









NGU Rapport 98.096

Assessment of soil and groundwater contamination at a former Soviet Military Base.

Valmieras Iela Armoured Vehicle Workshop, Riga, Latvia



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A former Soviet military armoured vehicle workshop has been subject to site investigation to examine soil and groundwater contamination. Site investigations have indicated that groundwater is contaminated by hydrocarbons, free phase LNAPL oil being found in one of the boreholes (borehole 3 beneath the scrapyard). Soils at the site are contaminated by oil and the heavy metals Pb, Cu, Zn and Cd. Risk assessment techniques have been applied to make a so-called "Tier 2" assessment of risk to human health and risk to water resources. The assessment has concluded that contamination from the site will not reach the River Daugava within 39 years, even without taking into account sorption and biodegradation.

The risk assessment concludes that the site can remain in its current usage or be redeveloped for commercial purposes without any risk to human health. The assessment predicts no unacceptable risk to off-site groundwater resources (well in Quaternary aquifer at 200 m distance or bore in Devonian at 500 m distance) or to the River Daugava from the site.

If the site is redeveloped for residential use or for open public access (parkland), an unacceptable human health risk may be present. If such redevelopment is proposed, either (a) a "Tier 3" risk assessment should be carried out to make a more refined, less conservative assessment of risk or (b) cleanup of selected areas should be carried out to cited risk-based clean-up levels.

The investigation has had three main shortcomings:

- (i) Lack of reproducibility of analytical data. Recommendation: that all national laboratories used for contamination assessments should take part in internationally recognised accreditation schemes and international ring tests. Sampling should include adequate provision for spiked samples and blanks.
- (ii) Lack of sensitivity analysis for modelling of groundwater contaminant transport and risk assessment. Recommendation: no model results or risk assessments should be accepted as the basis for decision-making unless accompanied by a quantitative sensitivity analysis or, at the very least, (i) some quantification of likely margins of error in the results or (ii) a full justification of the conservatism of the approach.
- (iii) Lack of modelling or risk assessment of evolution of LNAPL plume or risk therefrom. Recommendation: As LNAPL plumes frequently represent the greatest concentrations of contaminants at many former military bases, transport and risk models simulating LNAPL evolution should be assessed and implemented as a matter of urgency.

Emneord: Hydrogeologi	Geokjemi	Forurensning
Løsmasser	Risikovurdering	Olje
Grunnvannskvalitet	Grunnvann	Tungmetaller

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1. INTRODUCTION

This report comprises a desk study, site investigation and risk assessment of a former Soviet military armoured vehicle repair workshop at Valmieras iela, Riga, Latvia. This is one of two sites investigated as part of a joint project between

- the Defence Research Establishment of Norway (Forsvarets Forskningsinstitutt FFI),
- the Ministry of Environment of Latvia (via its daughter organisation, the Geological Survey of Latvia -GSL)
- and the Geological Survey of Norway (Norges geologiske undersøkelse NGU).

The main partners in the project have also contracted out parts of the project to subconsultants, namely:

- Dames and Moore (UK) who have carried out the risk assessment of both sites, and
- Geo-Konsultants (Latvia) who have carried out the geophysical investigations.

NGU, Dames and Moore and GSL have been jointly responsible for preparing this report. The project has been financed by the Ministry of Foreign Affairs in Norway and the Ministry of Environment in Latvia.

The project has comprised three parts:

- (i) Introducing the Norwegian-developed "Waste" Database to Latvia.
- (ii) Carrying out a first-pass audit and hazard ranking of contamination at known military bases in Latvia.
- (iii) Developing methodologies for more detailed assessments of contaminated bases, which have been demonstrated at two military bases in Riga (a) Viestura Prospekts fuel depot and (b) Valmieras iela maintenance workshop for armoured vehicles.

These two sites under (iii) have been chosen, not because they represent the worst contaminated military bases in Latvia, but because they are typical of a number of registered sites, easily accessible and were expected to exhibit a range of contamination, both organic (e.g. Viestura) and inorganic (Valmieras).

