováky – Military repair business (5)                                 | -461850                 | -1224500                | SK/EZ/PD/628                   |
| 295 | Partizánske – ZDA – store of chemicals (3)                            | -475827                 | -1235527                | SK/EZ/PE/639                   |
| 296 | Prešov – former ZPA (2)                                               | -262377                 | -1210538                | SK/EZ/PO/689                   |
| 297 | Prešov – panel industry (2)                                           | -260942                 | -1206646                | SK/EZ/PO/690                   |
| 298 | Prešov – Solivary (2)                                                 | -261737                 | -1210750                | SK/EZ/PO/693                   |
| 299 | Poprad – fuel pump station – Slovak bus transportation (3)            | -332711                 | -1198112                | SK/EZ/PP/700                   |
| 300 | Svit – fuel pump station (3)                                          | -338754                 | -1197768                | SK/EZ/PP/709                   |
| 301 | Magnezitovce – pesticide storage (1)                                  | -339036                 | -1241871                | SK/EZ/RA/733                   |
| 302 | Lubochňa – forest area (7)                                            | -414009                 | -1186614                | SK/EZ/RK/742                   |
| 303 | Ružomberok – SCP area – SUPRA plant (2)                               | -401452                 | -1191184                | SK/EZ/RK/747                   |
| 304 | Ružomberok – area TEXICOM – black oil management (2)                  | -405359                 | -1190485                | SK/EZ/RK/748                   |
| 305 | Jestice – pesticide storage (1)                                       | -354630                 | -1290045                | SK/EZ/RS/762                   |



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| ID  | Environmental burden                                          | Coord x_jtsk | Coord y_jtsk | ID Slovak Environmental Agency |
|-----|---------------------------------------------------------------|--------------|--------------|--------------------------------|
| 306 | Krásnohorské Podhradie – sarcophagus under Kaplna (7)         | -311699      | -1246575     | SK/EZ/RV/783                   |
| 307 | Lipany – ZVL area (2)                                         | -282202      | -1190783     | SK/EZ/SB/808                   |
| 308 | Holíč – oil-fired boiler room (7)                             | -562446      | -1207768     | SK/EZ/SL/852                   |
| 309 | Dubová – stock of agrochemicals (1)                           | -246399      | -1169149     | SK/EZ/SK/864                   |
| 310 | Soboš – stock of agrochemicals (1)                            | -239002      | -1193345     | SK/EZ/SK/875                   |
| 311 | Stročín – former chemical cleaning (2)                        | -235623      | -1179615     | SK/EZ/SK/876                   |
| 312 | Jarabina – stock of agrochemicals (1)                         | -303251      | -1168447     | SK/EZ/SL/883                   |
| 313 | Stará Ľubovňa – SKRUTKÁREŇ – EXIM (2)                         | -302023      | -1172391     | SK/EZ/SL/891                   |
| 314 | Krompachy – Kovohuty (2)                                      | -289402      | -1215735     | SK/EZ/SN/897                   |
| 315 | Osadné – pesticide storage (1)                                | -195862      | -1196516     | SK/EZ/SV/926                   |
| 316 | Strihovce – stock of chemicals of former farm Podvihorlat (1) | -187300      | -1222870     | SK/EZ/SV/935                   |
| 317 | Trenčín – Air Repair Shops (4)                                | -499067      | -1206515     | SK/EZ/TN/957                   |
| 318 | Trenčín – Slovak bus transportation (4)                       | -498796      | -1204498     | SK/EZ/TN/959                   |
| 319 | Trstená – former fuel storage Hámričky (3)                    | -380720      | -1162440     | SK/EZ/TS/973                   |
| 320 | Horné Orešany – Majdan – former chemical factory (2)          | -548362      | -1247043     | SK/EZ/TT/977                   |
| 321 | Veľká Čalomija – pesticide storage (1)                        | -418840      | -1300534     | SK/EZ/VK/1003                  |
| 322 | Bystre – former brick factory TEMAKO (7)                      | -241976      | -1207333     | SK/EZ/VT/1007                  |
| 323 | Čaklov – former farm area (7)                                 | -234973      | -1220542     | SK/EZ/VT/1009                  |
| 324 | Čičava – farm area (7)                                        | -232083      | -1218209     | SK/EZ/VT/1011                  |
| 325 | Hencovce – Bukocel – extraction of black oil (2)              | -226557      | -1225335     | SK/EZ/VT/1016                  |
| 326 | Komárany – stock of agrochemicals (1)                         | -233325      | -1219033     | SK/EZ/VT/1021                  |
| 327 | Sačurov – old steam mill (2)                                  | -229710      | -1230091     | SK/EZ/VT/1032                  |
| 328 | Vranov nad Topľou – Čemerné – brick factory (2)               | -231842      | -1223851     | SK/EZ/VT/1042                  |
| 329 | Vranov nad Topľou – Petrol station Dlhá ulica (3)             | -229454      | -1223467     | SK/EZ/VT/1045                  |
| 330 | Rosina – fly ash dump – tailing pond (1)                      | -442726      | -1177075     | SK/EZ/ZA/1062                  |
| 331 | Žilina – ZVL (2)                                              | -444569      | -1175813     | SK/EZ/ZA/1067                  |
| 332 | Žilina – Trnové – fly ash dump (2)                            | -440570      | -1175360     | SK/EZ/ZA/1840                  |
| 333 | Žilina – locomotive depo, Cargo (4)                           | -443734      | -1171117     | SK/EZ/ZA/1882                  |
| 334 | Hodruša-Hámre – Sandrik (2)                                   | -447688      | -1257504     | SK/EZ/ZC/1074                  |
| 335 | Nová Baňa – former Technical Glass Works (2)                  | -457576      | -1261832     | SK/EZ/ZC/1077                  |
| 336 | Žarnovica – former Preglejka (2)                              | -450639      | -1253362     | SK/EZ/ZC/1081                  |
| 337 | Zlaté Moravce – locomotive depo (4)                           | -477786      | -1263337     | SK/EZ/ZM/1118                  |
| 338 | Zvolen – army objects (5)                                     | -421876      | -1246923     | SK/EZ/ZV/1805                  |
| 339 | Bratislava – Devínska Nová Ves – quarry Srdce (2)             | -582001      | -1273892     | SK/EZ/B4/147                   |
| 340 | Brezno – Slovak Railways (4)                                  | -381656      | -1223727     | SK/EZ/BR/61                    |
| 342 | Plešivec – locomotive depo, Cargo (4)                         | -326080      | -1254853     | SK/EZ/RV/1858                  |
| 343 | Jablonica – depo (4)                                          | -546305      | -1231942     | SK/EZ/SE/831                   |
| 344 | Voderady – landfill (1)                                       | -538372      | -1269889     | SK/EZ/TT/1847                  |

