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^-, NH_4^+ and conductivity. The highest content of TOC (1,460 $mg.l^{-1}$) as an indicator of organic pollution was found at the site Komárno – area after the Soviet Army. Extremely high levels of COD_{Mn} (above 50 $mg.l^{-1}$) 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 – Vrakuňa – CHZJD 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, Sereď – landfill dump and former Nickel plant area, Zlaté Moravce – Calex, Bojná – landfill A.
- Urban et al. (2015a,b): locality Bratislava – Vrakuňa – landfill CHZJD, Bánovce nad Bebravou – railway station.

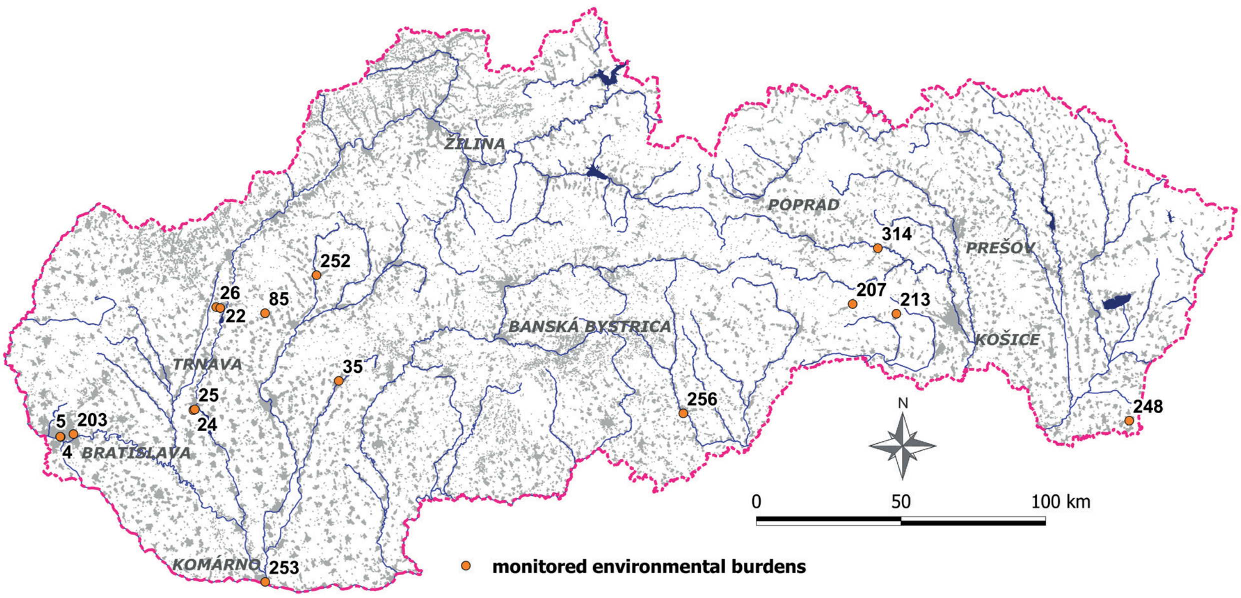

Fig. 1.1 Map of selected monitored environmental burdens with strong groundwater and/or surface water pollution

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_4^+, COD_{Mn}, TOC, conductivity, PAH, dichloromethane, tetrachloroethene	Chemical industry
5	Bratislava – Gumon	NH_4^+, COD_{Mn}, TOC, C_{10}-C_{40}, anthracene, chrysene, carbon tetrachloride	Rubber industry
22	Piešťany – Chirana	NH_4^+, 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_4^+, 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_4^+, COD_{Mn}, cis 1,2-dichloroethene, trans 1,2-dichloroethene, tetrachloroethene, trichloroethene, vinyl chloride	Production of refrigerators
85	Bojná – landfill – part A	As, Ba, B, Cl^-, NH_4^+, COD_{Mn}, TOC, conductivity	Waste management equipment
203	Bratislava – Vrakuňa – CHZJD landfill	As, F^-, NH_4^+, NO_2^-, TOC, C_{10}-C_{40}, 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^{3+}, As, Co, Cu, Ni, Zn, conductivity, pH	Pollution from mineral extraction
213	Poproč – Petrova dolina Valley	Al^{3+}, As, Cd, Ni, Sb, Zn, pH	Pollution from mineral extraction
248	Čierna nad Tisou – transshipment station	Cl^-, C_{10}-C_{40}, NEL-UV, benzene, ethylbenzene, toluene, xylene, carbon tetrachloride	Transport
252	Bánovce nad Bebravou – railway station	NH_4^+, TOC, cis 1,2-dichloroethene, tetrachloroethene, trichloroethene	Transport
253	Komárno – area after the Soviet Army	NH_4^+, TOC, C_{10}-C_{40}, 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	Krompachy – Kovohuty	Al^{3+}, B, As, Cd, Co, Cu, Hg, Ni, Pb, Sb, Zn, Cl^-, F^-, NH_4^+, TOC, C_{10}-C_{40}, conductivity, pH, SO_4^{2-}, Fe-tot., Mn	Metallurgical industry

Notes: PAH – polycyclic aromatic hydrocarbons, C_{10}-C_{40} – 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 Krompachy – 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 NH_4^+, Cl^- and EC and organic indicators for TOC, COD_{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 Cl^- dominate, which affect the elevated EC values (460 $mS.m^{-1}$ to 520 $mS.m^{-1}$). 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 $\mu g.l^{-1}$ (Tab. 1.3). The maximum value (846 $\mu g.l^{-1}$) 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_4^+	mg.l^{-1}	1.82	0.64	2.87	<0.05	13.6	39	1.2	2.4	3	10
Cl^-	mg.l^{-1}	171	131	200	24.2	1,121	39	150	250	10	3
TOC	mg.l^{-1}	10.3	3.1	14.8	<0.5	68.9	33	2	5	4	15
COD_{Mn}	mg.l^{-1}	7.38	1.59	10.9	<0.5	37.3	31	5	10	2	8
surfactants	mg.l^{-1}	0.48	0.14	1.11	0.02	6.1	35	0.25	0.5	7	6
hydrocarbon index (C_{10}-C_{40})	mg.l^{-1}	236	0.17	981	<0.02	4,715	38	0.25	0.5	4	11
1,1-dichloroethene	µg.l^{-1}	0.44	0.2	1.59	<0.1	10	38	10	20	0	0
cis 1,2-dichloroethene	µg.l^{-1}	4.76	1	8.57	<0.1	41.1	38	25	50	1	0
tetrachloroethene	µg.l^{-1}	12.4	0.7	30.7	<0.2	170	38	10	20	2	7
trichloroethene	µg.l^{-1}	2.82	0.2	5.23	<0.1	22.7	38	25	50	0	0
chloroethene	µg.l^{-1}	2.62	0.2	8.89	<0.1	50.8	38	5	10	2	2
benzene	µg.l^{-1}	7.87	<0.2	31.4	<0.2	176	32	15	30	0	2
chlorobenzene	µg.l^{-1}	16.8	0.2	83.0	<0.1	471	32	15	30	0	1
toluene	µg.l^{-1}	1.88	<0.2	8.79	<0.2	50	32	350	700	0	0
xylene	µg.l^{-1}	1.67	<0.2	5.33	<0.2	30	32	250	500	0	0
anthracene	µg.l^{-1}	7.82	0.021	45.7	<0.003	278	37	5	10	1	1
phenanthrene	µg.l^{-1}	73.2	0.163	436	<0.003	2,652	37	5	10	3	2
fluoranthene	µg.l^{-1}	4.20	0.018	23.7	<0.003	144	37	25	50	0	1
fluorene	µg.l^{-1}	10.1	0.1	57.6	<0.015	351	37				
chrysene	µg.l^{-1}	7.79	0.01	45.5	<0.003	277	37	0.1	0.2	1	8
naphthalene	µg.l^{-1}	2.77	0.105	12.8	<0.03	82.4	42	25	50	0	1
pyrene	µg.l^{-1}	16.1	0.036	91.7	<0.006	558	37	25	50	1	1
benzo(a)anthracene	µg.l^{-1}	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_4^+	mg.l^{-1}	1.00	0.565	2.03	<0.05	11.6	42	1.2	2.4	2	3
Cl^-	mg.l^{-1}	110	85.5	167	21.6	1,030	34	150	250	0	1
TOC	mg.l^{-1}	5.73	5.5	3.14	0.7	14.6	38	2	5	10	23
COD_{Mn}	mg.l^{-1}	5.84	3.39	5.72	<0.5	21.9	36	5	10	4	9
surfactants	mg.l^{-1}	0.64	0.605	0.44	<0.05	1.99	38	0.25	0.5	8	22
hydrocarbon index (C_{10}-C_{40})	mg.l^{-1}	42.0	0.075	225	<0.02	1,410	40	0.25	0.5	1	10
1,1-dichloroethene	µg.l^{-1}	0.52	<0.2	1.03	<0.2	5.8	40	10	20	0	0
cis 1,2-dichloroethene	µg.l^{-1}	0.43	<0.2	0.72	<0.2	3.7	40	25	50	0	0
tetrachloroethene	µg.l^{-1}	0.69	<0.2	0.99	<0.2	4.7	40	10	20	0	0
trichloroethene	µg.l^{-1}	0.78	<0.2	3.30	<0.2	21.1	40	25	50	0	0
chloroethene	µg.l^{-1}	1.60	<0.2	7.19	<0.2	45	40	5	10	1	1
benzene	µg.l^{-1}	9.10	0.2	33.1	<0.1	191	40	15	30	2	2
chlorobenzene	µg.l^{-1}	0.54	0.2	0.96	<0.1	4.5	40	15	30	0	0
toluene	µg.l^{-1}	19.4	0.2	103	<0.1	646	40	350	700	1	0
xylene	µg.l^{-1}	2.42	0.2	7.56	<0.1	39	40	250	500	0	0
anthracene	µg.l^{-1}	0.43	0.003	2.28	<0.003	13.3	34	5	10	0	1
phenanthrene	µg.l^{-1}	2.52	0.027	12.1	<0.003	70.6	34	5	10	1	1
fluoranthene	µg.l^{-1}	0.22	0.0075	1.09	<0.003	6.39	34	25	50	0	0
fluorene	µg.l^{-1}	0.96	0.015	3.66	<0.015	21.1	34				
chrysene	µg.l^{-1}	0.27	0.003	1.39	<0.003	8.14	34	0.1	0.2	0	3
naphthalene	µg.l^{-1}	0.34	0.04	1.13	<0.03	6.48	34	25	50	0	0
pyrene	µg.l^{-1}	0.26	0.0195	1.08	<0.006	6.29	34	25	50	0	0
benzo(a)anthracene	µg.l^{-1}	0.38	0.003	1.99	<0.003	11.6	34				

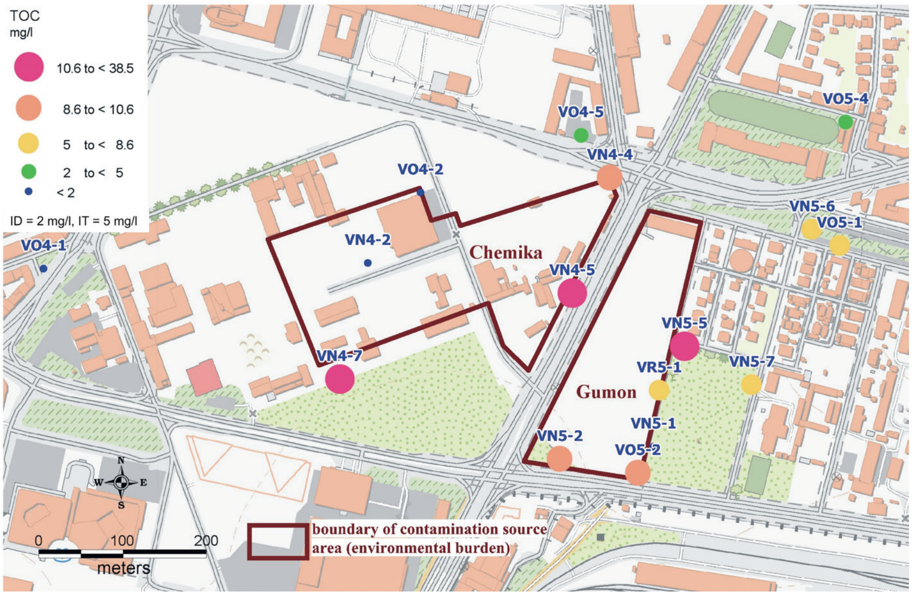

Fig. 1.2 TOC distribution in groundwaters (median concentrations) – sites Bratislava – Chemika and Bratislava – Gumon (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

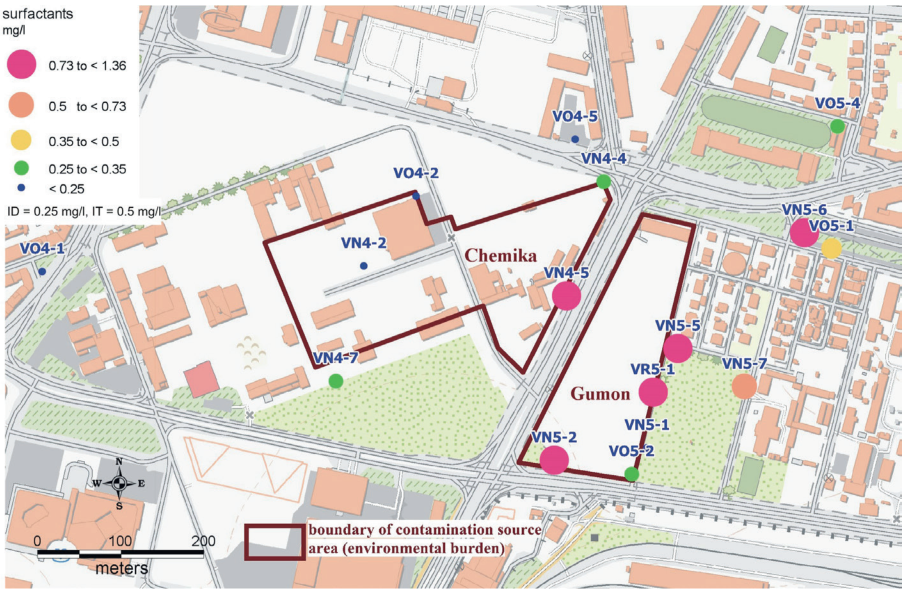

Fig. 1.3 Distribution of surfactants in groundwaters (median concentrations) – sites Bratislava – Chemika and Bratislava – Gumon (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

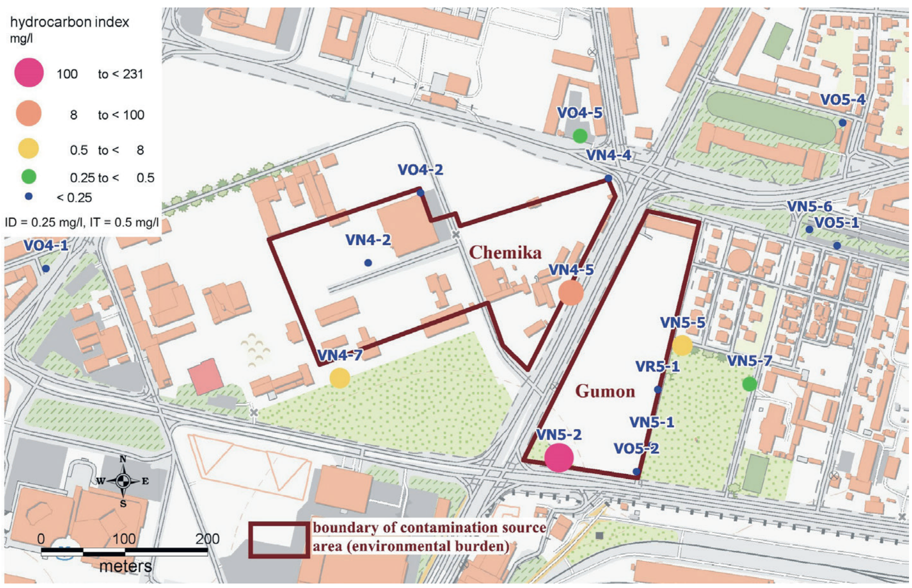

Fig. 1.4 Distribution of hydrocarbon index in groundwaters (median concentrations) – sites Bratislava – Chemika and Bratislava – Gumon (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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 $\mu g.l^{-1}$ at the site Piešťany – former factory Chirana). The surface area of groundwater pollution is large (reaches several km^2), 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 Sereď – landfill dump and former Nickel plant area (loc. No. 24 and 25)

The Sereď 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 Sereď.

Groundwater pollution is monitored in 25 boreholes. Mainly elevated or high contents of SO_4^{2-}, NH_4^+, NO_3^- 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 >ID**	**number of samples >IT**
Cl^-	$mg.l^{-1}$	48.1	51.5	20.6	8.17	125	80	150	250	0	0
SO_4^{2-}	$mg.l^{-1}$	144	154	51.3	28.6	244	80				
1,1-dichloroethene	$\mu g.l^{-1}$	1.02	0.2	1.67	<0.1	13.1	117	10	20	1	0
cis 1,2-dichloroethene	$\mu g.l^{-1}$	166	80.1	206	<0.1	846	117	25	50	6	65
trans 1,2-dichloroethene	$\mu g.l^{-1}$	2.13	0.8	4.17	<0.1	31.2	117	25	50	1	0
dichloromethane	$\mu g.l^{-1}$	3.02	0.2	12.9	<0.1	82.5	59	15	30	0	2
tetrachloroethene	$\mu g.l^{-1}$	1.51	0.2	2.37	<0.1	11.4	117	10	20	1	0
1,1,2-trichloroethene	$\mu g.l^{-1}$	30.2	2.7	62.6	<0.1	344	111	25	50	3	23
chloroethene	$\mu g.l^{-1}$	25.1	1.3	107	<0.1	760	112	5	10	5	21
chloroform	$\mu g.l^{-1}$	2.39	0.2	13.8	<0.1	111	70				
Piešťany – Tesla	**$mg.l^{-1}$**	**mean**	**median**	**standard deviation**	**minimum**	**maximum**	**number**	**ID value**	**IT value**	**number of samples >ID**	**number of samples >IT**
Cl^-	$mg.l^{-1}$	71.2	56.0	67.5	9.89	301	36	150	250	0	3
SO_4^{2-}	$\mu g.l^{-1}$	168	146	82.9	0.61	294	36				
1,1-dichloroethene	$\mu g.l^{-1}$	0.3	0.2	0.31	<0.1	1.2	47	10	20	0	0
cis 1,2-dichloroethene	$\mu g.l^{-1}$	27.2	12.4	41.5	0.2	180	47	25	50	7	6
trans 1,2-dichloroethene	$\mu g.l^{-1}$	0.57	0.2	0.54	<0.1	2.3	47	25	50	0	0
dichloromethane	$\mu g.l^{-1}$	1.13	0.2	3.35	<0.1	15.8	23	15	30	1	0
tetrachloroethene	$\mu g.l^{-1}$	0.6	0.2	0.70	<0.1	3.5	47	10	20	0	0
1,1,2-trichloroethene	$\mu g.l^{-1}$	6.39	2.75	10.1	<0.1	44.1	44	25	50	3	0
chloroethene	$\mu g.l^{-1}$	5.87	0.4	19.4	<0.1	129	46	5	10	5	5
chloroform	$\mu g.l^{-1}$	2.04	0.2	6.85	<0.1	33.1	27				