2. SITE SIZE AND LOCATION

The site has a total area of an estimated 3.2 Ha. It is divided into two areas. The northern, "Factory" site is approximately square in plan and forms a "courtyard" surrounded by various buildings. It is bordered by Valmieras iela, Vagonu iela, Matisa iela and Bruninieku iela. Of these Valmieras iela is a major (though single carriageway) road. Grass verges exist on the verges of Vagonu and Matisa iela. The main gate is from Vagonu iela, and other gates exist from Matisa and Bruninieku iela.

The second, southern or "Scrapyard" side of the site lies along Bruninieku iela and has an area of approx. 1.5 Ha. Access is via a gate from Bruninieku iela opposite the end of Vagonu. Rail access is at the extreme southern end of the site.

The site is located slightly east of central Riga in a light industrial and residential zone (see Figure 1).

3. TOPOGRAPHY

Site topography is shown on the map in Figure 2. The site is generally flat at an altitude of between 5 and 7 m above sea level (m a.s.l.). There is a slight gradient to the west (i.e. towards the River Daugava) with a difference of slightly over 2 m from east to west of the factory site.

4. LAND USE

The site's known history commenced in 1913. The northern "Factory" part of the site was occupied by the Russo-Balt Vagon Zavod (Russo Balt Coach Factory), which is believed to have supplied Baltic and Russian railways with rolling stock (possibly locomotives?).

This usage continued into the Soviet period, but during the 2nd World War, the entire site was taken into military ownership. The reported usage was for repair (and possibly production?) of military vehicles, including armoured vehicles. The southern "Scrapyard" part is reported to have been used as a scrapyard where is dismantling of oil-containing equipment took place. This lubricating and/or cooling oil is alleged to have been allowed to seep into the ground in the vicinity of soil sample sites 16 & 17 (see Fig. 3).

Since 1993 the site has fragmented into smaller businesses (Figure 4). The entire southern half of the site is in use as a scrapyard. Scrap of varying types (ranging from cars to shell casings) enters by rail via the southern rail gates. Scrap is moved around the site by a large rail-mounted mobile crane. Workers work amongst the scrap and along the sides of the scrap storage area dismantling the scrap into its component parts. Rubber is burned off tyres to retrieve steel reinforcement wire. Safety procedures for site workers appear to be lacking.

The majority of the "Factory" part of the site, including the Russo Balt sheds, is owned by a light industrial firm, retaining the name Russo-Balt VZ, producing a variety of metal objects including trailers, axes etc. Production appears to be taking place at a small fraction of the potential capacity and the large Russo-Balt carriage sheds appear largely unused (except for a stored amphibious armoured vehicle which was attempted sold to NGU's hydrogeologists). The eastern part of the "Factory" site houses the factory's offices. The northern corner of the site is occupied by a residential block. A fuel pump cluster stands in the centre of the site. Towards the western part of the site, bins for various types of materials and waste (steel, coloured metals, swarf, waste) are located, as is the factory's (presumably oil-fired) heating plant. A water tower also stands in the west of the site. It was formerly fed by a borehole drilled to the Devonian aquifer beneath the site. The borehole is believed by the factory owner to be some 200 m deep and formerly abstracted 100,000 m³/yr. It is currently disused. The

factory now consumes only $1000 \text{ m}^3/\text{yr}$ mains water - a reflection of the current industrial depression in Riga.

Smaller, apparently independent businesses occupy the marginal buildings on the southern corner (along Bruninieku and Vagonu iela) of the "Factory" part of the site. These include auto repair workshops (including Alaska Auto) and a tyre workshop with remoulding facility. During sampling in June 1997 it was noted that another small business had occupied the buildings adjacent to the Matisa iela gate: "Sia Lauktehnika" apparently trading in spare parts, including agricultural machinery, building materials and shelf units.

The Scrapyard arm of the site has a perimeter fence and a manned gate. The Factory part of the site is enclosed by buildings and all entrance gates are locked and/or manned. The entry of all but the most determined trespassers is thus unlikely.