**List of 309 monitored environmental burdens (at SGIDŠ)**

| <b>ID</b> | <b>Environmental burden</b>                                 | <b>Coord x_jtsk</b> | <b>Coord y_jtsk</b> | <b>ID Slovak Environmental Agency</b> |
|-----------|-------------------------------------------------------------|---------------------|---------------------|---------------------------------------|
| 346       | Čierna nad Tisou – locomotive depo, Cargo (4)               | -204427             | -1275767            | SK/EZ/TV/1861                         |
| 501       | Bratislava – Devínska Nová Ves – landfill at Volkswagen (1) | -580506             | -1270858            | SK/EZ/B4/152                          |

Explanations:

1 – waste disposal facilities, 2 – industrial production, 3 – storage and distribution of goods, 4 – transportation, 5 – military base, 6 – mining of mineral resources, 7 – other



## Instructions to authors

### General instructions

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### Text layout

The text should be arranged as follows: full name of the author(s); title of the paper, number of supplements (in brackets, below the title, e.g. 5 figs., 4 tabs.); key words - maximum 6 key words arranged successively from general to special terms; abstract (max. 300 words presenting principal results, without references); in a footnote of the first page, name of the author(s) as well as her/his/their professional or private address.

The extent of the article is limited to 30 manuscript pages including references, figures and explanations. Publishing of longer articles must be agreed by the Editorial Board.

The text of the paper should be logically divided. Text must be sectionalized by headlines, the position of the main headlines is in the centre of the page, associated headlines start from the left side of the page. The hierarchy of headings can contain maximum three levels (1 - highest level, 2 - lower, 3 - lowermost), being indicated by pencil at the particular heading. Text of the article has to contain the introduction, characterization (state) of investigated problem, used methodology, obtained data, discussion, conclusion and references.

The references in the text should be used preferably in parentheses. Names of cited authors in the text are written without first names or initials (e.g. Matula, 1969); the names of the co-authors are divided (e.g. Mišík & Sýkora, 1981). The name(s) is followed by a comma. If there are more authors, the first one, or the first two only are cited, adding et al. and publication year.

**Mathematical and physical symbols** of units, such as m, °C should be preceded by a space, e.g. 20 m, 50 °C, etc. In the case of % and ‰, the exemption shall be made: 10%, 2‰. SI units are preferred. Abbreviations of the units such as second, liter, etc. should be written without a period. Compass readings may be substitute by the abbreviations E, W, NW, SSE, etc. Brackets (parentheses) are to be indicated as should be printed, i.e. square brackets, parentheses or compound. Dashes should be typed as double hyphens. Please, use comma, as a 3-digit group separator (10,000) and decimal point, as separator of the fractional part of decimal number (0.1)

Text of the article must be sent to Editorial office printed in two copies with line spacing 2, as well as on CD. Please for using preferable MS Word editor for PC. Figs. and Tabs. must be delivered in digital form in separate files. Paragraphs are marked with 1 tab space from the left margin, or by a typographic symbol. Greek character in the text must be visualized in the text by its name [e.g. Ω (omega)]. Indices and exponents should be properly marked.