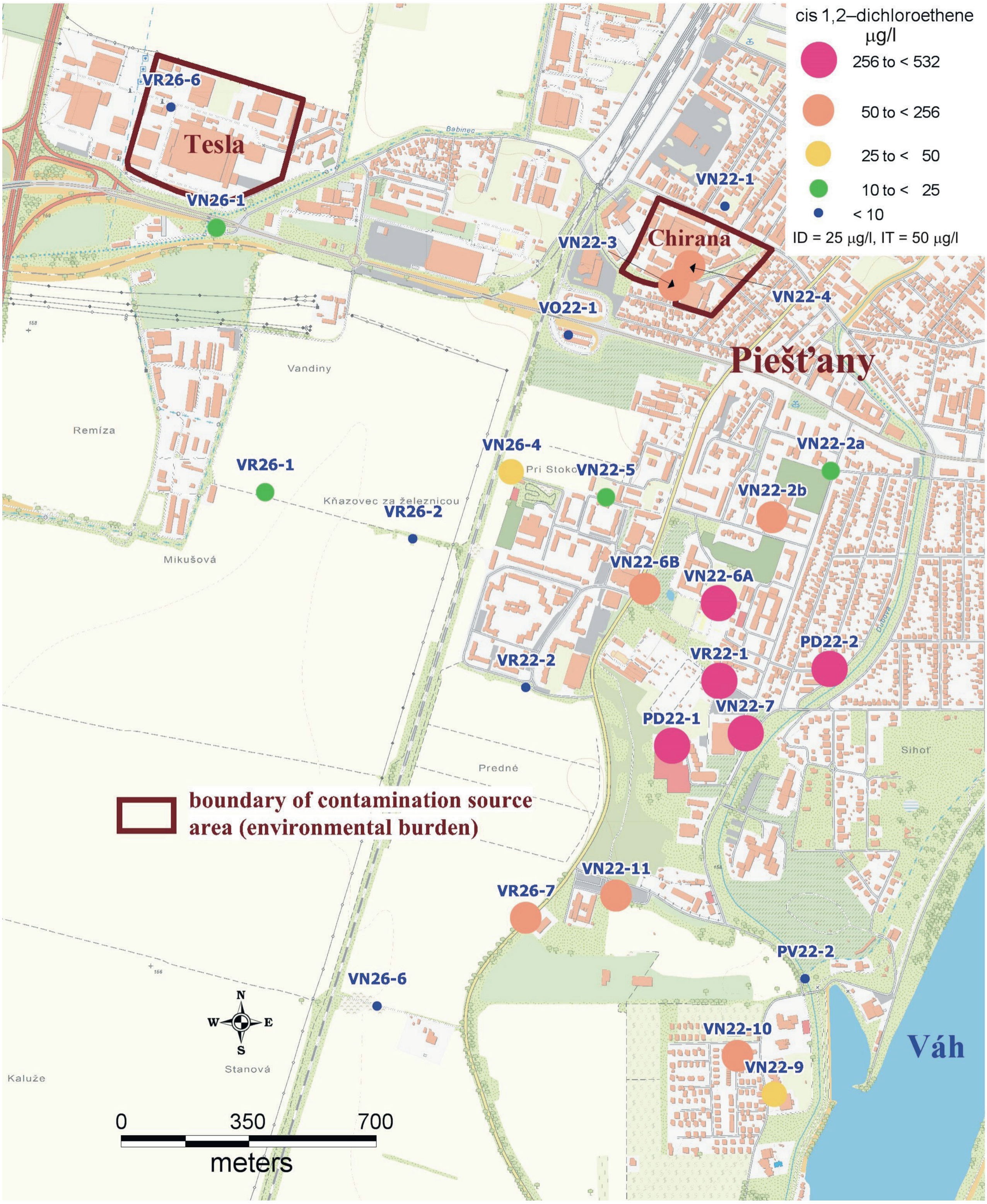

Fig. 1.5 Distribution of cis 1,2-dichloroethene in groundwaters (median concentrations) – sites Piešťany – former factories Chirana and Tesla (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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 NH_4^+ and Ni were found. Borehole VR24-2 also contains SO_4^{2-}, Na^+, Zn and B, and the wells in the downstream groundwater south and southeast of the pollution sources had elevated levels of NO_3^-, NH_4^+ and 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 NH_4^+, Ni and 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 $mg.l^{-1}$) 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 $mg.l^{-1}$ 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 Sereď – landfill dump and former Nickel plant area

Landfill dump	**unit**	**mean**	**median**	**standard deviation**	**minimum**	**maximum**	**number**	**ID value**	**IT value**	**number of samples >ID**	**number of samples >IT**
NH_4^+	$mg.l^{-1}$	12.9	8.98	12.1	0.02	47.3	97	1.2	2.4	0	73
NO_3^-	$mg.l^{-1}$	61.7	68	52.5	<0.5	161	97				
Cl^-	$mg.l^{-1}$	80.4	69.5	49.2	32.5	282	97	150	250	5	3
SO_4^{2-}	$mg.l^{-1}$	213	161	194	42.8	1,145	97				
Fe_{total}	$mg.l^{-1}$	0.02	0.01	0.02	<0.002	0.088	90				
Mn	$mg.l^{-1}$	0.49	0.136	0.68	<0.002	3.49	90				
B	$mg.l^{-1}$	0.27	0.173	0.29	<0.02	1.496	83	0.5	5	14	0
Ni	$\mu g.l^{-1}$	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 >ID**	**number of samples >IT**
NH_4^+	$mg.l^{-1}$	5.77	4.16	6.30	<0.02	21.7	96	1.2	2.4	3	52
NO_3^-	$mg.l^{-1}$	10.8	4.69	19.4	<0.5	91.4	96				
Cl^-	$mg.l^{-1}$	33.3	30.2	20.9	3.31	91.8	96	150	250	0	0
SO_4^{2-}	$mg.l^{-1}$	188	81.0	387	7.62	3,237	96				
Fe_{total}	$mg.l^{-1}$	1.49	0.016	4.47	<0.002	25.4	92				
Mn	$mg.l^{-1}$	1.71	0.624	4.02	<0.003	23.9	92				
B	$mg.l^{-1}$	0.31	0.135	0.56	<0.02	3.29	87	0.5	5	12	0
Ni	$\mu g.l^{-1}$	3,107	3	12,369	<2	80,523	93	100	200	1	20

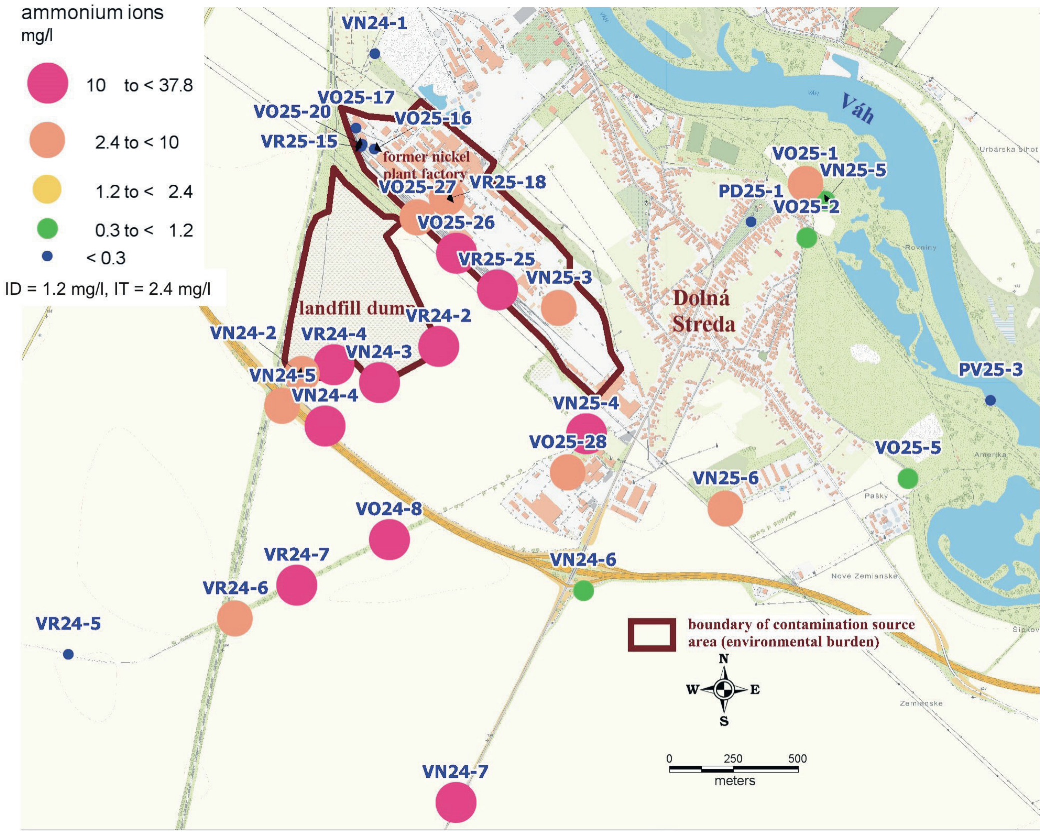

Fig. 1.8 Distribution of NH_4^+ in groundwaters (median concentrations) – sites Sereď – landfill dump and former Nickel plant area (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

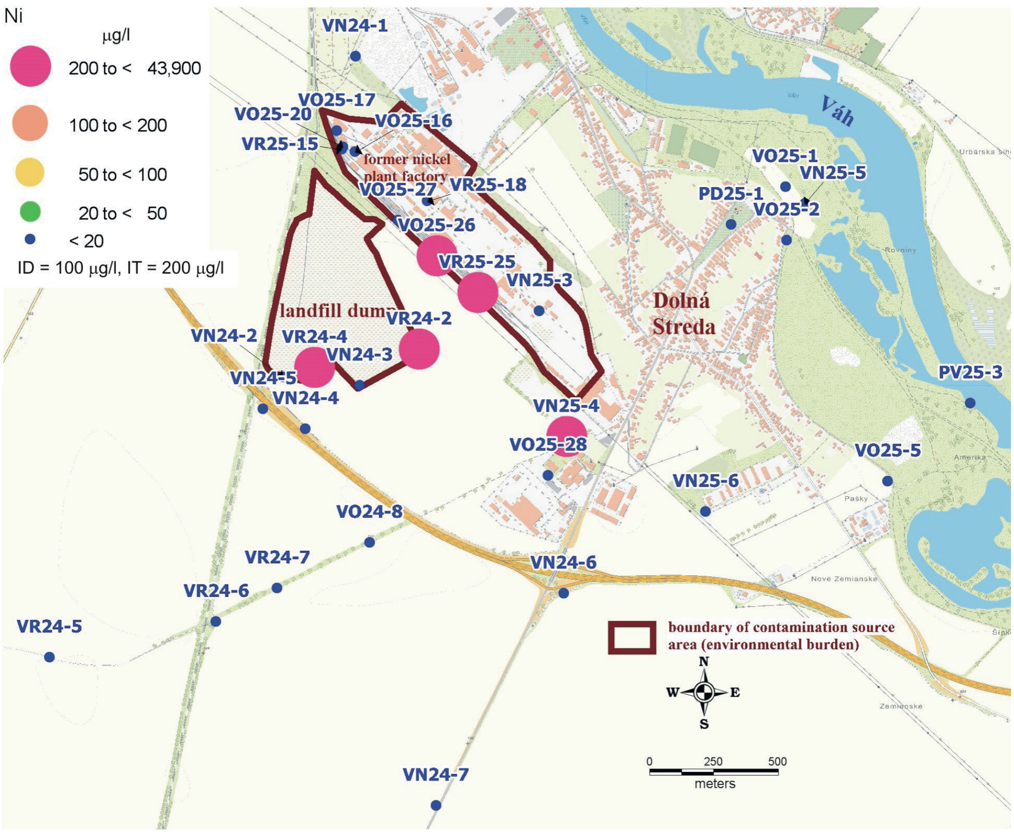

Fig. 1.9 Distribution of Ni in groundwaters (median concentrations) – sites Sereď – landfill dump and former Nickel plant area (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

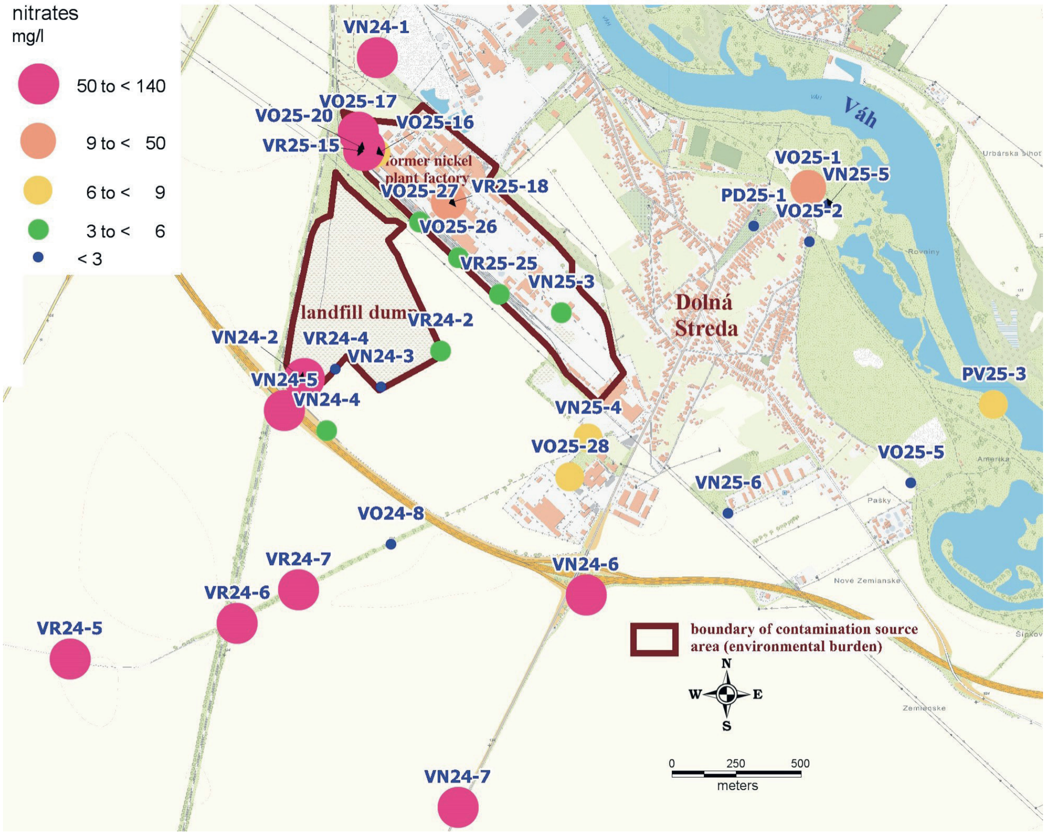

Fig. 1.10 Distribution of NO_3^- in groundwaters (median concentrations) – sites Sereď – landfill dump and former Nickel plant area (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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^3 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 >ID	number of samples >IT
TOC	mg.l^{-1}	2.02	1.7	1.23	0.3	6.6	118	2	5	40	4
COD_{Mn}	mg.l^{-1}	2.59	1.12	3.15	<0.5	15.3	76	5	10	4	5
1,1-dichloroethene	µg.l^{-1}	1.61	0.2	4.38	<0.1	32.5	124	10	20	6	1
cis 1,2-dichloroethene	µg.l^{-1}	522	0.85	3,185	<0.1	34,190	124	25	50	2	27
trans 1,2-dichloroethene	µg.l^{-1}	3.71	0.2	13.2	<0.1	121	124	25	50	3	2
tetrachloroethene	µg.l^{-1}	249	9.55	846	<0.2	6,482	124	10	20	7	52
trichloroethene	µg.l^{-1}	4,056	8.6	13,313	<0.1	85,200	124	25	50	6	49
chloroethene	µg.l^{-1}	84.5	<0.2	517	<0.2	5,186	124	5	10	2	19

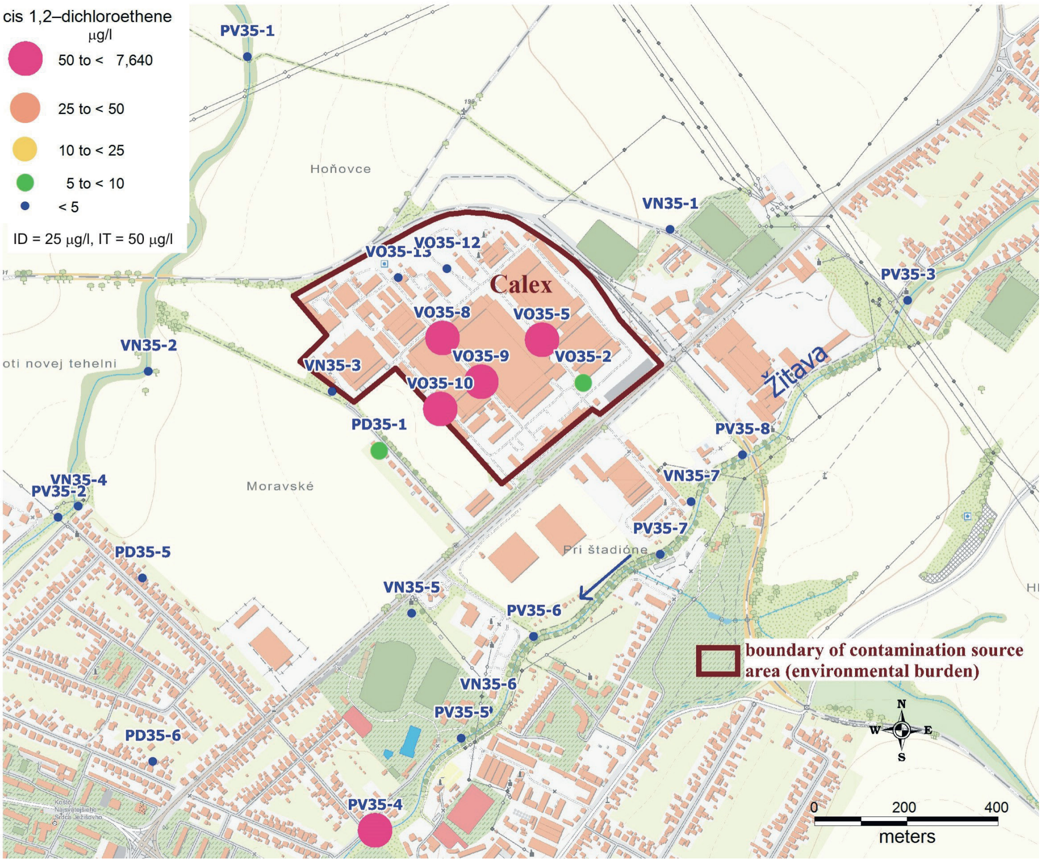

Fig. 1.11 Distribution of cis 1,2-dichloroethene in groundwaters (median concentrations) – site Zlaté Moravce – Calex (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

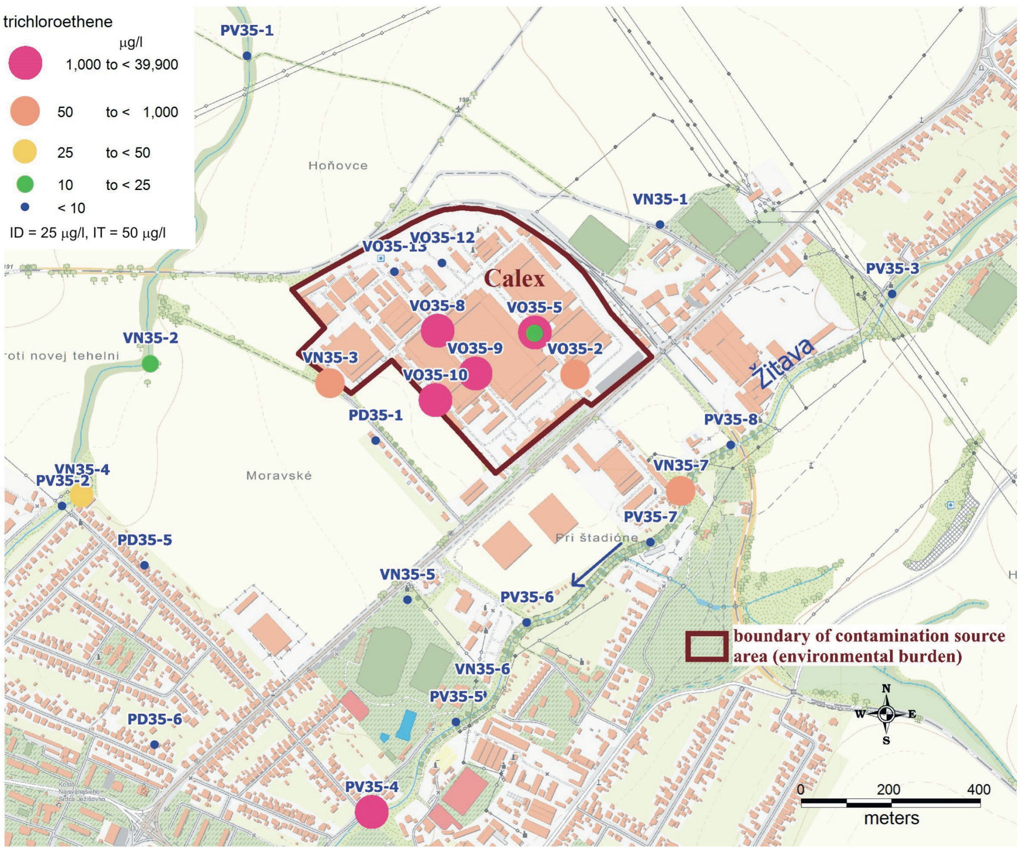

Fig. 1.12 Distribution of trichloroethene in groundwaters (median concentrations) – site Zlaté Moravce – Calex (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