Surrounding land-use is a mixture of industry, commerce and residential. To the east of Bruninieku iela by the Scrapyard site are the offices of the local Gas Board. To the west of Bruninieku iela at the Factory half of the site are a textiles factory (wool products - "A/S Saule") and a dairy products factory. On the SE side of Vagonu iela is another vehicle repair workshop. Residential properties occur along Vagonu and Matisa iela.

Future land use is unknown. 4 scenarios are presented for consideration in a risk assessment:

- (i) Current use (i.e.industrial, scrapyard). Groundwater-related sub-scenarios include:
 - (a) that the Devonian borehole is taken back into use for process and drinking water supply for the factory.
 - (b) that a borehole is drilled to the Devonian aquifer 500 m downgradient of the site for public supply
 - (c) that a domestic well in the Quaternary deposits is dug 200 m downgradient of the site for watering of a garden.
 - (d) the impact of contaminated groundwater in water quality in the River Daugava.
- (ii) Redevelopment for commercial (office) usage.
- (iii) Redevelopment for residential usage with and without garden
- (iv) Abandonment, with open access to the public.

5. HABITAT

The Valmieras iela site is almost totally anthropogenic with few remnants of natural habitats. Grass verges exist between Matisa iela and Vagonu iela and the perimeters of the Factory site.

New vegetation is beginning to establish itself in the derelict northern part of the Factory site.

6. CONTAMINANT SOURCES AND VISUAL EVIDENCE OF CONTAMINATION

The main likely contaminant sources are assumed to be as follows:

- (i) Leakage / spillage of lubricating oil / fuel from repair shops in NW part of factory site
- (ii) Leakage / spillage of lubricating, cooling oil or fuels from scrapyard activities .
- (iii) Leakage of fuel oil from firing house
- (iv) Leakage of petrol/fuel from fuel pump enclosure and associated tanks/pipelines.
- (v) Spillage of chlorinated or other solvents from tyre repair workshops or other vehicle/repair workshops
- (vi) Soil contamination by metals from scrapyard activities or from repair workshop activities

As regards contaminants of concern, six classes can be named:

- (i) Hydrocarbon fuel ranging from petrols, through diesel to heating oil
- (ii) Natural inorganic fuel components much Soviet oil is, for example, known to be rich in vanadium (Rankama & Sahama 1950)
- (iii) Fuel additives. These may include lead, halogenated hydrocarbons or MTBE (methyl *tert* butyl ether).
- (iv) Toxic metals from scrapyard- or workshop-related activities
- (v) Chlorinated or other solvents
- (vi) Natural components mobilised as a result of oil contamination. Biodegradation of hydrocarbons consumes oxygen (promoting reducing conditions and mobilisation of Fe, Mn and possibly other elements from the aquifer matrix) and produces CO₂ (leading to aggressive groundwaters and enhanced mineral weathering and solubilisation of components).

Subsidiary contamination could be related to washing of vehicles or battery storage.

Regarding visual evidence of contamination, oil contamination of soils could be observed in the area of the scrapyard (especially near soil sample 17) and in the oldest RBVZ repair shops (near sample 7). Analyses carried out by FFI in 1997 (Appendix 5) suggest that most the hydrocarbon contamination found in groundwater at the site bears the character of degraded diesel.

7. PREVIOUS CONTAMINATION INCIDENTS AND INVESTIGATIONS

No previous contamination assessments are believed to have been carried out at the site.

8. REGIONAL GEOLOGY AND HYDROGEOLOGY

Thickness of Quaternary deposits in the Riga Region typically varies between 20 and 50 m (Gosk et al. 1996).

Holocene and Upper Pleistocene alluvial deposits are found along river valleys, particularly those of the Gauja, Daugava and Lielupe, reaching their maximum thickness in the delta areas. These deposits range from sand to pebbles, with fine sands and silts in flood-plain deposits. The deposits are rich in organic matter, promoting reducing conditions and high iron contents, organic matter, H₂S and ammonia may cause groundwater quality problems. The aquifer is used by Gauja-I and Gauja experimental wellfields.

The Baltic Ice Lake deposits are mainly medium- to fine-grained sands of thickness 20-40 m and hydraulic conductivity ranging from a few m/d (fine sand) to 20-30 m/d (medium sand). Unpolluted water quality is generally satisfactory. The aquifer is used by Baltezers, Baltezers I, Baltezers II, Rembergi and Zakumuiza wellfields.