### Figures and tables

The high quality of illustrations is required. Their aim is the most effective documenting and explaining the text. When drawing them by hand or computer their maximum width 81 mm (width of column) or 170 mm (width of page) must be taken into account. Properly adapted figure (dimensions of letters, thickness of lines) can be reproduced also in the scale 1: 1, but there is recommended to prepare figures in larger scale. The pen-drawn figures must be prepared by black ink using the template for figures. The minimum acceptable size of capitals and numbers in camera-ready figure is 2 mm. Maximum dimension of illustration in journal is 170 x 240 mm. Overlapping of illustrations should be avoided.

Figures compiled using the computer must be printed by high resolution laser printer (min. 300 DPI). For figures drawing the editorial office recommends the Corel Draw software. The very thin lines (hair lines) as well as automatic filling of objects are not allowed. The filling must consist from separately set objects. The raster-type filling of planes is either appropriate.

Each illustration including photographs must contain graphic (metric) scale. Grouped figures, e.g. photographs and diagrams must be compiled as one figure with separate parts designated a, b, c, etc. They are referred to as one picture.

Photographs must be sharp, preferably black & white, contrast, in the form of JPG or TIFF files having resolution of at least 600 DPI.

All figures must contain their number, description and name of author; in the case of maps and sketches an arrow indicating their orientation, and scale.

The explanations used for a series of several maps and profiles should correspond to that in the first figure. Description to figures should be inserted in the text on their proper place.

Each illustration and table must be referred in the text.

The high quality colour illustrations can be published after agreement by editorial office. The costs incurred will be charged to the account of the author (50 EUR for one page).

The Publisher reserves the right to return the graphic supplements back to author after language correction, resp. demand him to replace them by the higher quality ones.

Tables are submitted on separate page. Their layout is accepted in a size of up to A4. More widespread tables are not accepted.

Data are incorporated into table only when there is no possibility to incorporate them into text. The numbering of tables shall be gradual. Short explanation to a table should be included on the same sheet. If the text is longer, it should be typed on a separate sheet.

### References

The list of references should only include the works cited in the text. The references are stated in alphanumeric order, with hanging indent in the second and following lines. The denotation "in press" can be used only in the cases of acceptance of reviewed version of article by editorial board. The denotation "personal information" can be cited only in the text (e.g. Kováčik, pers. information, 2008). When referring the data by other author not being the co-author of referred publication, in the text he is cited in the following form: (Gerda in Kubka, 1975), though in the list of literature is stated only Kubka J., 1975.

### Examples of referring to:

#### Book

Gazda, L. & Čech, M., 1988: Paleozoic of the Medzev nappe. Bratislava, Alfa, 155 p.

#### Journal

Vrba, P., 1989: Shear zones in the metapelite complexes. Mineralia Slov., 21, p. 135 – 142.

#### Anniversary volume

Návesný, D., 1987: High-potassium rhyolites. In: Romanov, V. (ed.): Stratiform deposits of Gemericum. Spec. publ. Slov. Geol. Soc. Košice, p. 203 – 215.

#### Manuscript

Radvanský, F., Slivka, B., Viktor, J. & Srnka, T., 1985: Vein deposits of the Jedľovec nappe of Gemericum. Final report from the project SGR-geophysics. Manuscript-archive ŠGÚDŠ Spišská Nová Ves, 28 p.

### Proofs

The authors are obliged to correct the errors, which are due to typing and technical arrangements. The first proof is sent to author(s). The second proof is provided only to the editorial office. It can be sent to authors upon request.

The proofs must be marked clearly and intelligibly, to avoid further errors and doubts. Common typographic symbols are to be used; their list and meaning will be provided by editorial office. Each used symbol must also appear on the margin of the text, if possible on the same line where the error occurred. The deadline and conditions for proof-reading are subject to the contract, which is governed by the Chairman of the Editorial Board.

### Final remarks

These instructions are obligatory to all authors. Exceptions can be made by the Editorial Board or the Scientific Editor. Manuscripts not complying with these instructions shall be returned to the authors.

The Editorial Board reserves the right to publish preferentially invited manuscript and to assemble thematic volumes.

The manuscripts should be sent by e-mail to the address: slovak.geological.magazine[at]geology.sk.

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