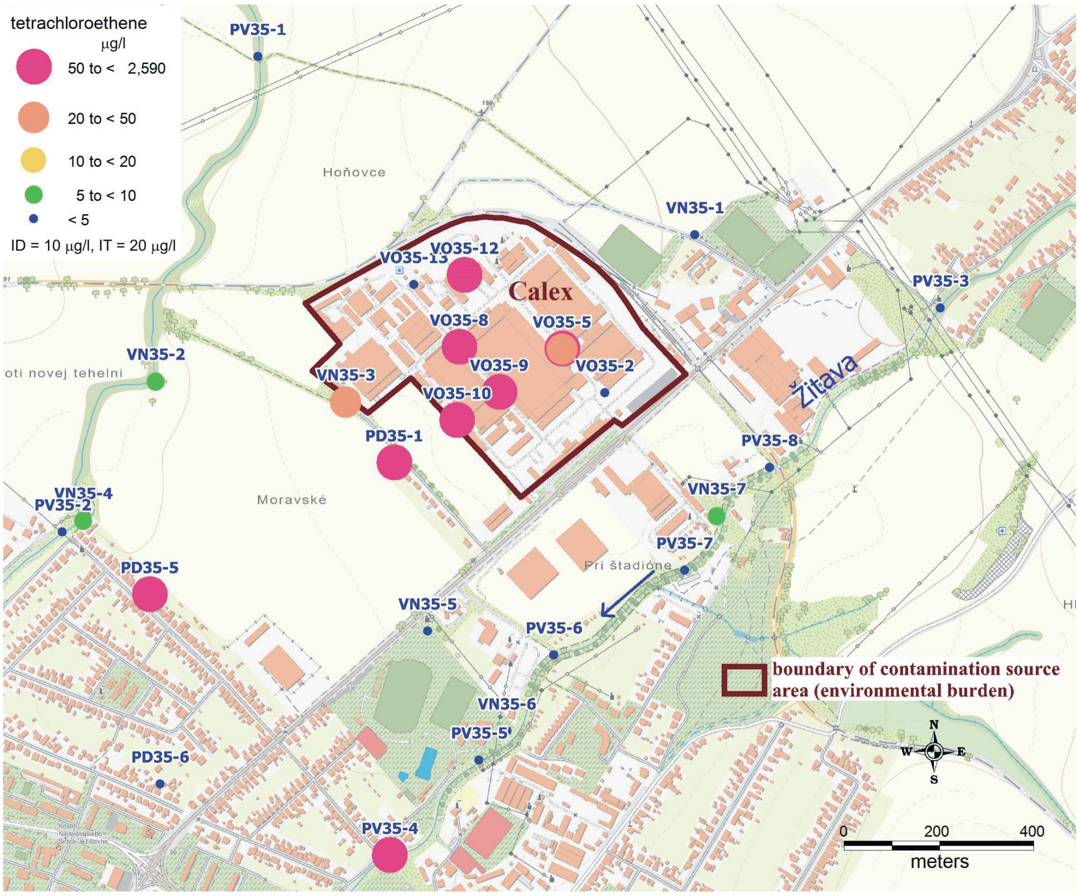

Fig. 1.13 Distribution of tetrachloroethene in groundwaters (median concentrations) – site Zlaté Moravce – Calex (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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_4^+	mg.l^{-1}	19.3	0.22	87.2	<0.04	779	95	1.2	2.4	9	18
Cl^-	mg.l^{-1}	402	218	515	2.28	2,168	95	150	250	9	42
SO_4^{2-}	mg.l^{-1}	93.9	45.4	130	2	669	95				
HCO_3^-	mg.l^{-1}	832	387	978	78.1	5,161	77				
TOC	mg.l^{-1}	32.0	8.9	55.0	0.1	296	90	2	5	8	57
COD_{Mn}	mg.l^{-1}	17.6	6.54	30.9	<0.5	150	83	5	10	12	31
Na^+	mg.l^{-1}	166	66.4	231	11.5	969	87				
K^+	mg.l^{-1}	24.7	2.15	91.1	0.71	602	87				
Ca^{2+}	mg.l^{-1}	208	110	174	21.3	719	87				
Mg^{2+}	mg.l^{-1}	73.4	36.7	71.5	6.82	287	87				
Fe_{total}	mg.l^{-1}	10.2	0.173	36.8	0.007	338	94				
Mn	mg.l^{-1}	0.93	0.134	1.90	<0.001	14.5	94				
B	mg.l^{-1}	0.95	0.162	1.59	<<0.01	8.09	90	0.5	5	27	2
As	μg.l^{-1}	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 Cl^-, NH_4^+, COD_{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 Cl^-, NH_4^+, COD_{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

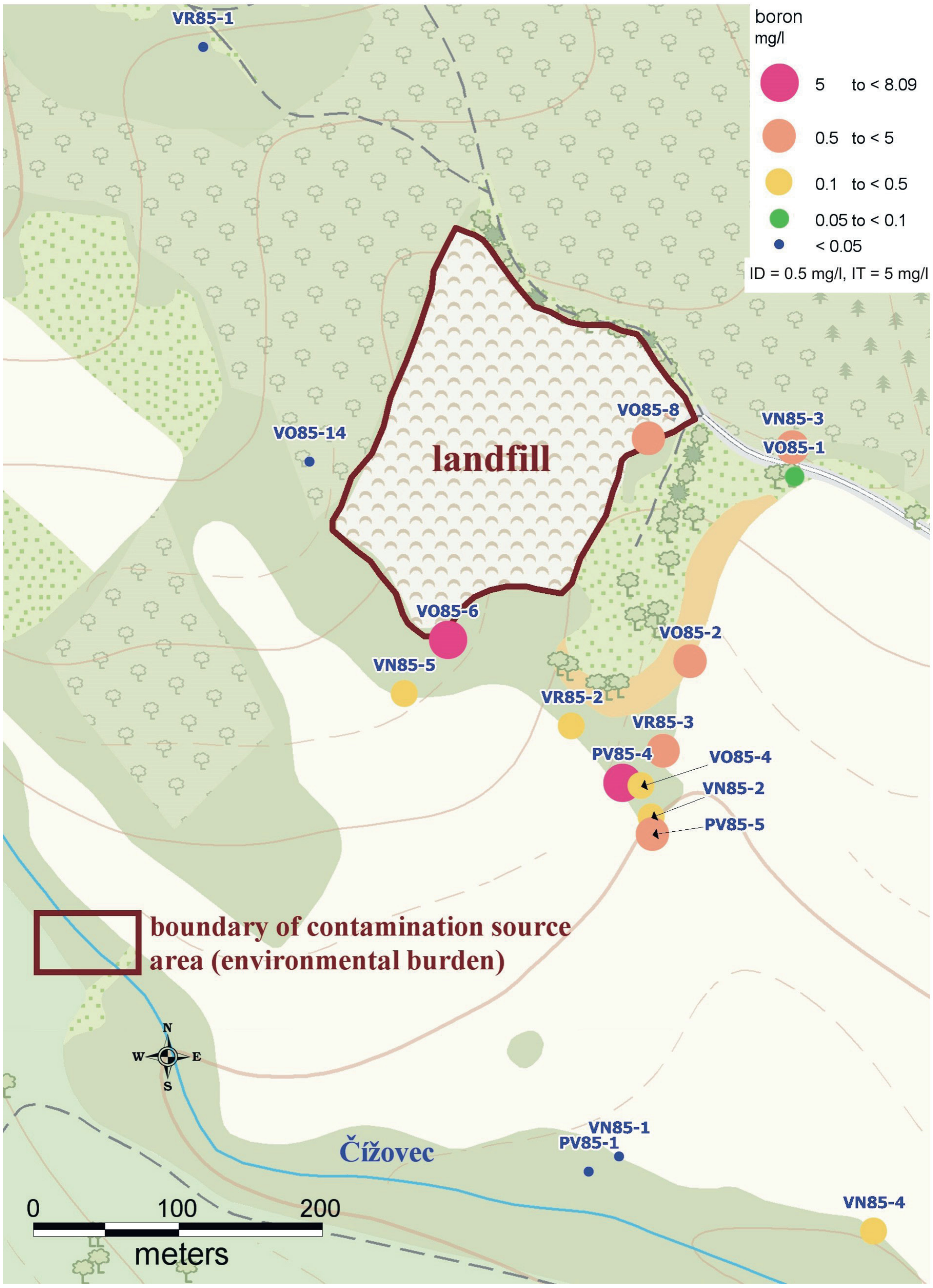

Fig. 1.14 Distribution of boron in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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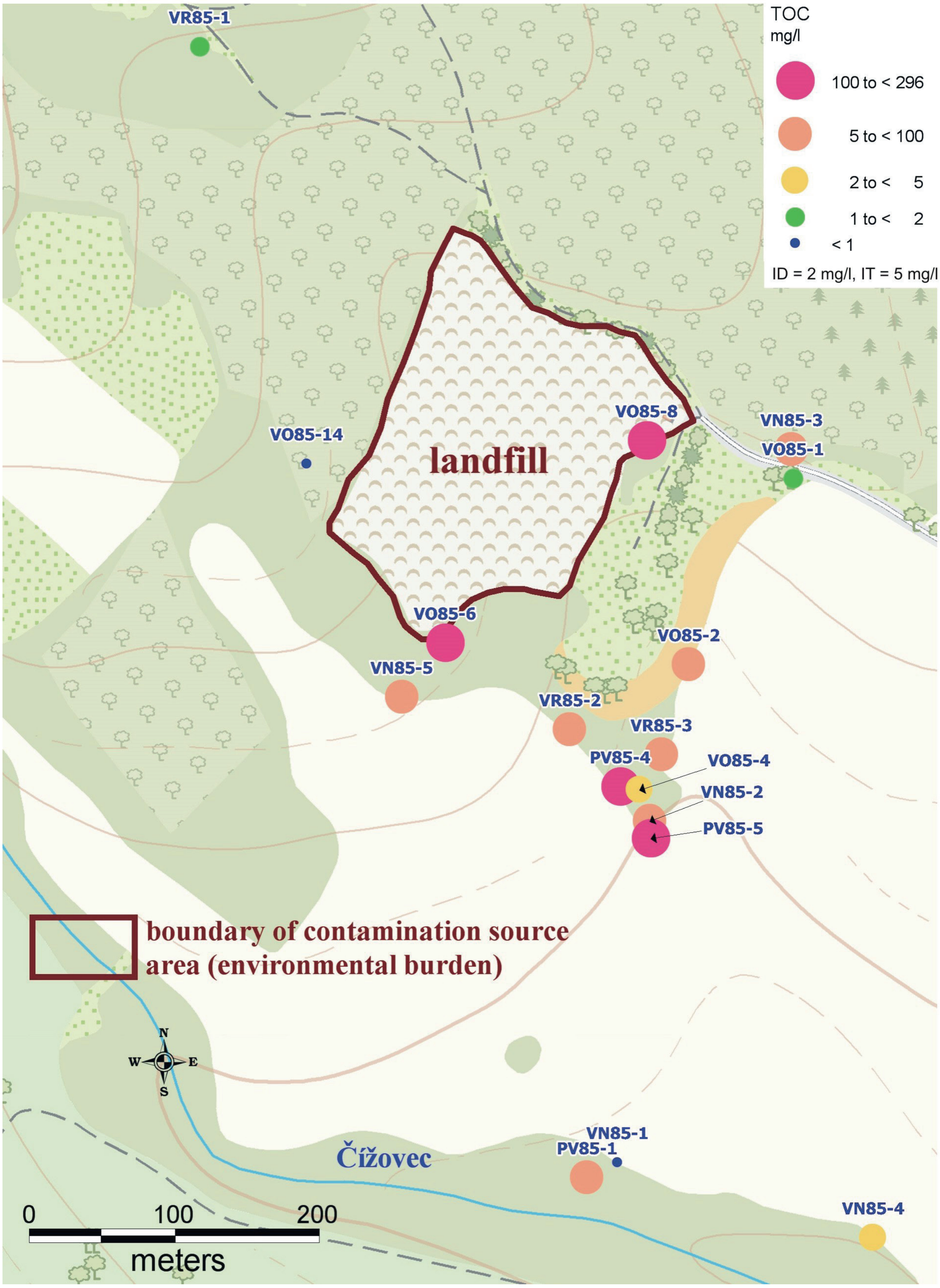

Fig. 1.15 Distribution of TOC in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

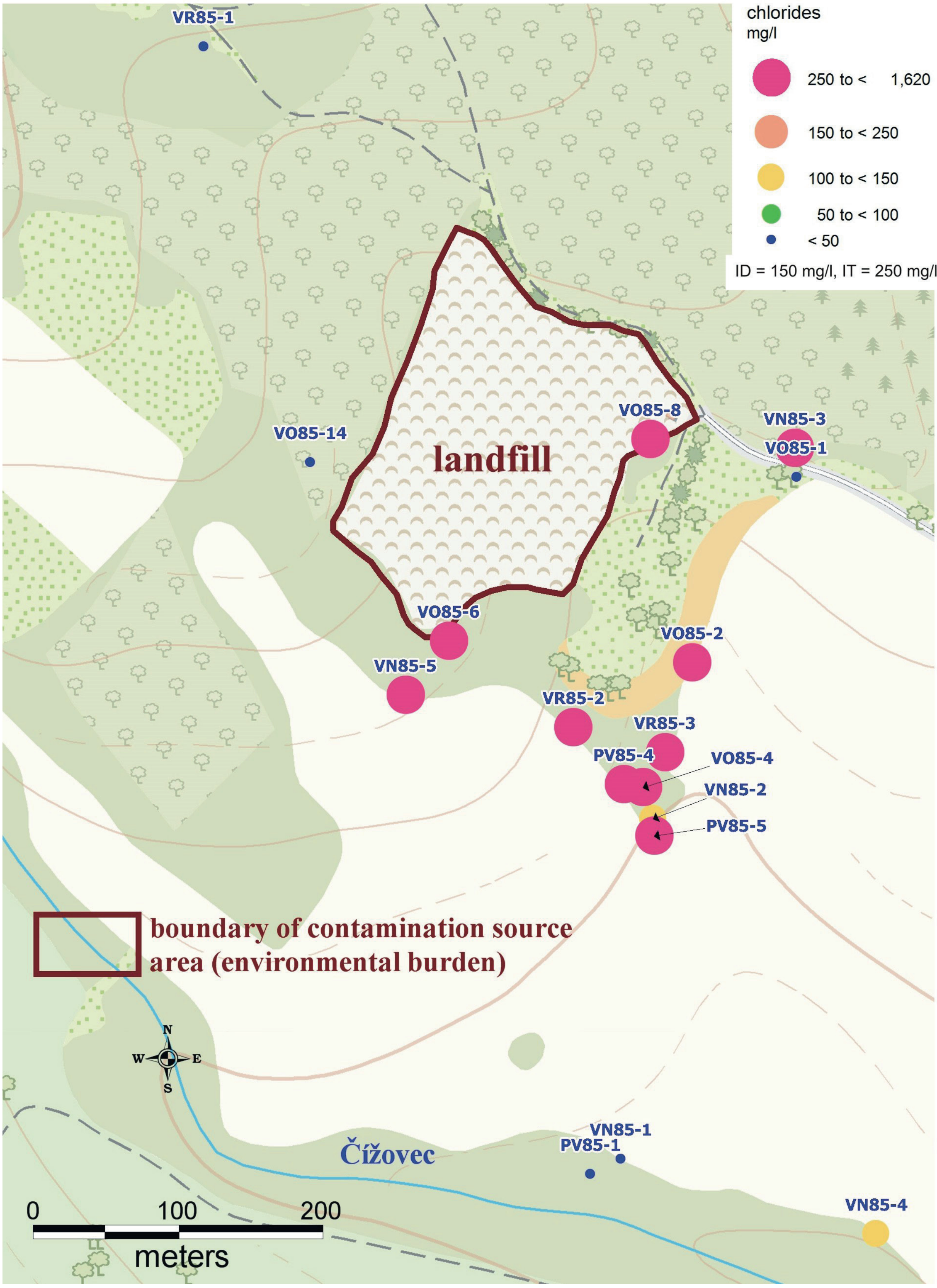

Fig. 1.16 Distribution of chlorides in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

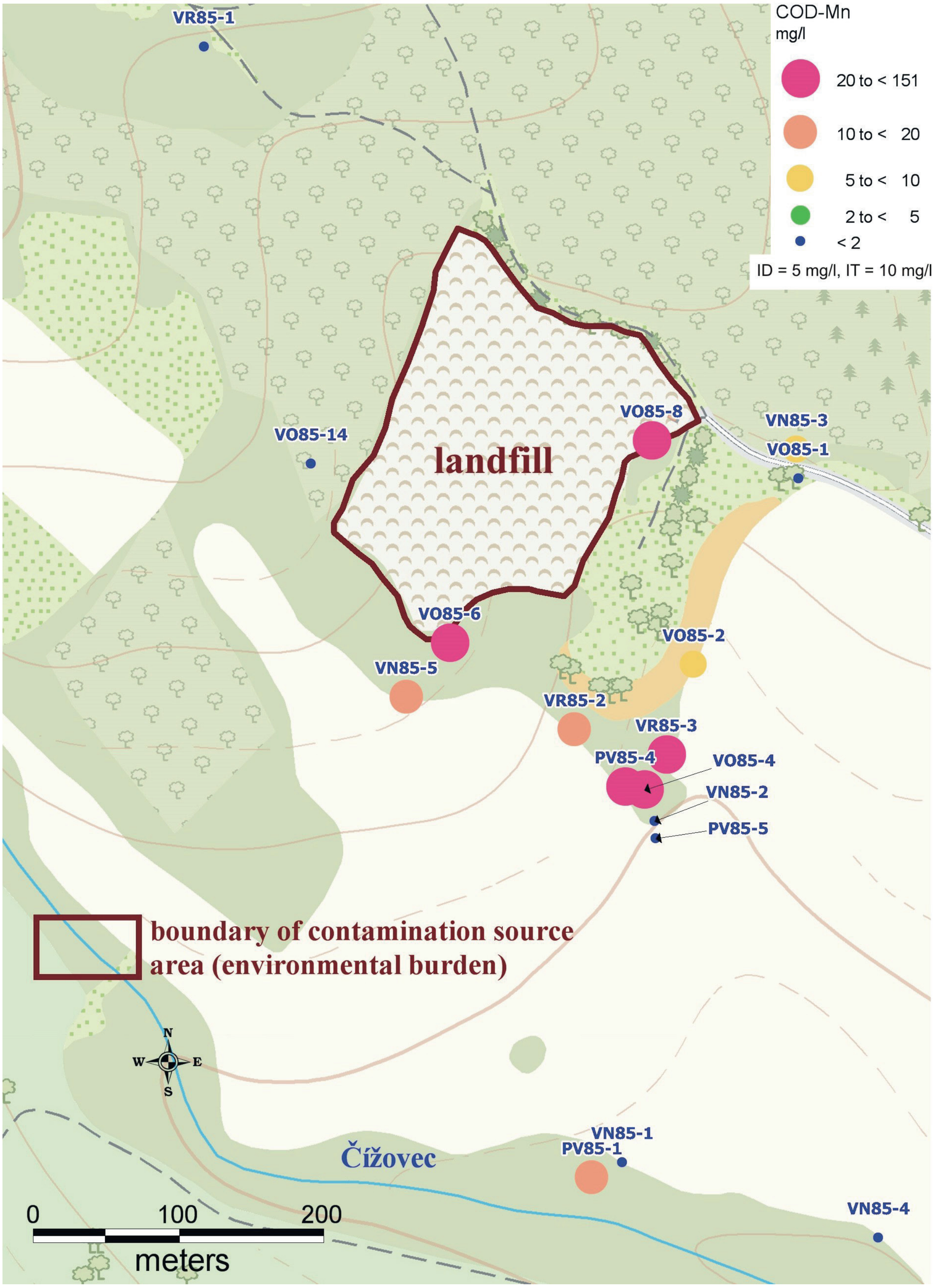

Fig. 1.17 Distribution of COD_{Mn} in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