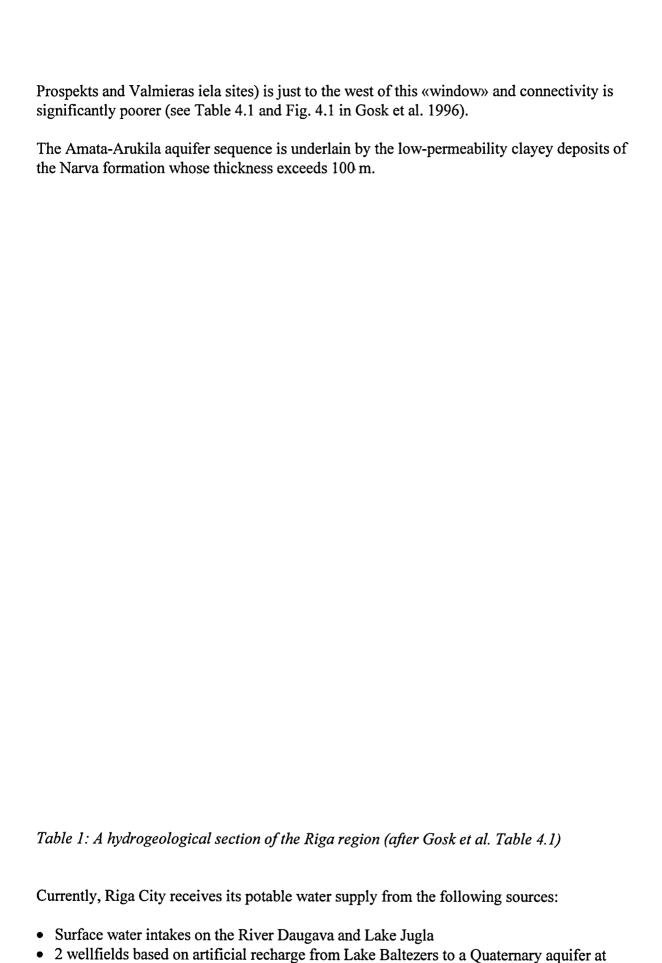
Lower permeability Quaternary deposits, including tills, often underlie the Quaternary aquifers, rendering hydraulic connectivity to the underlying Devonian aquifers limited.

The Middle to Upper Amata-Arukila multi-aquifer system occurs below Riga. In the northern and eastern parts of Riga region it directly underlies the Quaternary sequence; whereas elsewhere it is overlain by lower permeability Upper Devonian sedimentary rocks. The total thickness of the multi-aquifer system is 200-220 m, with sandstones comprising 50 - 85 %; i.e. a net sandstone thickness of not less than 120 m. Individual sandstone horizons are typically 20 - 30 m thick.

Recharge to the Devonian aquifer system occurs at outcrop in the Vidzemes Hills and in areas where the Quaternary aquifers directly overlie the Devonian aquifers, unimpeded by low permeability Quaternary or Upper Devonian deposits. Sandstone hydraulic conductivity is typically 8 - 13 m/d and typical transmissivity of the full aquifer sequence is estimated as 600 - 800 m²/d. The head in the aquifer system increases eastwards, reaching up to 70 m asl 30 - 40 km east of Riga. The lowest heads are found in the central Riga region, associated with intensive groundwater withdrawal in Riga and Jelgava and discharge from the aquifer to major rivers and the Gulf of Riga. In 1993, for example, heads in the Gauja formation were below -5 m a.s.l. (i.e. 5 m below sea level) in the Riga City area. Specific yields of wells in the Devonian are typically up to c. 10 l/s/m.

The Gauja Formation is the most important aquifer horizon within the Amata-Arukila system, and can reach up to 80-100 m thickness. Its transmissivity varies from 300 - 600 m²/d. Head in the aquifer may be as low as - 8 m a.s.l. below Riga. The water quality is of calcium bicarbonate type with total dry residue of 200 - 400 mg/l. Iron concentrations typically vary in the range 0.3 - 3 mg/l. Beneath the Riga area, the top of the aquifer is around 40 - 60 m below ground level (b.g.l.).