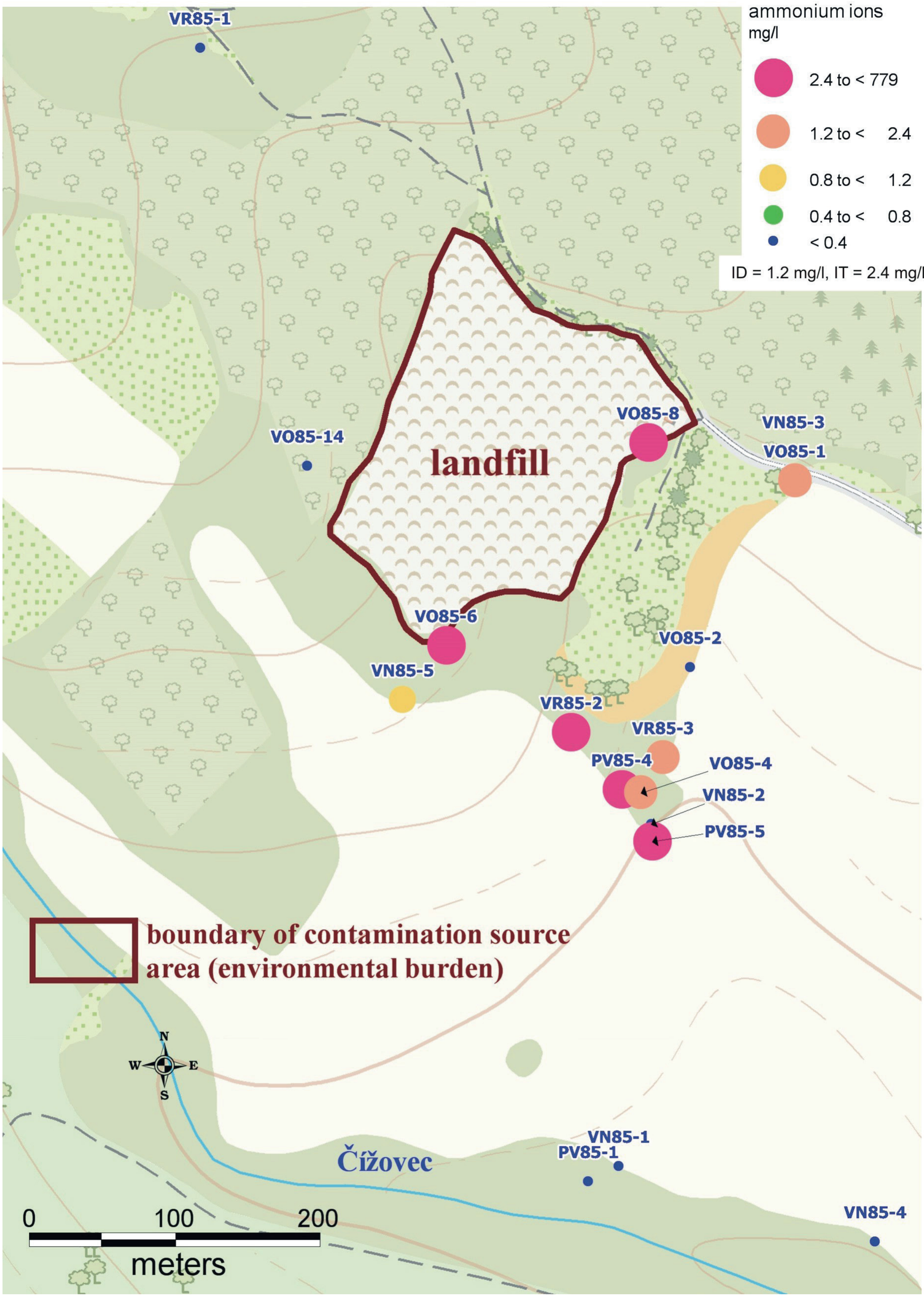

Fig. 1.18 Distribution of NH_4^+ in groundwaters (median concentrations) – site Bojná – landfill – part A (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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^3 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_4^+	$mg.l^{-1}$	1.90	0.125	4.93	<0.03	25.7	54	1.2	2.4	5	8
TOC	$mg.l^{-1}$	19.6	2.2	40.9	<0.5	219	81	2	5	12	29
As	$mg.l^{-1}$	58.5	0.5	202	<0.1	1,310	127	50	100	5	13
COD_{Cr}	$mg.l^{-1}$	108	23	212	6	993	43				
surfactants	$mg.l^{-1}$	1.16	0.235	2.81	<0.05	13.8	54	0.25	0.5	9	16
phenol index	$mg.l^{-1}$	0.51	<0.01	1.92	<0.01	11.4	77	0.015	0.06	7	18
hydrocarbon index (C_{10}-C_{40})	$mg.l^{-1}$	0.07	0.02	0.16	<0.02	1.33	100	0.25	0.5	1	3
tetrachloroethene	$\mu g.l^{-1}$	18.3	9.6	22.2	<0.2	110	138	10	20	27	40
tetrachloromethane	$\mu g.l^{-1}$	1.93	0.2	10.2	<0.1	91.8	84	5	10	5	1
trichloroethene	$\mu g.l^{-1}$	4.38	1.4	9.27	<0.2	47.6	137	25	50	5	0
chloroethene	$\mu g.l^{-1}$	3.14	0.5	9.45	<0.2	50	138	5	10	4	9
1,2-dichlorobenzene	$\mu g.l^{-1}$	1.15	0.2	3.70	<0.1	25.1	137	1.5	3	2	12
1,3-dichlorobenzene	$\mu g.l^{-1}$	0.81	0.2	2.17	<0.1	11.3	137	1.5	3	1	9
1,4-dichlorobenzene	$\mu g.l^{-1}$	3.05	0.2	10.5	<0.1	70.5	137	1.5	3	4	18
benzene	$\mu g.l^{-1}$	86.9	<0.2	350	<0.2	2,440	138	15	30	5	14
ethylbenzene	$\mu g.l^{-1}$	34.5	0.2	150	<0.1	1,140	138	150	300	2	5
chlorobenzene	$\mu g.l^{-1}$	250	1.3	906	<0.1	6,900	137	15	30	5	31
toluene	$\mu g.l^{-1}$	48.9	0.4	191	<0.2	1,700	138	350	700	3	3
xylene	$\mu g.l^{-1}$	85.4	0.5	333	<0.2	2,448	138	250	500	2	8
atrazine	$\mu g.l^{-1}$	90.9	0.03	538	<0.02	4,060	121	100	500	2	3
simazine	$\mu g.l^{-1}$	4.73	<0.02	27.5	<0.02	225	121	100	500	2	3
desethylatrazine	$\mu g.l^{-1}$	0.26	<0.02	1.36	<0.02	11.1	121	100	500	0	0
propazine	$\mu g.l^{-1}$	5.21	<0.02	26.2	<0.02	183	121	100	500	3	0
sebuthylazine	$\mu g.l^{-1}$	0.03	<0.02	0.04	<0.02	0.25	93	100	500	0	0
prometryne	$\mu g.l^{-1}$	118	0.12	781	<0.02	6,190	121	100	500	1	3
terbutryn	$\mu g.l^{-1}$	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^-, NH_4^+, 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).

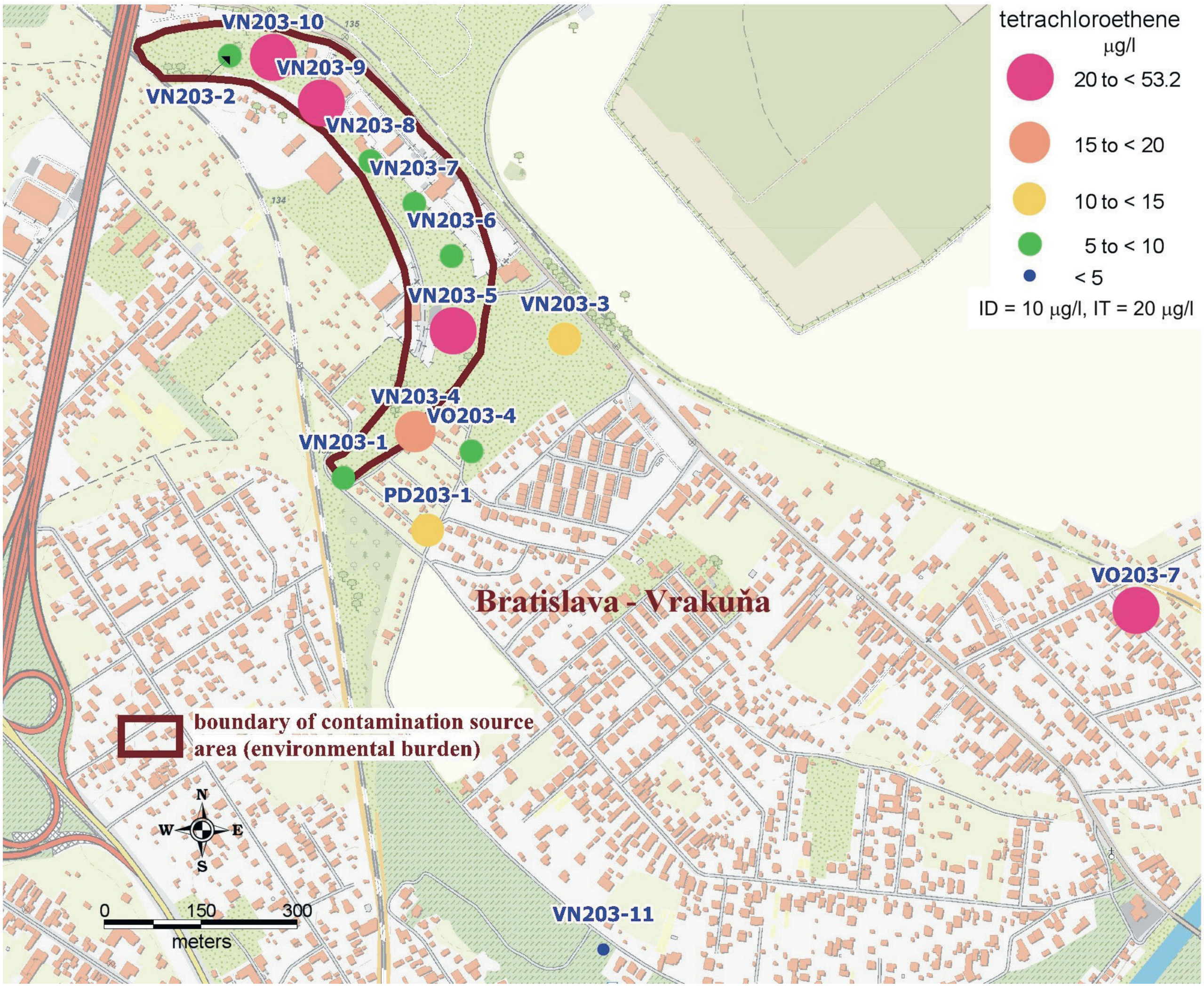

Fig. 1.19 Distribution of tetrachloroethene in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

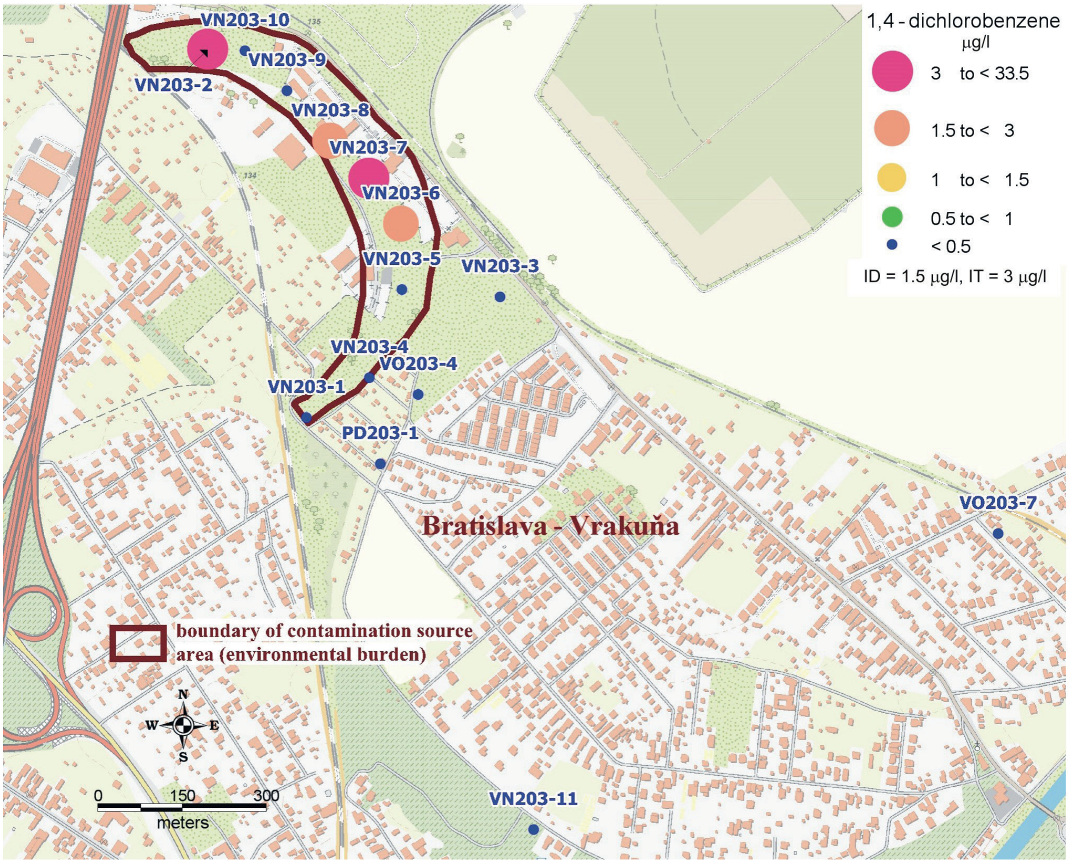

Fig. 1.20 Distribution of 1,4-dichlorobenzene in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

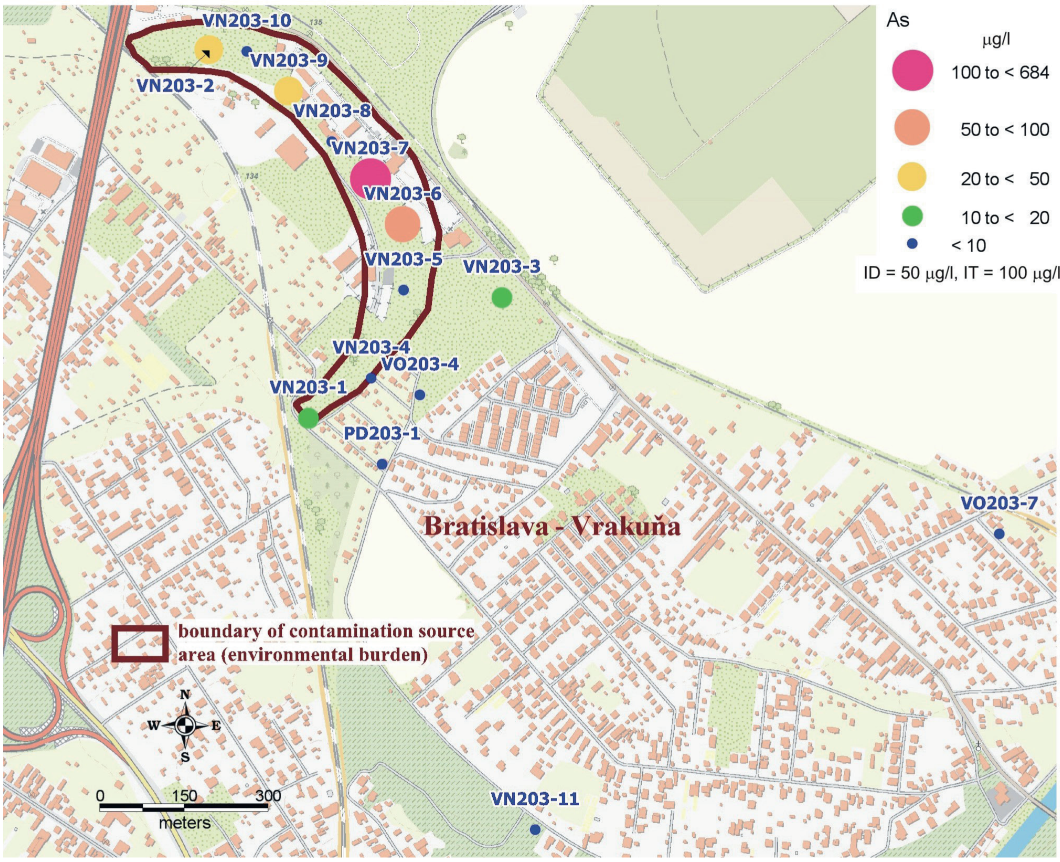

Fig. 1.21 Distribution of As in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

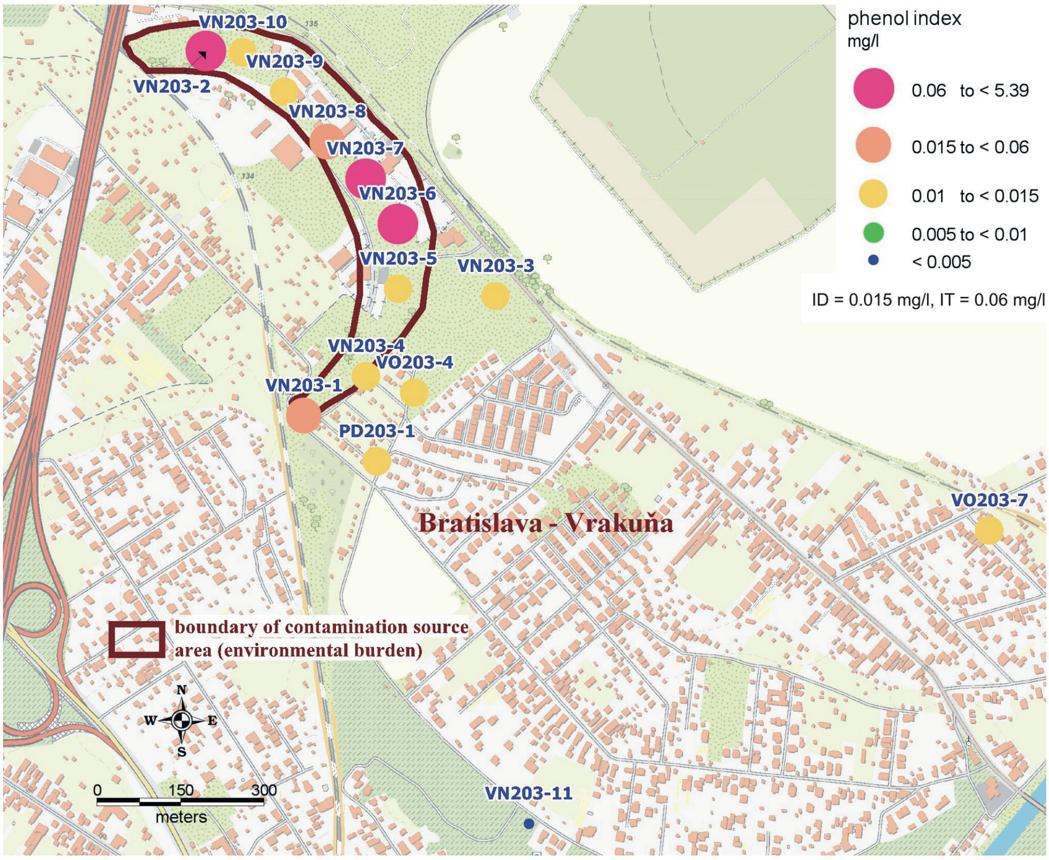

Fig. 1.22 Distribution of phenol index in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

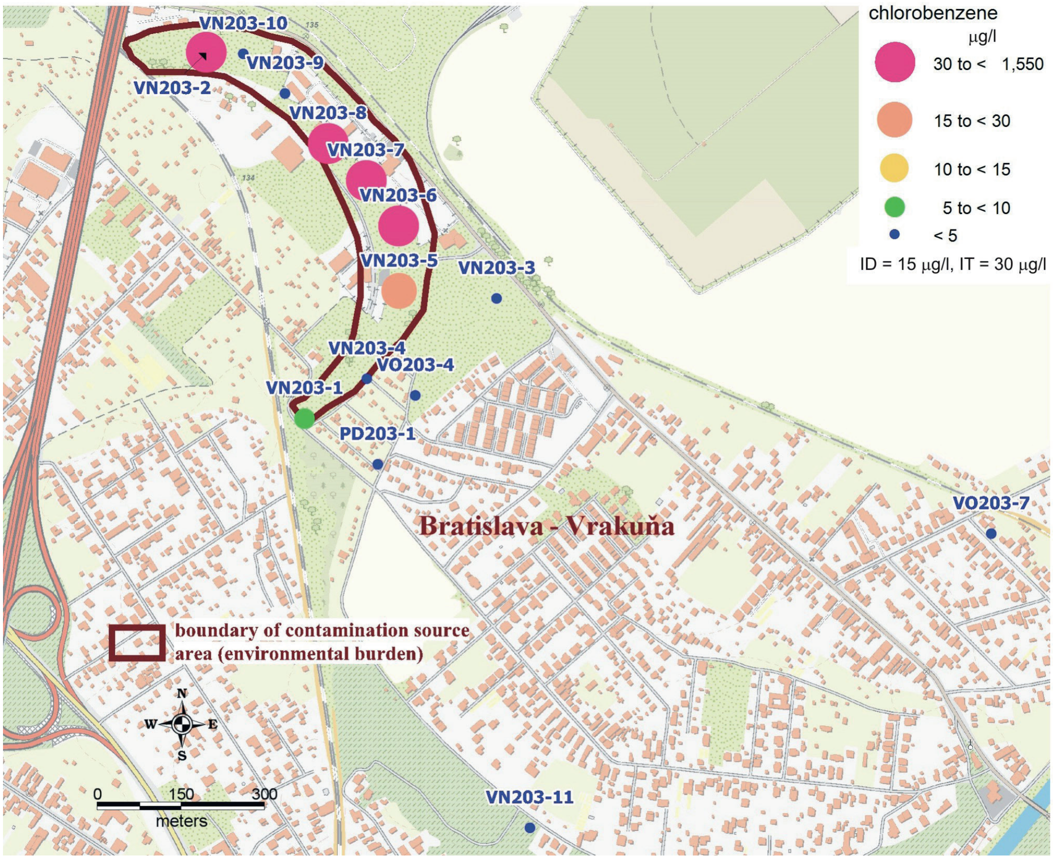

Fig. 1.23 Distribution of chlorobenzene in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

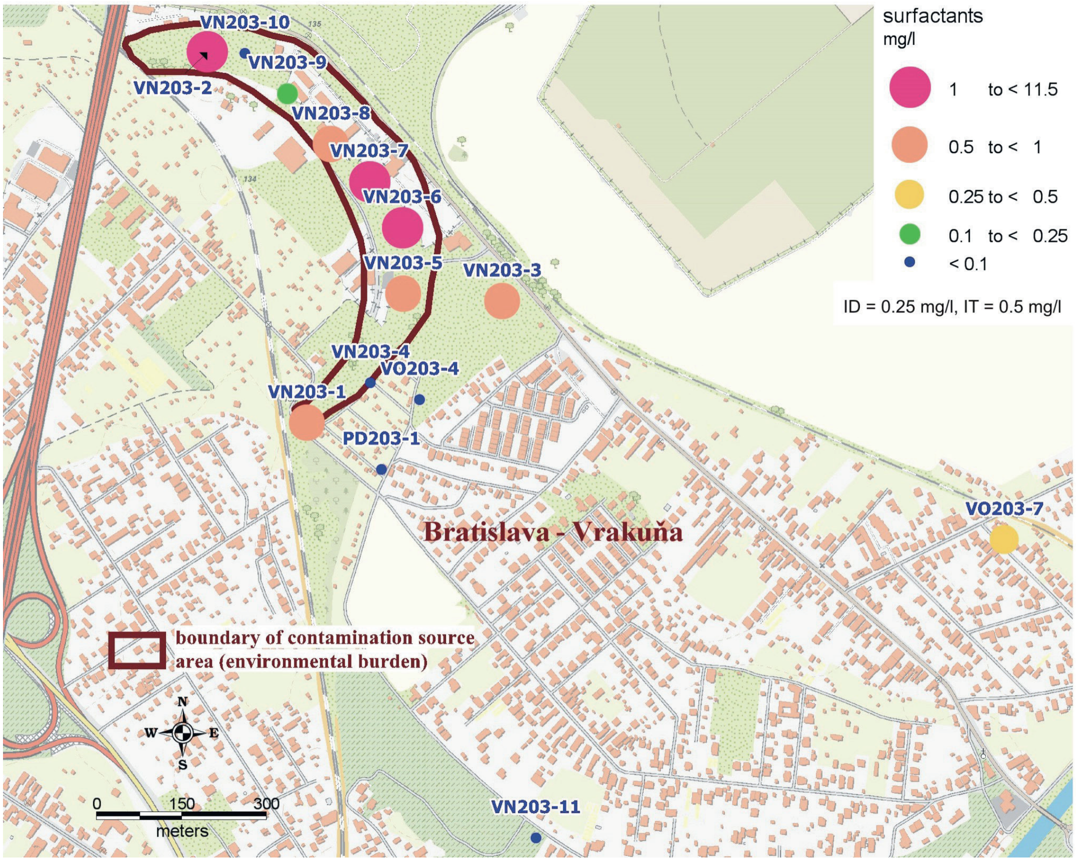

Fig. 1.24 Distribution of surfactants in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

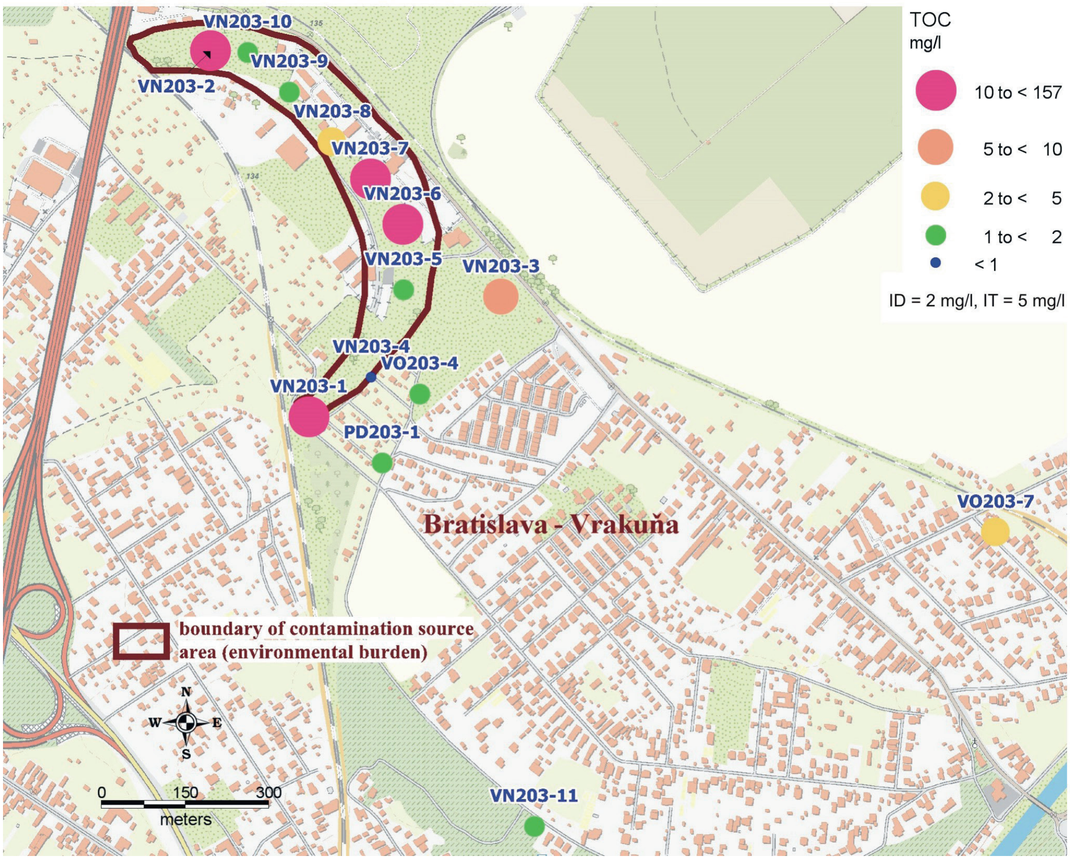

Fig. 1.25 Distribution of TOC in groundwaters (median concentrations) – site Bratislava – Vrakuňa – landfill CHZJD (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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 13th 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_{total}, Mn, Al, SO_4^{2-} (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_{total}, NO_2^-, NO_3^-, COD_{Mn} and hydrocarbon index (C_{10}-C_{40}). 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_4^{2-}	$mg.l^{-1}$	1,265	203	1,634	17.7	5,900	30				
Fe_{total}	$mg.l^{-1}$	79.6	5.68	154	0.021	590	30				
Mn^{2+}	$mg.l^{-1}$	6.26	1.59	8.03	0.021	25.6	30				
Al^{3+}	$mg.l^{-1}$	17.1	0.09	33.2	<0.01	110	30	0.25	0.4	1	10
As	$\mu g.l^{-1}$	23.2	0.95	44.1	<0.5	178	30	50	100	2	2
Cd	$\mu g.l^{-1}$	2.89	0.4	5.40	<0.1	17.6	30	5	20	4	0
Cu	$\mu g.l^{-1}$	853	34.5	1,885	<2	5,670	30	1,000	2,000	1	4
Ni	$\mu g.l^{-1}$	62.7	35	77.6	<2	232	30	100	200	4	4
Pb	$\mu g.l^{-1}$	5.91	0.5	13.8	<0.5	59.9	30	100	200	0	0
Co	$\mu g.l^{-1}$	77	20	117	<2	478	30	100	200	2	4
Zn	$\mu g.l^{-1}$	1,717	199	3,053	14	9,990	30	1,500	5,000	4	4

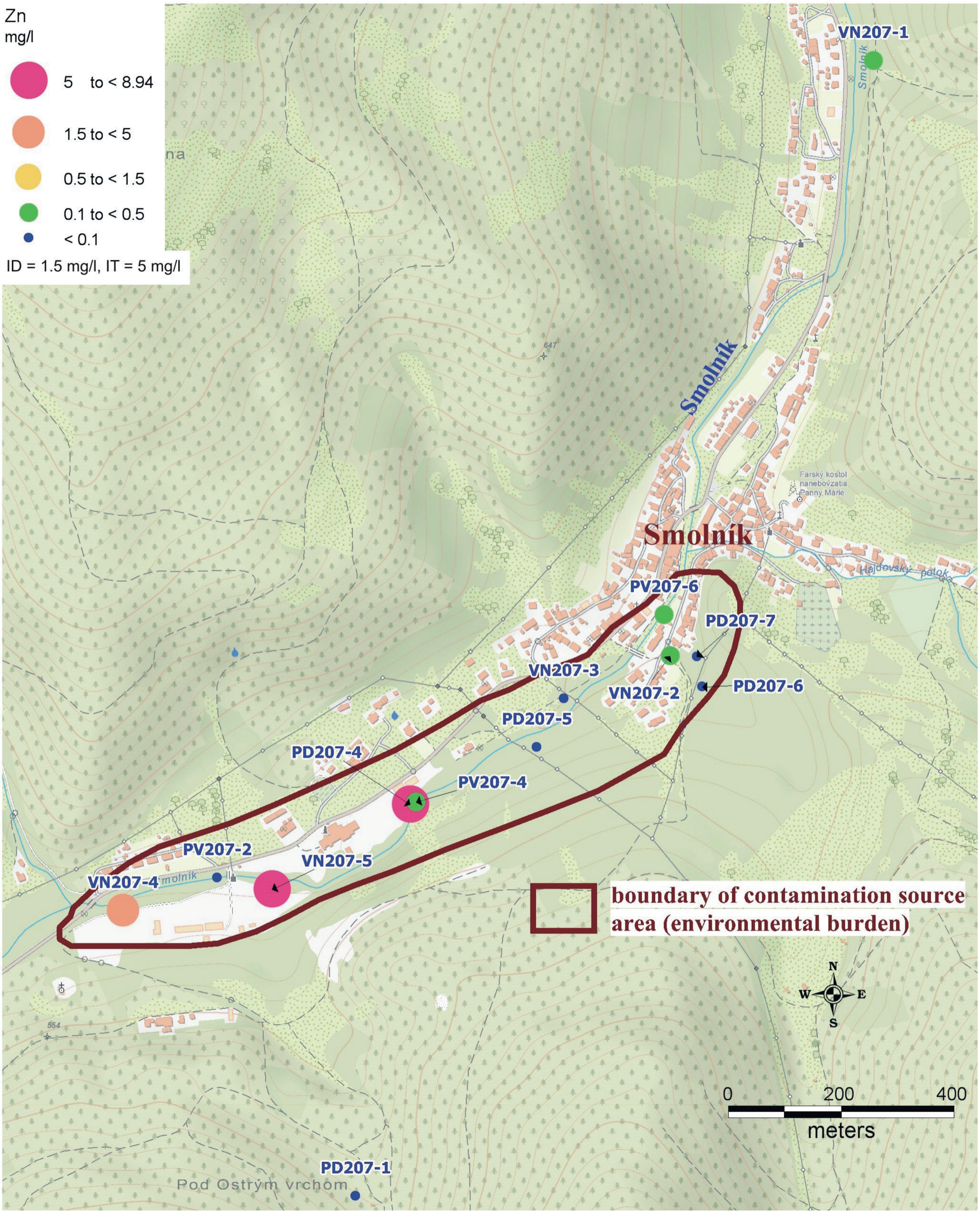

Fig. 1.26 Distribution of Zn in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

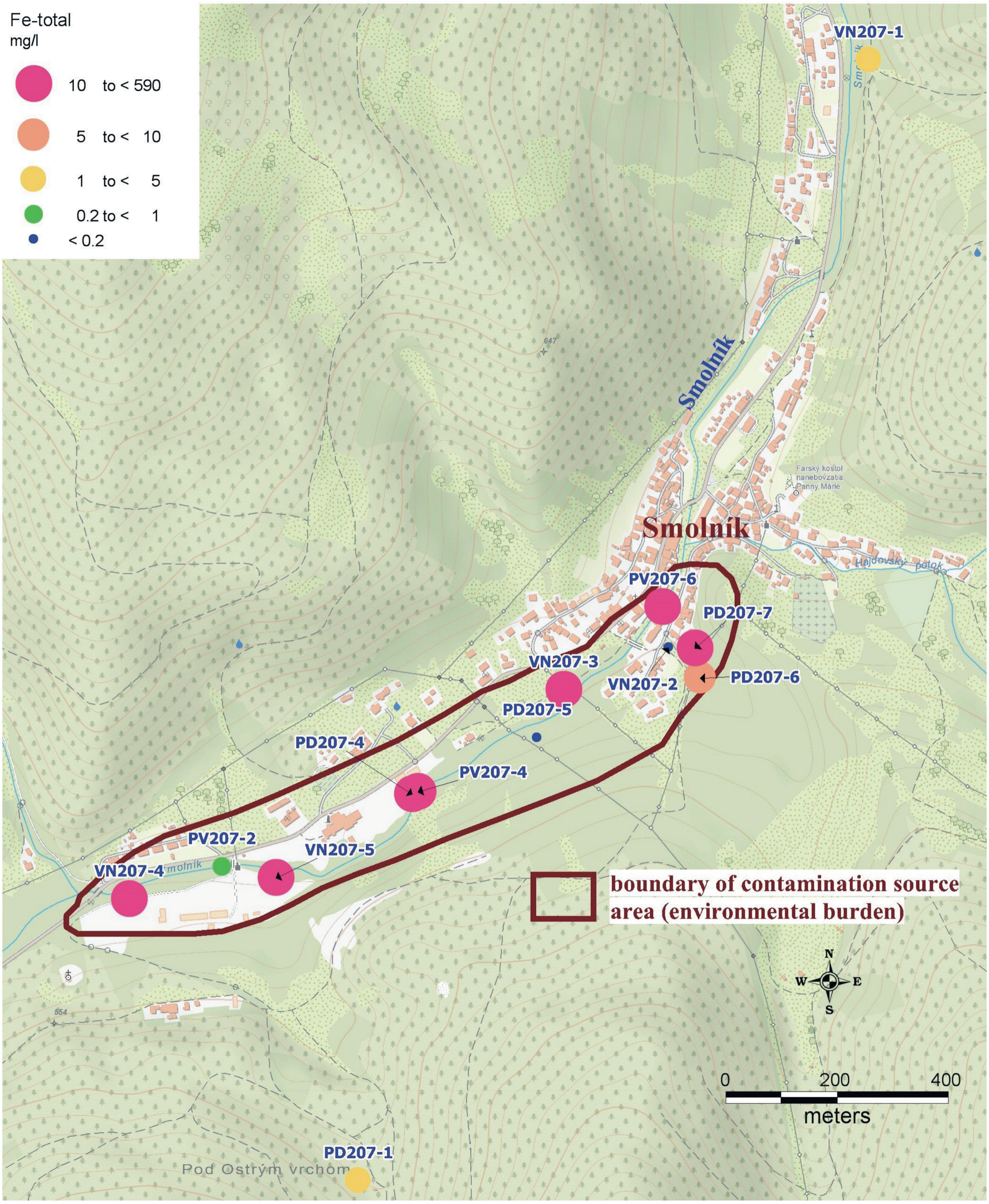

Fig. 1.27 Distribution of Fe in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

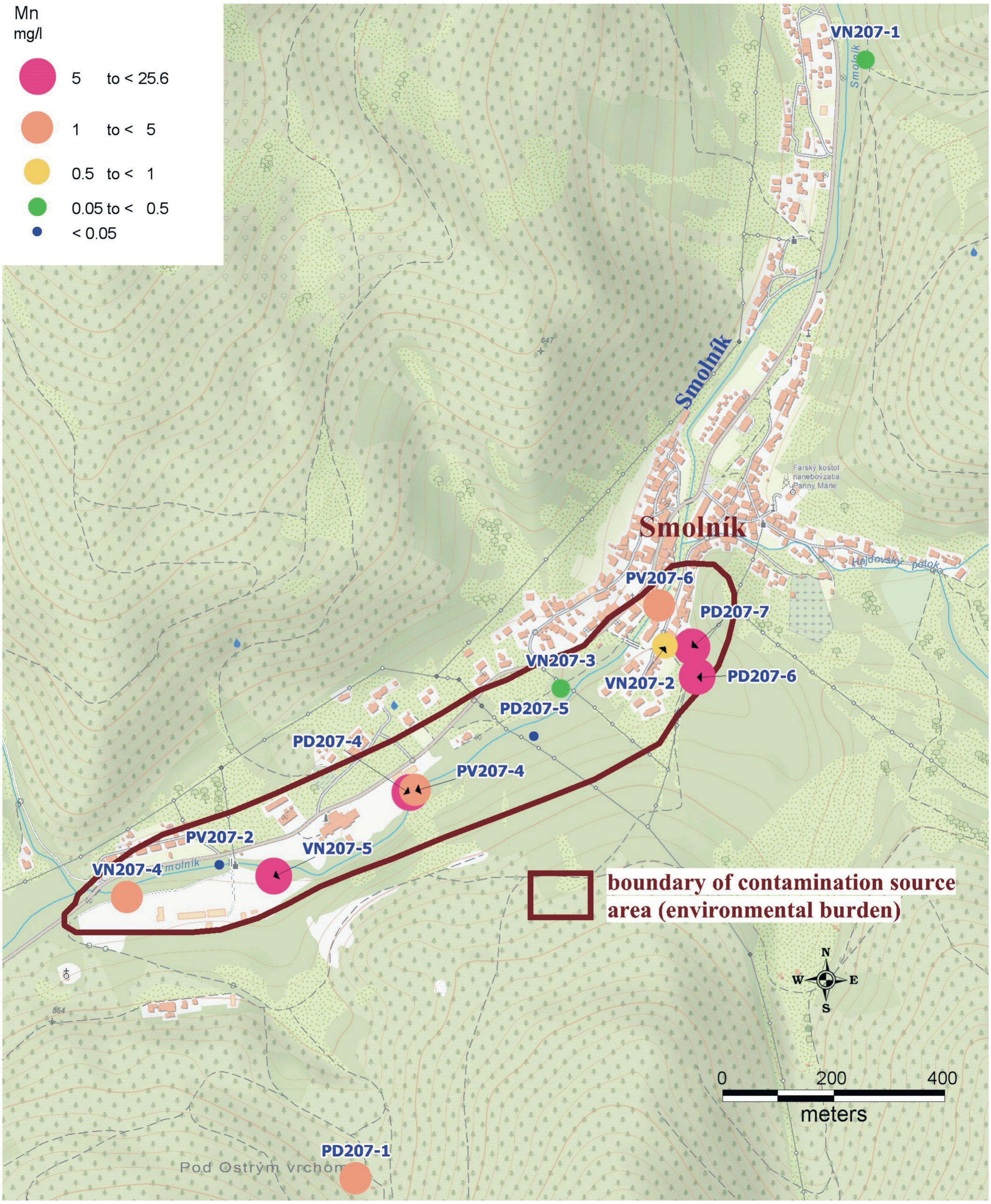

Fig. 1.28 Distribution of Mn in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

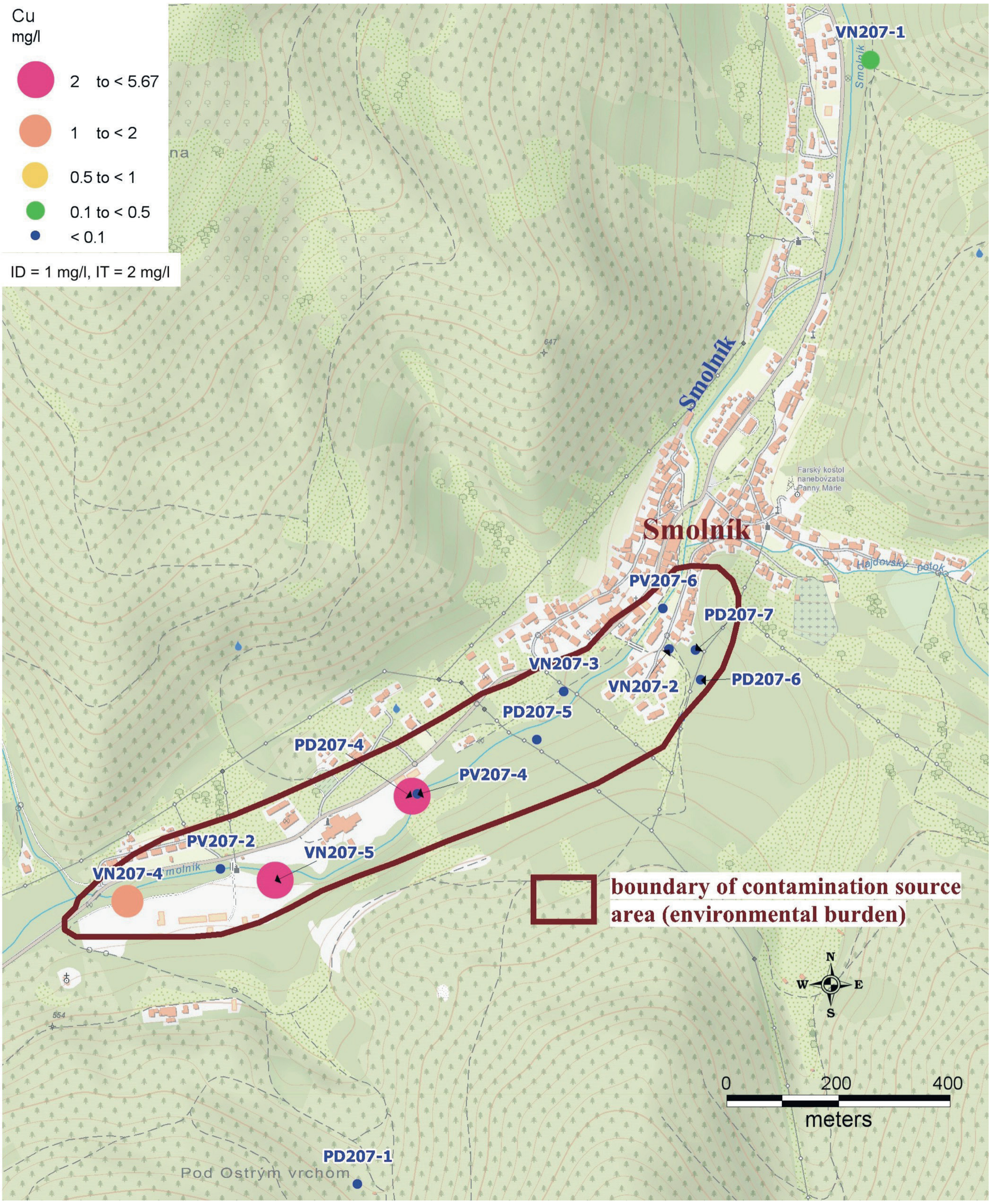

Fig. 1.29 Distribution of Cu in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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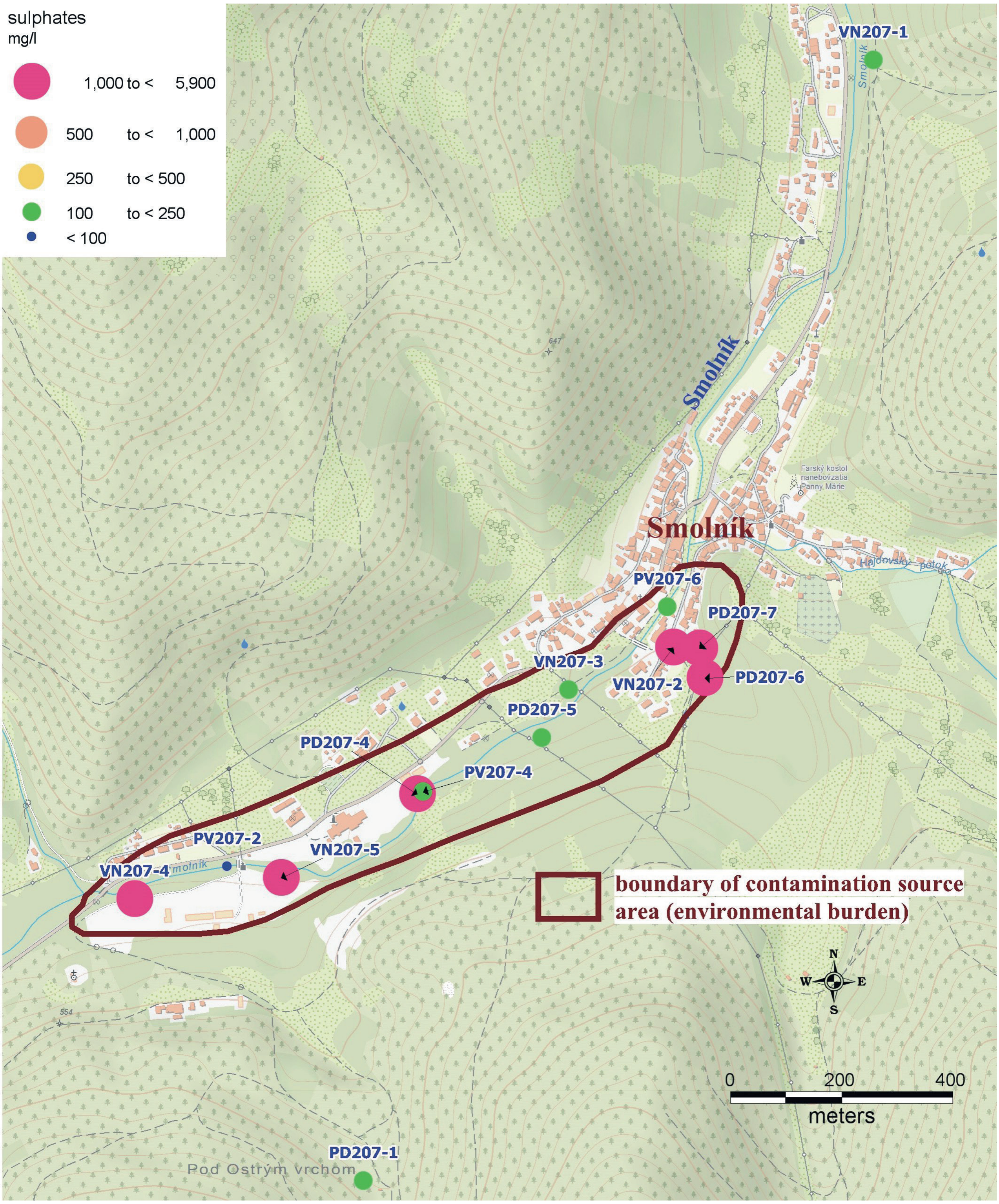

Fig. 1.30 Distribution of sulphates in groundwaters (sampled on 27.9.2018) – site Smolník – pyrite ores (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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 17th 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 $\mu g.l^{-1}$ for As, 406 $\mu g.l^{-1}$ for Sb) and maximum (7,250 $\mu g.l^{-1}$ for As, 7,176 $\mu g.l^{-1}$ 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. Fľaková 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_4^{2-}	$mg.l^{-1}$	137	87	167	11.1	863	38				
Fe_{total}	$mg.l^{-1}$	9.11	0.371	28.4	0.004	213	65				
Mn	$mg.l^{-1}$	0.92	0.209	1.82	0.002	10.5	65				
Al	$mg.l^{-1}$	1.23	0.05	4.33	<0.01	30.5	65	0.25	0.4	0	13
As	$\mu g.l^{-1}$	320	24.6	1,071	<0.5	7,250	65	50	100	8	19
Sb	$\mu g.l^{-1}$	406	199	922	<1	7,176	65	25	50	2	56
Cd	$\mu g.l^{-1}$	3.75	0.3	14.1	<0.1	107	65	5	20	3	3
Ni	$\mu g.l^{-1}$	27.3	2	69.3	<2	354	45	100	200	1	2
Pb	$\mu g.l^{-1}$	163	0.7	999	<0.5	7,810	65	100	200	1	2
Co	$\mu g.l^{-1}$	30.5	4	59.7	<2	258	39	100	200	4	1
Zn	$\mu g.l^{-1}$	536	19	1,693	<2	12,100	65	1,500	5,000	5	2

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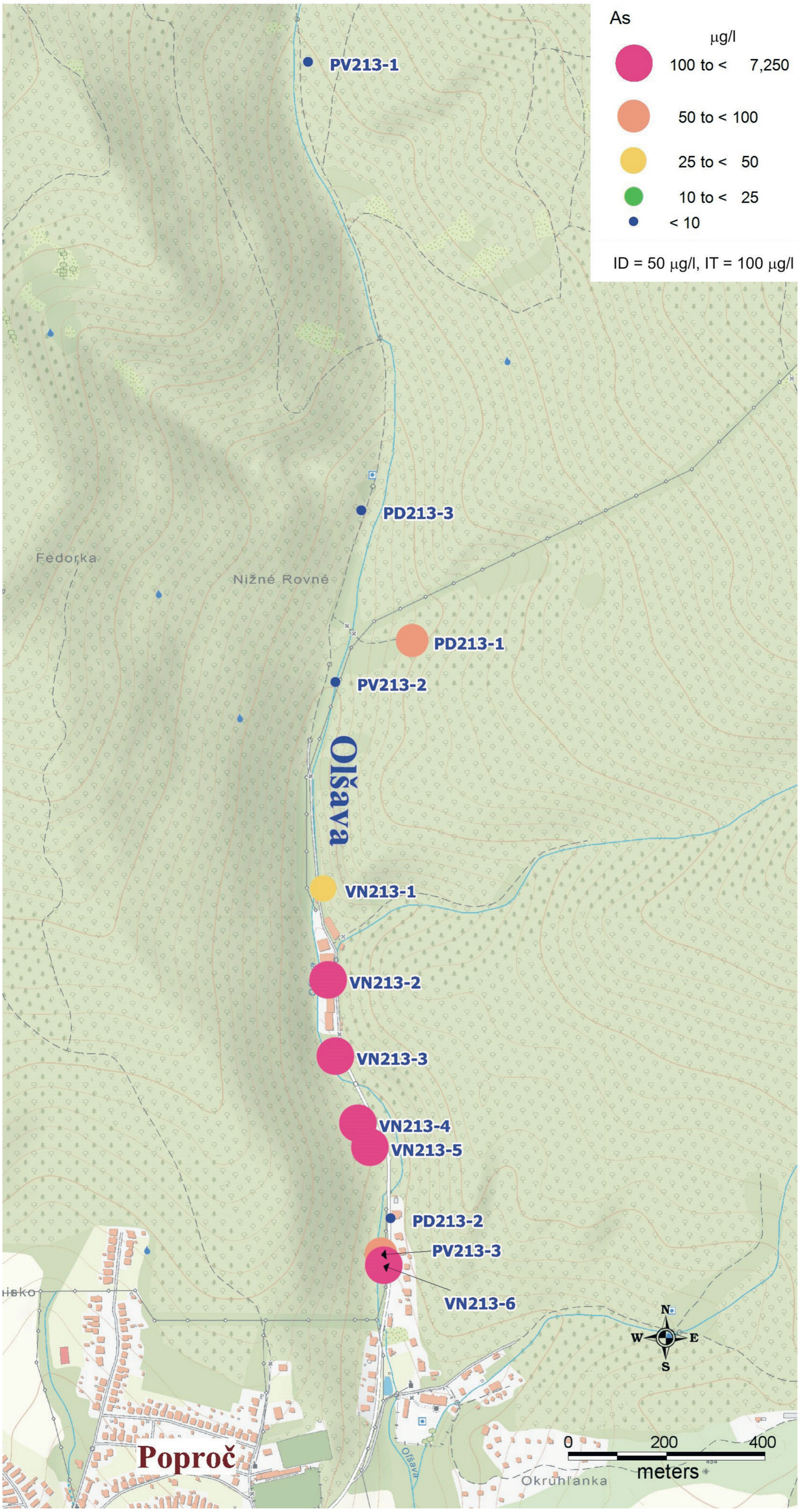

Fig. 1.31 Distribution of As in groundwaters (median concentrations) – site Poproč – Petrova dolina Valley (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

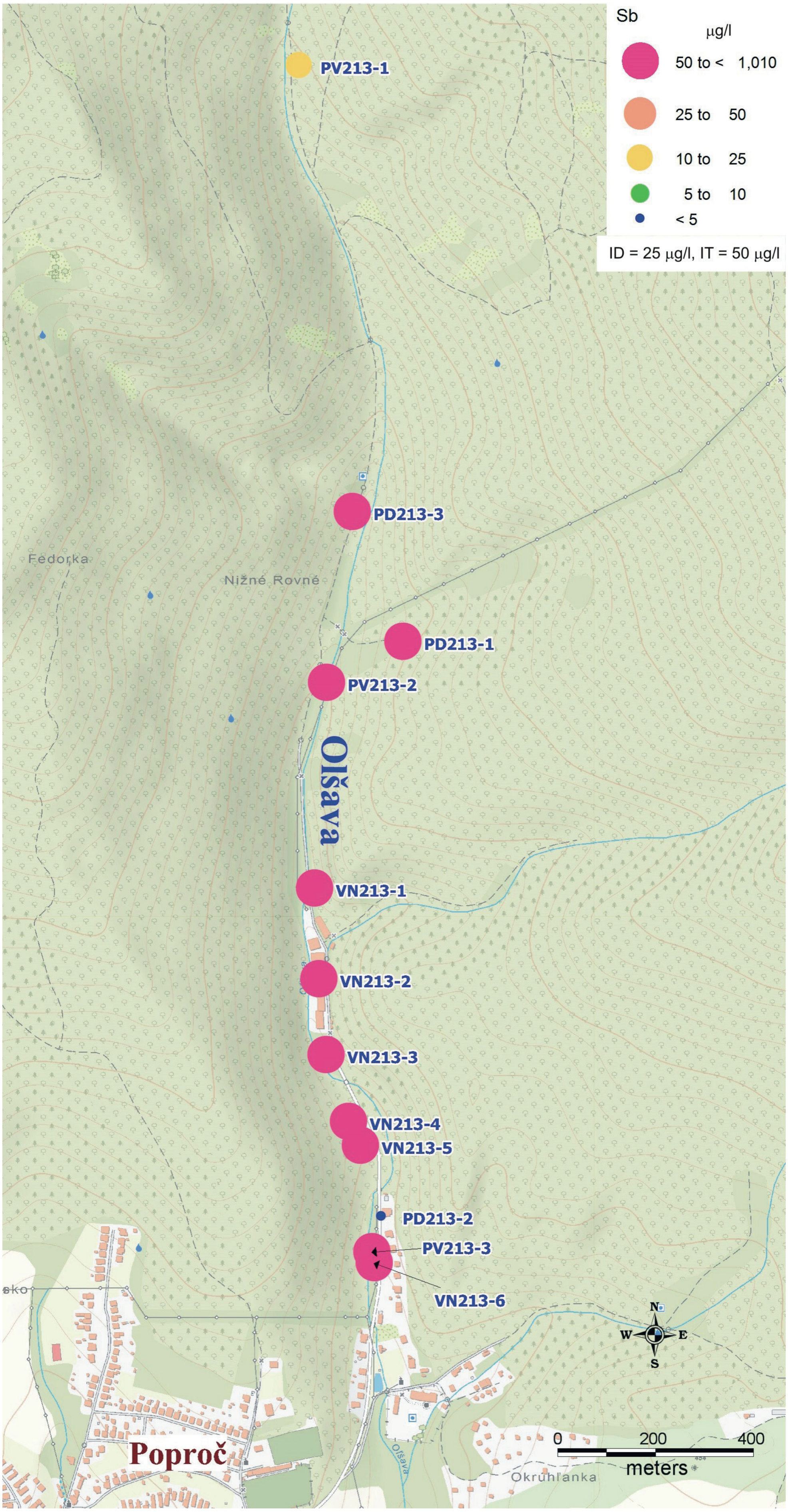

Fig. 1.32 Distribution of Sb in groundwaters (median concentrations) – site Poproč – Petrova dolina Valley (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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 $mg.l^{-1}$ for hydrocarbon index, 67.0 $mg.l^{-1}$ for NEL-UV) and maximum (689 $mg.l^{-1}$ for hydrocarbon index, 2,775 $mg.l^{-1}$ 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_3^-	$mg.l^{-1}$	12.2	1.37	47.7	1	335	72				
Cl^-	$mg.l^{-1}$	76.8	24.5	216	1	1,782	72	150	250	2	5
SO_4^{2-}	$mg.l^{-1}$	78.6	43.5	153	1.62	1,060	72				
Fe_{total}	$mg.l^{-1}$	9.49	0.53	16.9	0.018	67.3	71				
Mn	$mg.l^{-1}$	1.07	0.637	1.22	0.003	5.98	72				
hydrocarbon index (C_{10}-C_{40})	$mg.l^{-1}$	16.2	0.03	96.6	0.02	689	72	0.25	0.5	2	6
NEL-UV	$mg.l^{-1}$	67.0	0.105	395	0.05	2,775	72	0.5	1	9	16
tetrachloroethane	$\mu g.l^{-1}$	278	<0.2	2,359	<0.2	20,016	72				
dichloromethane	$\mu g.l^{-1}$	1.43	<0.2	4.01	<0.2	18.9	72	15	30	2	0
tetrachloromethane	$\mu g.l^{-1}$	16,099	<0.2	136,298	<0.2	1,156,560	72	5	10	1	3
trichloroethene	$\mu g.l^{-1}$	0.77	<0.2	3.26	<0.2	20.5	72	25	50	0	0
chloroethene	$\mu g.l^{-1}$	0.44	<0.2	1.06	<0.2	8	72	5	10	1	0
chloroform	$\mu g.l^{-1}$	3,405	<0.2	28,885	<0.2	245,100	72				
benzene	$\mu g.l^{-1}$	4,108	<0.2	33,975	<0.2	288,350	72	15	30	0	4
ethylbenzene	$\mu g.l^{-1}$	95.5	<0.2	764	<0.2	6,480	72	150	300	1	1
chlorobenzene	$\mu g.l^{-1}$	83.2	<0.2	703	<0.2	5,965	72	15	30	0	1
toluene	$\mu g.l^{-1}$	47.5	<0.2	394	<0.2	3,340	72	350	700	0	1
styrene	$\mu g.l^{-1}$	0.2	<0.2	0.00	<0.2	0.2	72	20	50	0	0
xylene	$\mu g.l^{-1}$	3,703	<0.2	30,912	<0.2	262,340	72	250	500	0	4

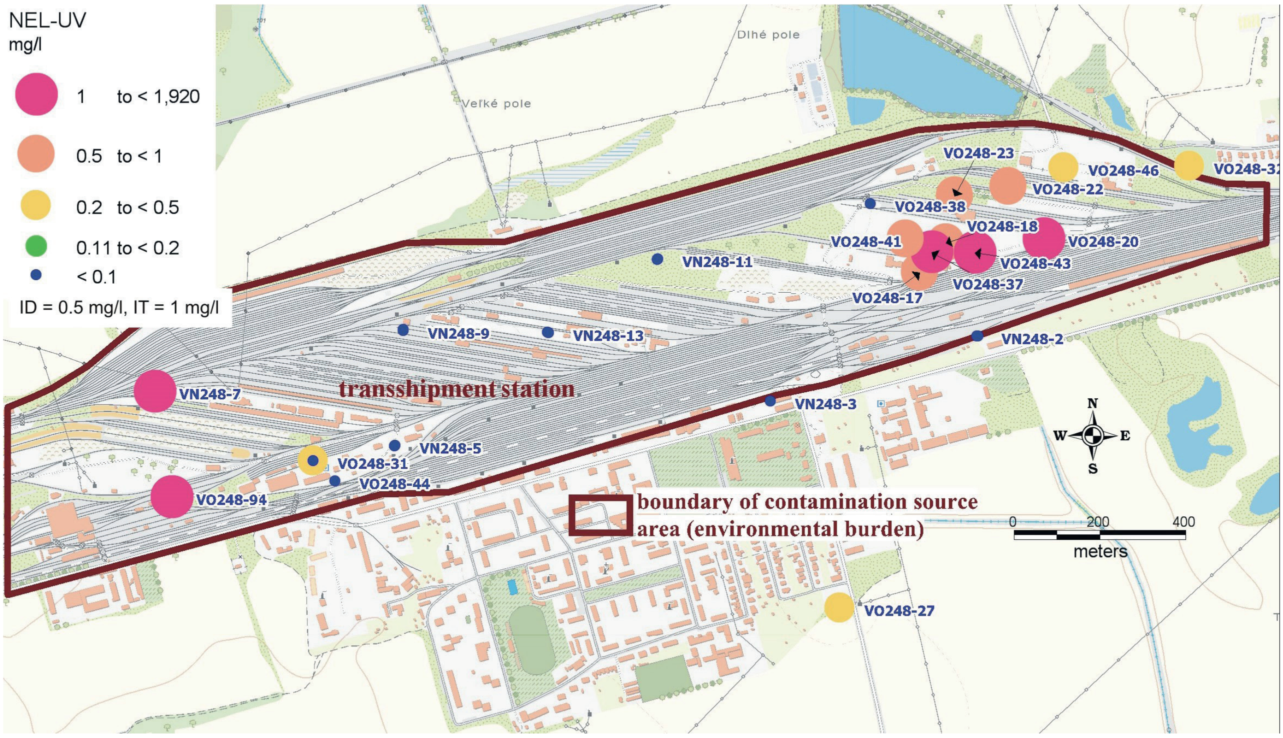

Fig. 1.33 Distribution of NEL-UV in groundwaters (sampled in 2018) – site Čierna nad Tisou – transshipment station (most contaminated boreholes; Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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 $\mu g.l^{-1}$ for cis 1,2-dichloroethene, 57.3 $mg.l^{-1}$ 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 >ID	number of samples >IT
NH_4^+	$mg.l^{-1}$	0.82	0.115	1.88	<0.03	7.7	34	1.2	2.4	0	4
TOC	$mg.l^{-1}$	2.74	2.55	1.16	1.1	5.9	34	2	5	20	2
cis 1,2-dichloroethene	$\mu g.l^{-1}$	15.4	9.05	17.7	<0.2	61.8	34	25	50	5	3
tetrachloroethene	$\mu g.l^{-1}$	57.3	5	111	<0.2	413	34	10	20	2	14
trichloroethene	$\mu g.l^{-1}$	50.2	6.45	95.0	<0.2	421	34	25	50	4	8
chloroethene	$\mu g.l^{-1}$	1.36	<0.2	2.51	<0.2	9.1	34	5	10	4	0

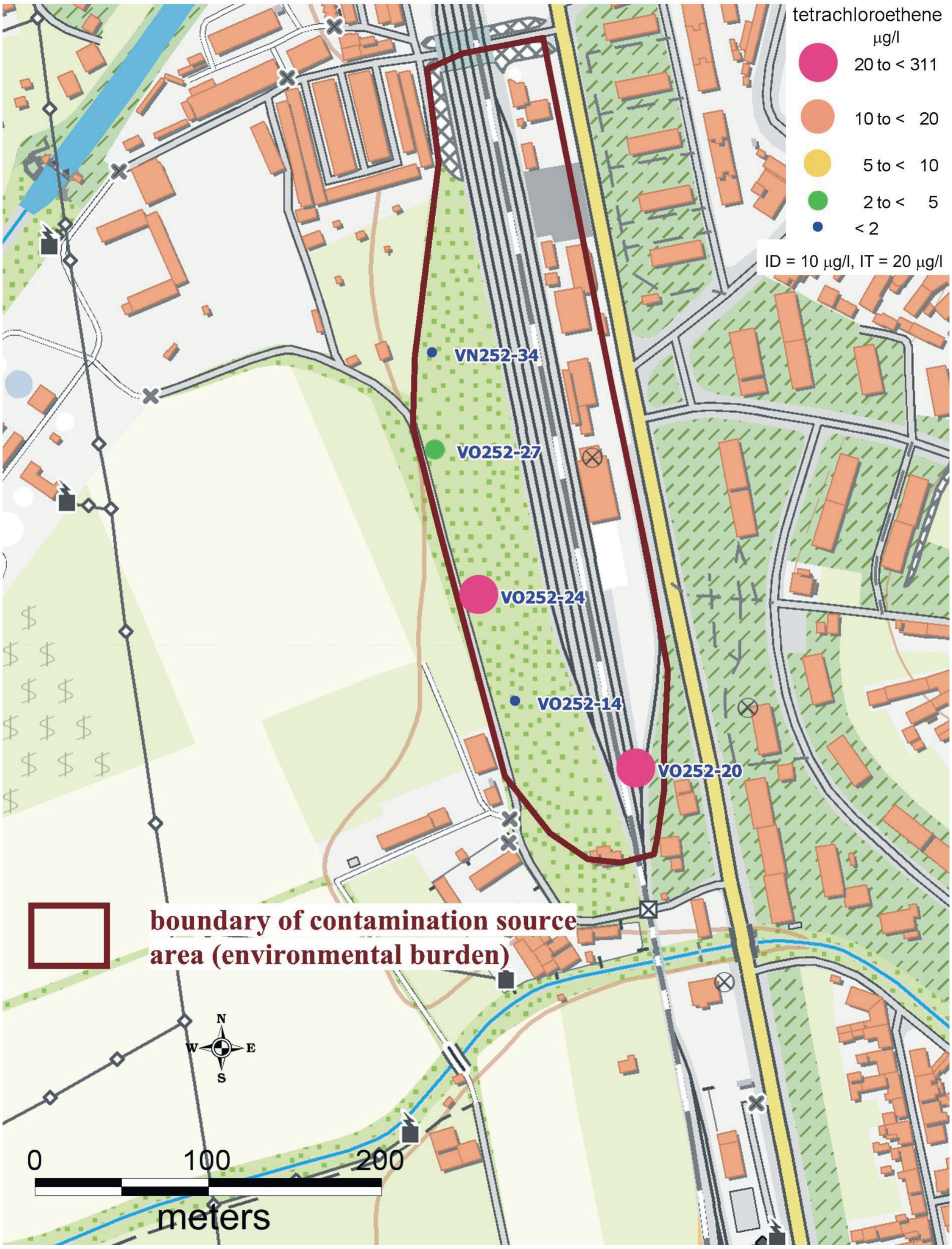

Fig. 1.34 Distribution of tetrachloroethene in groundwaters (median concentrations) – site Bánovce nad Bebravou – Railway station (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

50.2 mg.l^{-1} for trichloroethene) and maximum (61.8 µg.l^{-1} for cis 1,2-dichloroethene, 413 µg.l^{-1} for tetrachloroethene, 421 µg.l^{-1} 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 NH_4^+, TOC, hydrocarbon index (C_{10}-C_{40}), tetrachloroethene, benzene, benzo(b)fluoranthene, benzo(g,h,i)perylene, phenanthrene and chrysene. The extremely high concentrations of 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 >ID	number of samples >IT
NH_4^+	$mg.l^{-1}$	3.67	0.425	6.27	<0.02	34.6	226	1.2	2.4	6	84
TOC	$mg.l^{-1}$	20.8	10.8	79.0	0.862	1,460	370	2	5	89	270
hydrocarbon index (C_{10}-C_{40})	$mg.l^{-1}$	10,285	0.1	101,541	<0.005	1,193,000	388	0.25	0.5	20	65
tetrachloroethene	$\mu g.l^{-1}$	1.04	<0.1	5.98	<0.1	107	423	10	20	15	2
tetrachloromethane	$\mu g.l^{-1}$	0.21	<0.1	1.12	<0.1	19.3	404	5	10	2	1
trichloroethene	$\mu g.l^{-1}$	0.44	<0.1	2.46	<0.1	29.1	423	25	50	3	0
chloroethene	$\mu g.l^{-1}$	0.25	<0.1	1.05	<0.1	12.7	423	5	10	2	2
benzene	$\mu g.l^{-1}$	2.26	<0.1	13.3	<0.1	153	385	15	30	4	8
ethylbenzene	$\mu g.l^{-1}$	1.96	<0.1	12.4	<0.1	147	385	150	300	0	0
xylene	$\mu g.l^{-1}$	15.9	<0.1	102	<0.1	1,405	385	250	500	3	4
benzo(a)pyrene	$\mu g.l^{-1}$	0.01	<0.001	0.02	<0.001	0.133	385	0.1	0.2	1	0
benzo(b)fluoranthene	$\mu g.l^{-1}$	0.09	<0.001	0.61	<0.001	8.64	385	0.25	0.5	2	12
benzo(g,h,i)perylene	$\mu g.l^{-1}$	0.01	<0.001	0.04	<0.001	0.4	385	0.1	0.2	12	2
benzo(k)fluoranthene	$\mu g.l^{-1}$	0.01	<0.001	0.06	<0.001	0.85	385	0.1	0.2	3	3
phenanthrene	$\mu g.l^{-1}$	3.49	0.003	22.9	<0.001	297	385	5	10	4	15
chrysene	$\mu g.l^{-1}$	0.44	<0.001	2.93	<0.001	37.5	385	0.1	0.2	4	21
naphthalene	$\mu g.l^{-1}$	2.12	<0.001	14.2	<0.001	182	385	25	50	2	7
pyrene	$\mu g.l^{-1}$	0.798	0.004	5.79	<0.001	74.1	385	25	50	1	2

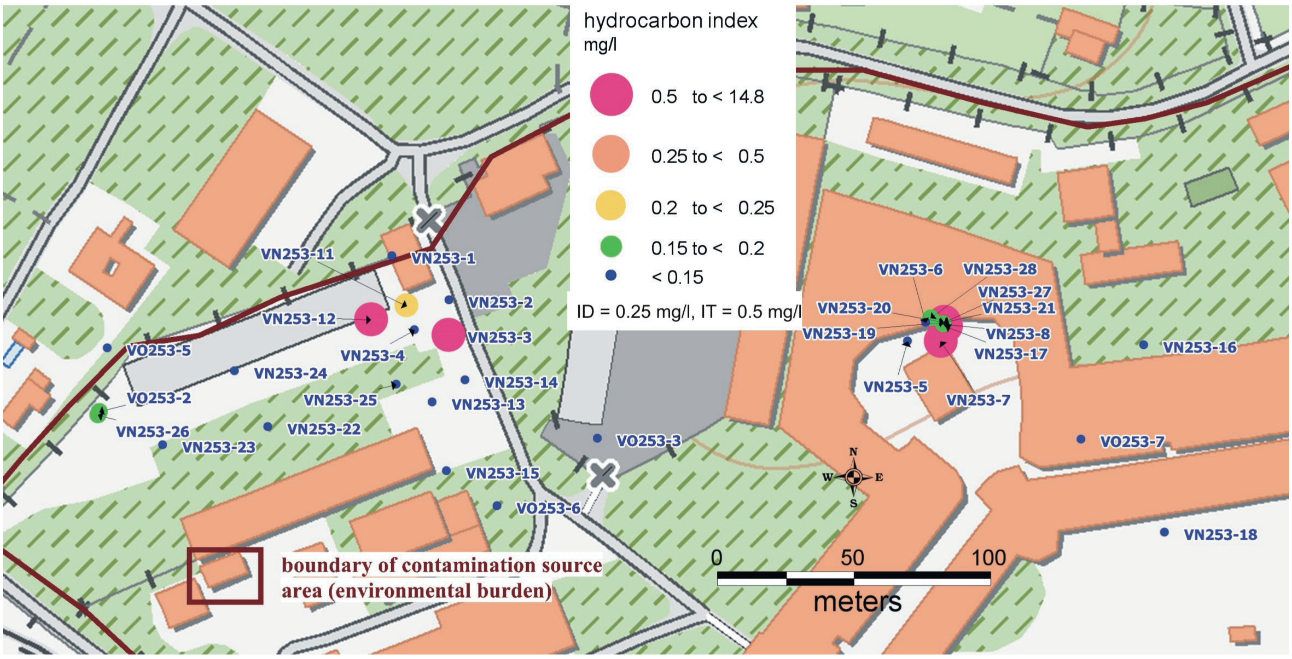

Fig. 1.35 Distribution of hydrocarbon index in groundwaters (median concentrations) – site Komárno – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

TOC, hydrocarbon index and xylene in groundwater (Tab. 1.12) were observed (maximum values 34.6 mg.l^{-1} for NH_4^+, 1,460 mg.l^{-1} for TOC, 1,193,000 µg.l^{-1} for hydrocarbon index, 1,405 µg.l^{-1} for xylene).

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

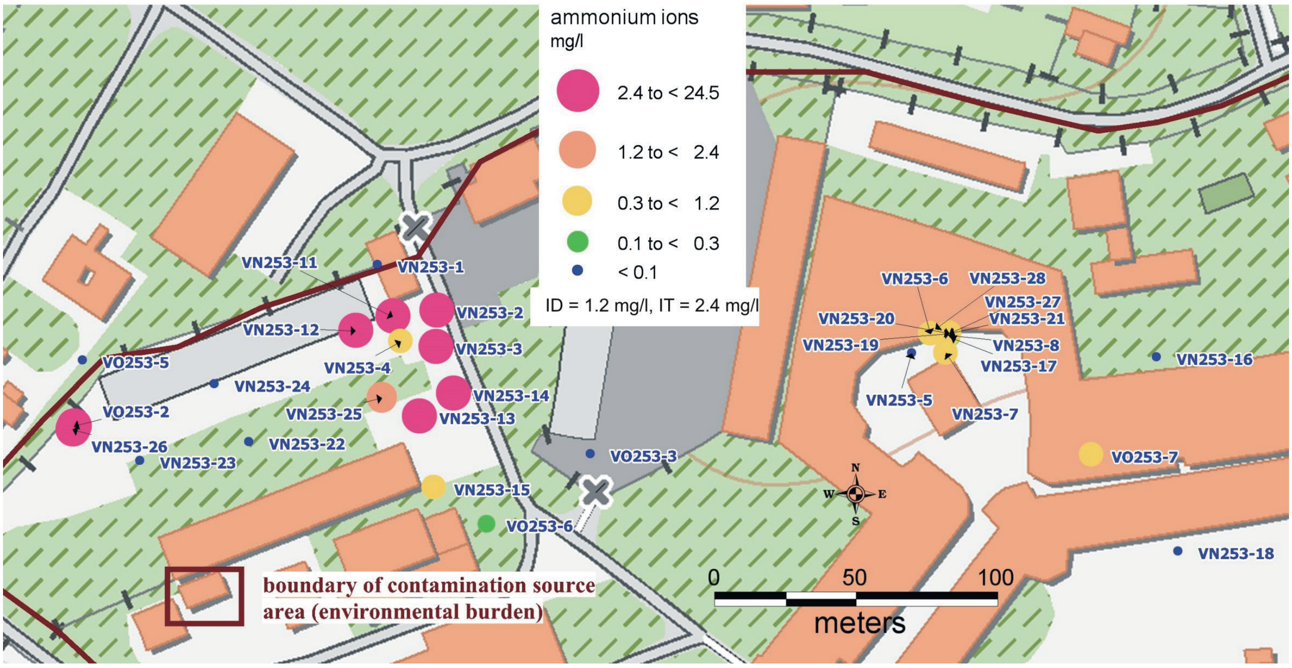

Fig. 1.36 Distribution of NH_4^+ in groundwaters (median concentrations) – site Komárno – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

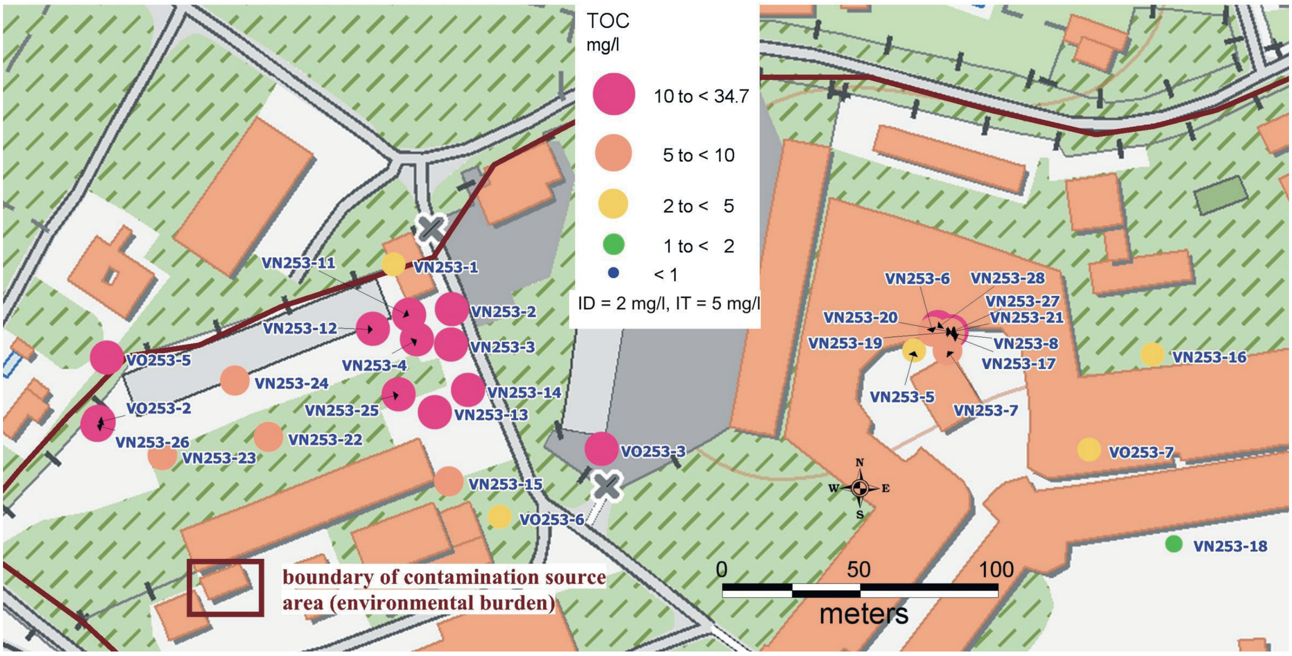

Fig. 1.37 Distribution of TOC in groundwaters (median concentrations) – site Komárno – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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})	$mg.l^{-1}$	0.03	0.02	0.04	0.02	0.32	91	0.25	0.5	2	0
cis 1,2-dichloroethene	$\mu g.l^{-1}$	38.9	1.8	111	<0.2	770	91	25	50	2	16
tetrachloroethene	$\mu g.l^{-1}$	7.10	<0.2	27.1	<0.2	213	91	10	20	0	8
trichloroethene	$\mu g.l^{-1}$	6.69	<0.2	31.4	<0.2	275	91	25	50	2	4
chloroethene	$\mu g.l^{-1}$	7.73	1.6	16.0	<0.2	103	91	5	10	10	17

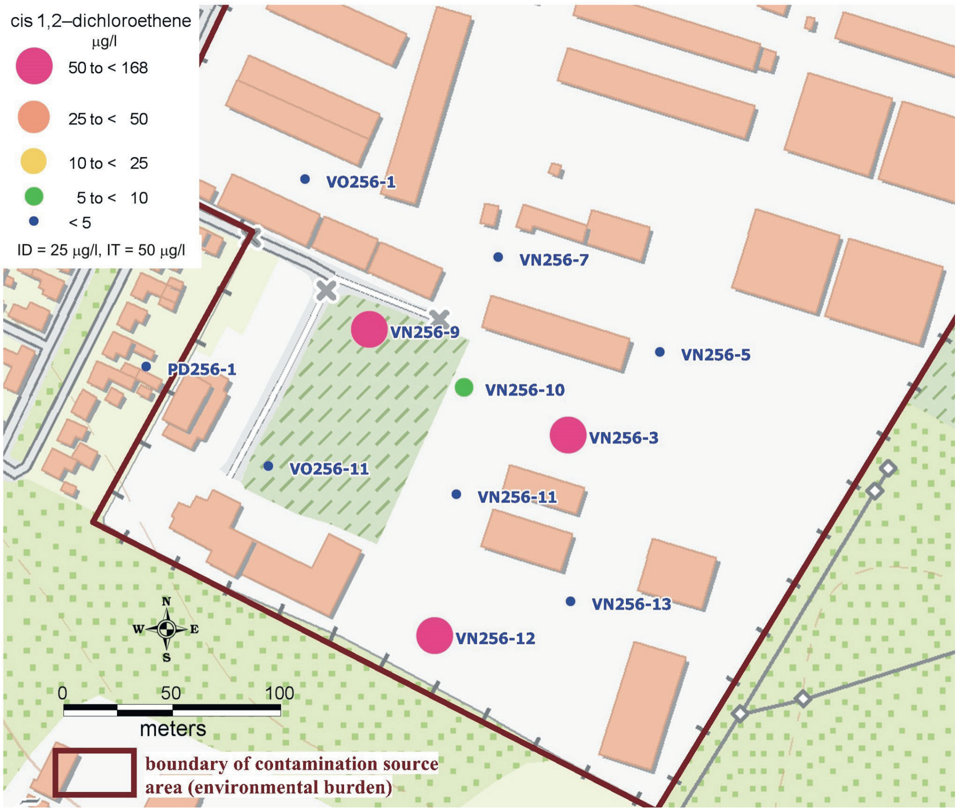

Fig. 1.38 Distribution of cis 1,2-dichloroethene in groundwaters (median concentrations) – site Rimavská Sobota – area after the Soviet Army (Topographic background: ZB-GIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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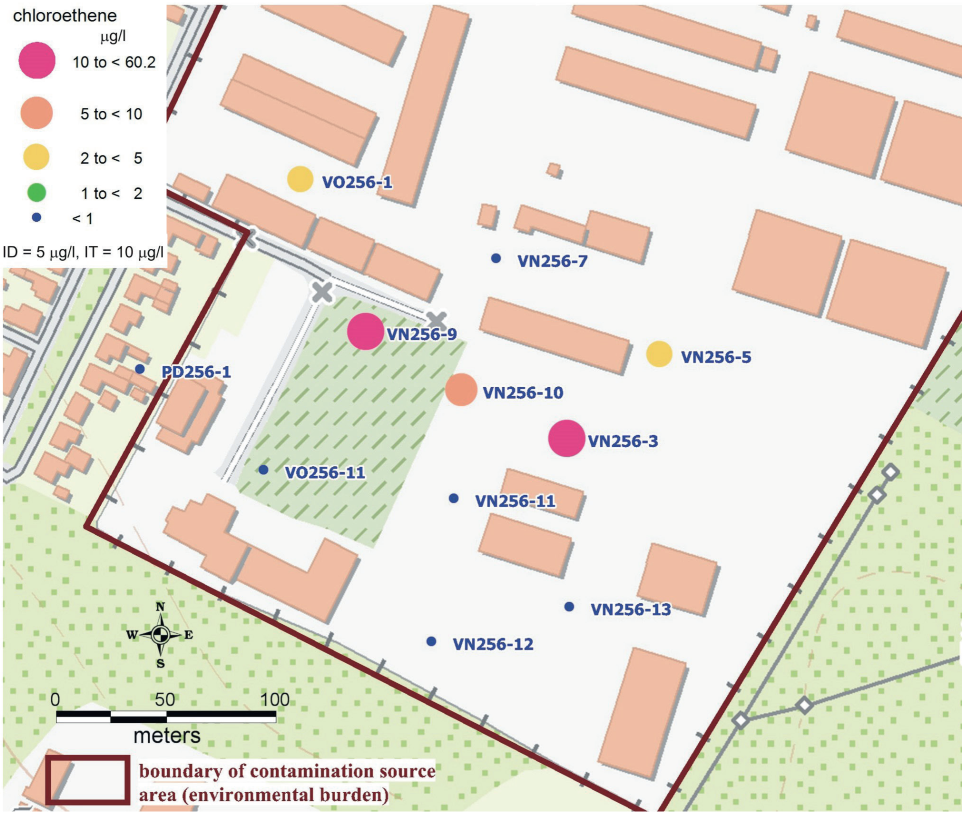

Fig. 1.39 Distribution of chloroethene in groundwaters (median concentrations) – site Rimavská Sobota – area after the Soviet Army (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

chloroethene. Elevated maximum concentrations of cis 1,2-dichloroethene (770 $mg.l^{-1}$), tetrachloroethene (213 $mg.l^{-1}$), trichloroethene (275 $mg.l^{-1}$) and chloroethene (103 $mg.l^{-1}$) 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_4^+ 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 $mS.m^{-1}$), VO314-23 (917.7 $mS.m^{-1}$), VN314-2 (278 $mS.m^{-1}$), VO314-28 (293.3 $mS.m^{-1}$). Mean sulphate concentrations above extremely high value of 1,000 $mg.l^{-1}$ were observed in many monitored boreholes: VN314-1, VN314-2, VN314-10, VN314-19, VO314-23 (the highest mean value of about 5,020 $mg.l^{-1}$), VO314-24, VO314-25, VO314-26, VO314-28, VO314-30. Elevated mean contents of arsenic (above 100 $\mu g.l^{-1}$) were monitored in boreholes VN314-17, VO314-26 and VO314-30 (the highest mean value of about 1,774 $\mu g.l^{-1}$). Extremely high mean concentration was observed in borehole VO314-26 (2,254 $\mu g.l^{-1}$) for antimony, in borehole VO314-23 (4,367 $\mu g.l^{-1}$) for cadmium, in boreholes VN314-17 (6,436 $\mu g.l^{-1}$) and VO314-26 (13,533 $\mu g.l^{-1}$) for copper. Mean nickel contents above very high value of 1,000 $\mu g.l^{-1}$ were observed in monitored boreholes: VN314-1, VN314-2 (the highest mean value at level 9,405 $\mu g.l^{-1}$), 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	$mS.m^{-1}$	208	169	180	37	1,170	243	200	300	82	21
NH_4^+	$mg.l^{-1}$	1.95	0.21	3.81	<0.05	19.2	99	1.2	2.4	2	21
Cl^-	$mg.l^{-1}$	86	35	164	2.12	1,490	146	150	250	12	10
F^-	$mg.l^{-1}$	0.73	0.17	1.62	<0.1	8.4	81	2	4	4	5
SO_4^{2-}	$mg.l^{-1}$	1,140	750	1,446	28	12,649	155				116*
Fe-total	$mg.l^{-1}$	12.1	0.12	42.6	<0.002	257	146				43**
Mn	$mg.l^{-1}$	4.92	2.29	6.56	0.001	31.8	146				107***
Al	$mg.l^{-1}$	0.15	0.05	0.24	0.01	1.44	116	0.25	0.4	4	15
B	$mg.l^{-1}$	0.53	0.21	0.63	0.02	2.24	116	0.5	5	32	0
As	$\mu g.l^{-1}$	46.3	5	208	<0.5	2,010	232	50	100	15	15
Sb	$\mu g.l^{-1}$	57.3	2.4	274	<0.5	2,410	213	25	50	9	25
Cd	$\mu g.l^{-1}$	215	1.1	977	<0.1	6,680	232	5	20	40	31
Cu	$\mu g.l^{-1}$	778	32	2,619	<2	16,700	232	1,000	2,000	4	14
Ni	$\mu g.l^{-1}$	865	18	2,329	<2	12,200	232	100	200	12	76
Zn	$\mu g.l^{-1}$	189,752	136	936,162	3	7,090,000	232	1,500	5,000	29	16
Pb	$\mu g.l^{-1}$	19	1	78	<0.05	862	232	100	200	5	7
Co	$\mu g.l^{-1}$	28.7	1	82	<2	532	167	100	200	6	7
Hg	$\mu g.l^{-1}$	1.1	0.2	3.2	<0.1	23.5	230	2	5	8	15
TOC	$mg.l^{-1}$	32	7	92	0.5	513	79	2	5	10	44
hydrocarbon index (C_{10}-C_{40})	$mg.l^{-1}$	0.07	<0.02	0.12	<0.02	0.74	161	0.25	0.5	9	3

* *Number of samples > 250 $mg.l^{-1}$ (national normative value according to 247/2017 Coll.)*

** *Number of samples > 0.5 $mg.l^{-1}$ (national normative value according to 247/2017 Coll.)*

*** *Number of samples > 0.2 $mg.l^{-1}$ (national normative value according to 247/2017 Coll.)*

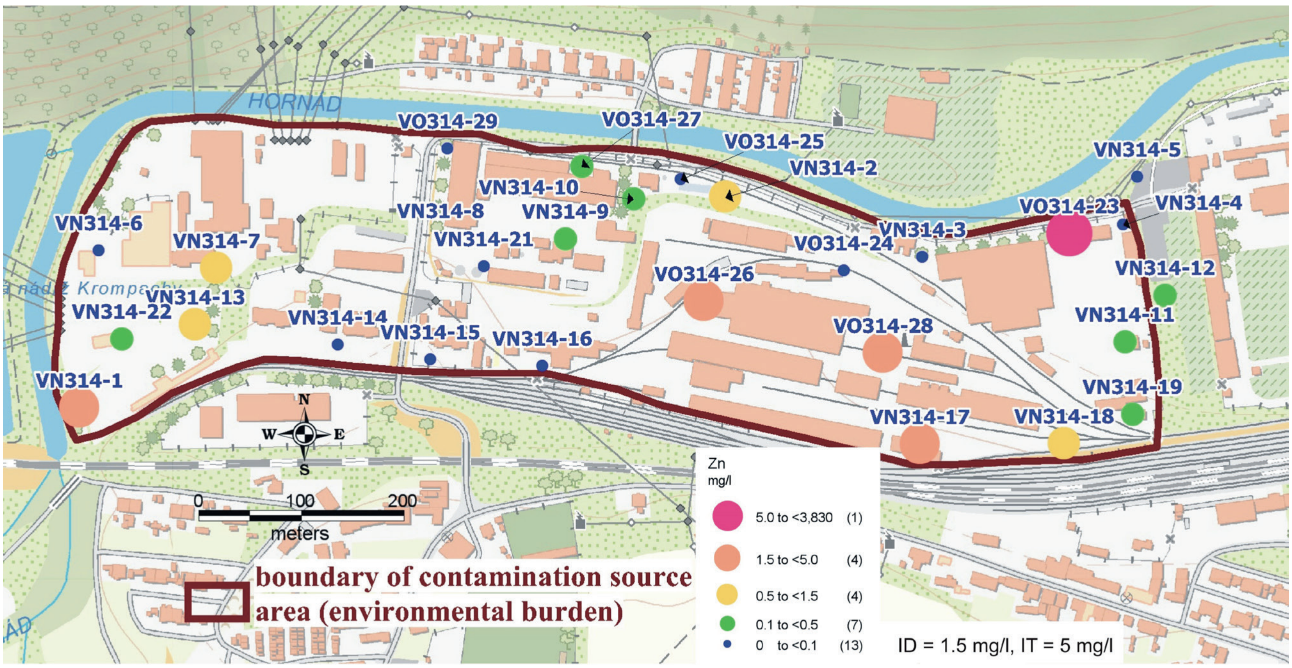

Fig. 1.40 Distribution of Zn in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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

Borehole	conductivity	NH_4^+	Cl^-	SO_4^{2-}	As	Sb	Cd	Cu	Ni	Zn	B	TOC
	$mS.m^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$	$\mu g.l^{-1}$	$\mu g.l^{-1}$	$\mu g.l^{-1}$	$\mu g.l^{-1}$	$\mu g.l^{-1}$	$\mu g.l^{-1}$	$mg.l^{-1}$	$mg.l^{-1}$
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

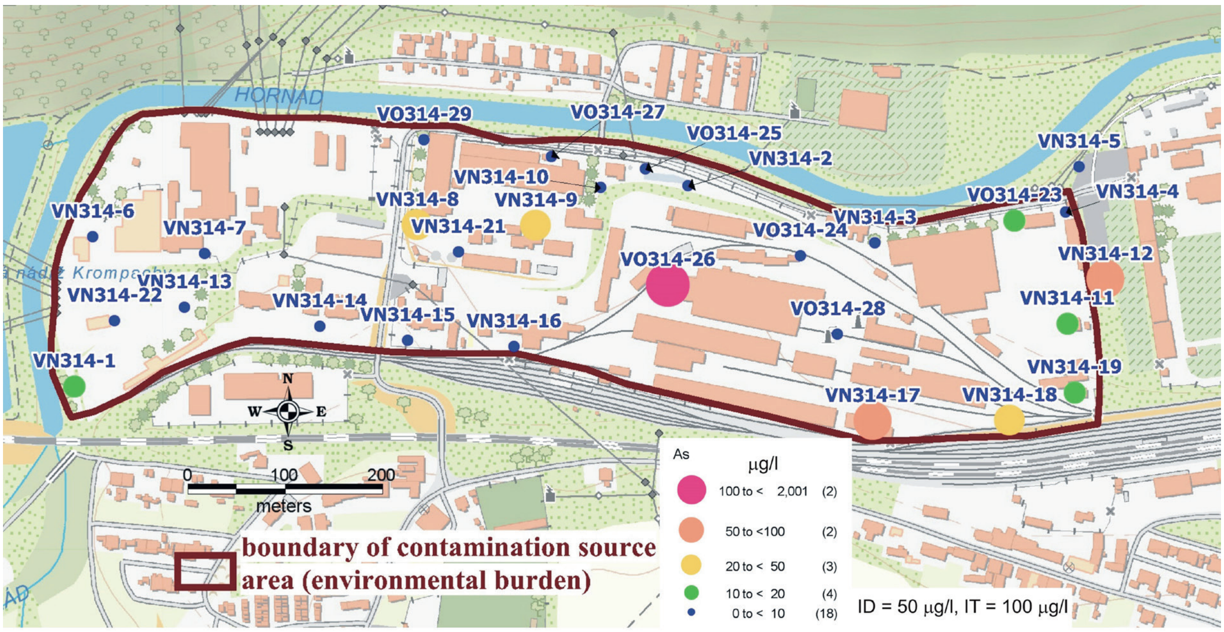

Fig. 1.41 Distribution of As in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

mean concentration was calculated in borehole VO314-23 (3,980,455 μg.l[-1]). Mean zinc contents above 1,000 μg.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

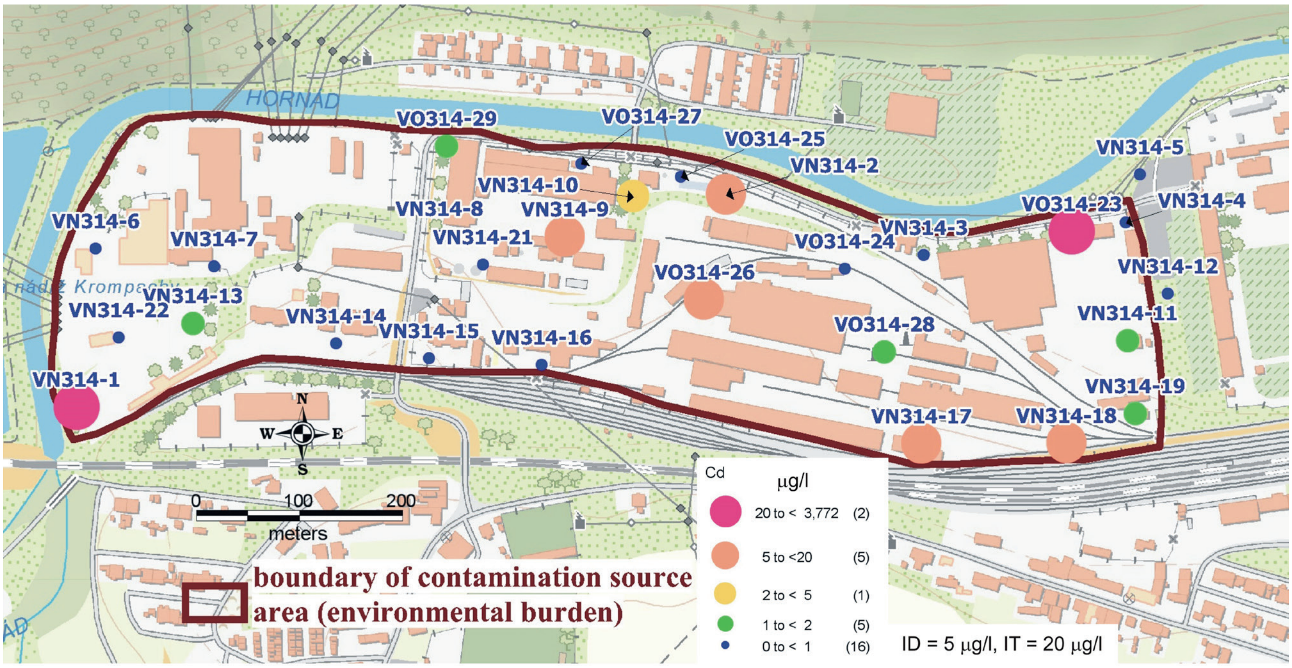

Fig. 1.42 Distribution of Cd in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

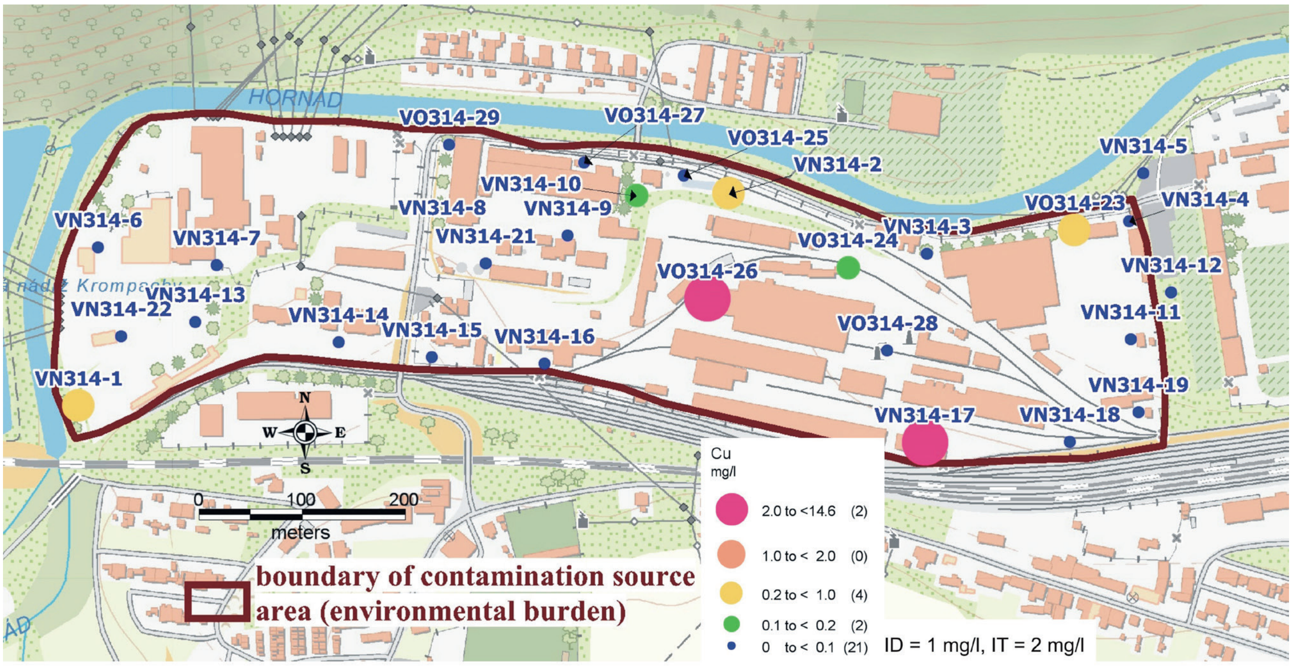

Fig. 1.43 Distribution of Cu in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

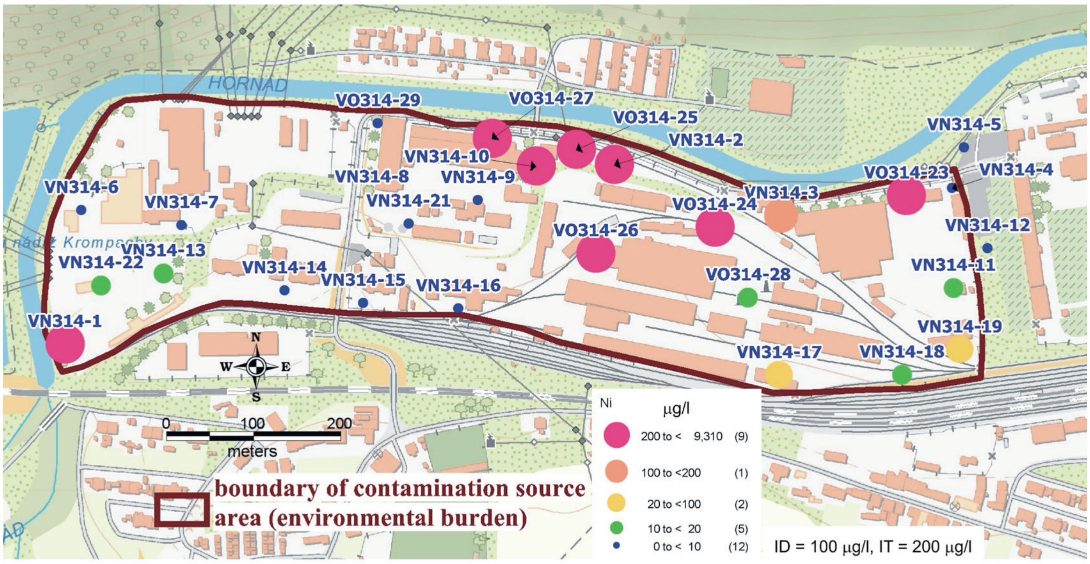

Fig. 1.44 Distribution of Ni in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

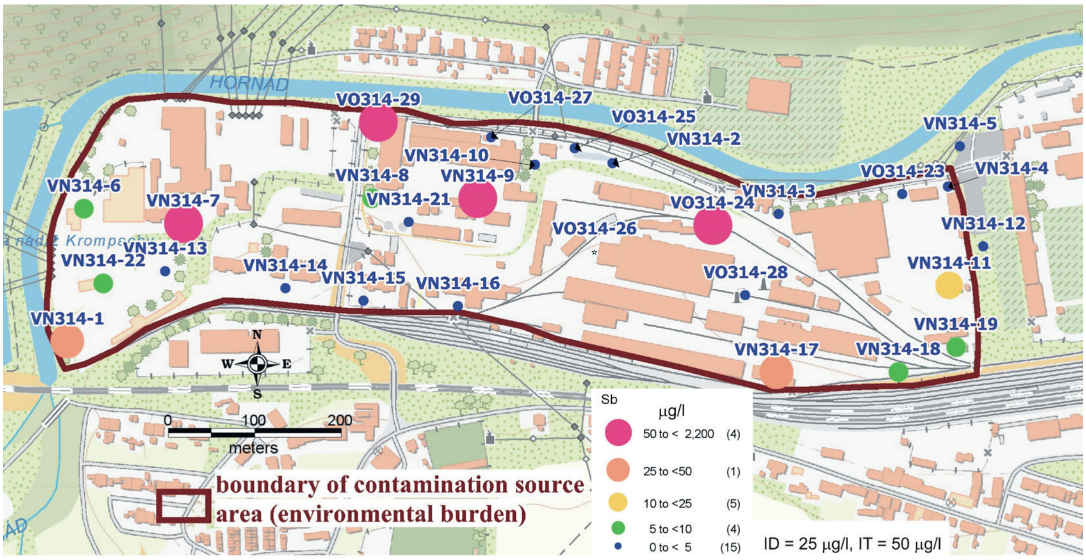

Fig. 1.45 Distribution of Sb in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

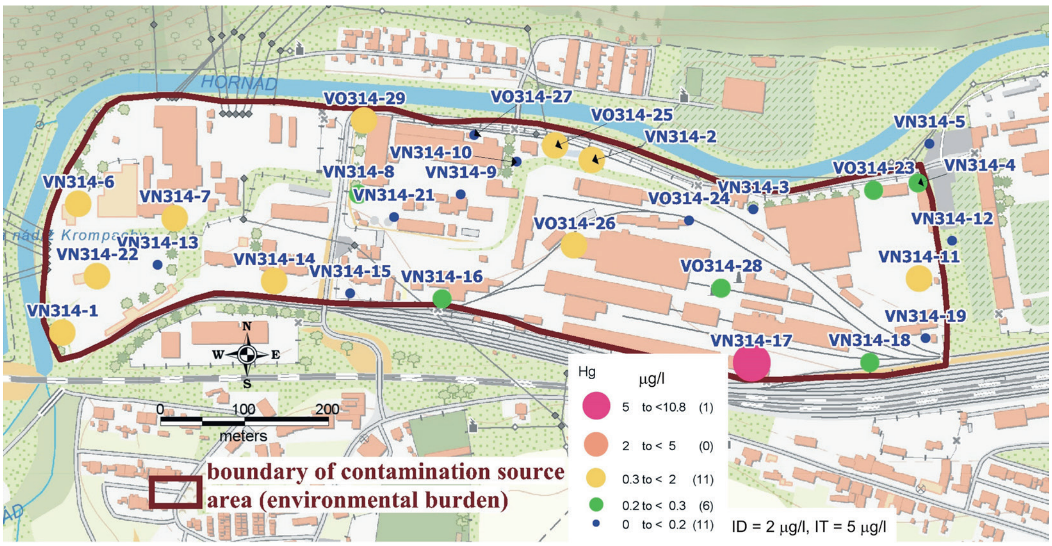

Fig. 1.46 Distribution of Hg in groundwaters (median concentrations) – site Krompachy – Kovohuty (Topographic background: ZBGIS®, The Geodesy, Cartography and Cadastre Authority of the Slovak Republic)

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^-, NH_4^+ and conductivity. As an example, extremely high contents of B (above 5 $mg.l^{-1}$) and NH_4^+ (above 100 $mg.l^{-1}$) were observed at the site Bojná – landfill – part A.

Pollution with organic substances (which is indicated by TOC and COD_{Mn}) 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 $mg.l^{-1}$) was found at the site Komárno – area after the Soviet Army. Extremely high levels of TOC (above 50 $mg.l^{-1}$) were also determined at the sites Bojná – landfill – part A and Bratislava – Vrakuňa – CHZJD landfill. Extremely high levels of COD_{Mn} (above 50 $mg.l^{-1}$) 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 $mg.l^{-1}$), trichloroethene (above 1 $mg.l^{-1}$), tetrachloroethene (above 1 $mg.l^{-1}$) and chloroethene (above 0.1 $mg.l^{-1}$) were found at the site Zlaté Moravce – Calex. Very high concentrations of chloroethene (above 0.1 $mg.l^{-1}$) and dichloromethane (above 0.02 $mg.l^{-1}$) were observed at the site Piešťany – Chirana. Very high contents of dichloromethane (above 0.02 $mg.l^{-1}$) were determined at the site Bratislava – Vrakuňa – CHZJD landfill. Extremely high levels of C_{10}-C_{40} (above 10 $mg.l^{-1}$) 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), trichlorethene (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 $mg.l^{-1}$) 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 $mg.l^{-1}$) 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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