To the north-east and east of Riga, the Gauja aquifer is believed to be in good hydraulic connection with the unconfined Quaternary aquifers. Central Riga (including the Viestura



Baltezers and Baltezers II.

- 2 wellfields in Quaternary deposits drawing on bank infiltration from the River Gauja at Gauja I and Gauja experimental.
- Baltezers I wellfield where groundwater is abstracted from unconfined Quaternary deposits
- 2 wellfields where groundwater is abstracted from both unconfined Quaternary and confined Devonian aquifers, at Zakumuiza and Rembergi.
- Katlakalns wellfield where groundwater is abstracted from the confined Devonian.
- 200 groundwater wells providing decentralised water supply throughout the city area, mostly from confined aquifers. These supply 8.1 % (26,300 m³/d) of the total supply (almost 300,000 m³/d) to Riga.

9. LOCAL GEOLOGY

Across much of the site, a significant layer of anthropogenic "soil" occurs, often over 1 m thick. This is detailed in the drilling reports in Appendix 9. Much of the site is underlain by asphalt and /or concrete hard standing.

Below these anthropogenic layers occur silt/fine-medium sand deposits of the Quaternary Baltic Ice Lake. The Baltic Ice Lake sediments appear to be rather homogeneous although interlayering of silt and fine-to-medium grained sands may occur. The thickness of the Baltic Ice Lake sand sequence is estimated at 11 m by the Latian Geological Survey. GSL also estimate a hydraulic conductivity in the range 8 - 10 m/d for the sands, although this is essentually an educated guess (although a rather good one as later hydraulic tests were to prove).

Below the Baltic Ice Lake sands sequence occur tills comprising sandy clays and clayey sands with gravel/pebble clasts. The thickness of this lower permeability Lower Quaternary sequence is reported by the Geological Survey of Latvia (Lacis pers. comm. 1997) as some 5 m, giving a total Quaternary thickness of some 16 m.

The Quaternary deposits overlie sedimentary rocks of the Devonian system, comprising an estimated 6 m of rather low-permeability marl, with gypsum interlayers. This overlies a dolomite aquifer (top of aquifer at estimated 22 m b.g.l.) of Upper Devonian age (see Table 1).

10. HYDROGEOLOGY

The hydrogeology at the contaminated site essentially consists of two aquifer horizons, the Baltic Ice Lake sands and the Devonian Dolomite, separated by a ca. 11 m thick aquitard sequence of Quaternary sandy clays and Devonian gypsiferous marl.

Georadar profiles calibrated against water-level determinations in boreholes indicate a westerly water table gradient oriented towards the River Daugava (Fig. 5).

Meteorological records from the station at the University of Latvia (Merkela street, Riga) indicate an annual average precipitation of some 705 mm (Table 2). Of this, GSL suggest that around 400 mm/a is evapotranspired, leaving a potential 300 mm to recharge (or runoff).

	J	F	M	Α	M	J	J	Α	S	0	N	D	Annual
Long-term average	44	38	34	44	51	72	89	83	71	64	63	52	705
1995	69	53	59	31	68	109	32	65	41	86	58	34	705

Table 2. Precipitation measurements (mm), University of Latvia, Riga.

In addition to precipitation recharge, another source of groundwater recharge in the Riga area might be leakage from water mains. Gosk et al. (1996) report an estimate of leakage rate in Riga at 27 %, although they also believe that this is likely to be optimistic.

11. SITE INVESTIGATION METHODOLOGY

11.1 Existing Observation Wells

No existing observation boreholes were located at the site. The existing factory water supply borehole from the Devonian was not in operation and not accessible for monitoring.

11.2 Topographical Survey

A topographical survey of the entire Valmieras iela site was carried out by the firm Geo-Konsultants. The result of this survey is shown in Figs. 2 and 3. The map indicates a gentle fall in topography towards the west.

11.3 GeoRadar Survey

A Georadar survey was undertaken by the firm Geo-Konsultants. The Georadar survey was carried out in a series of topographically-controlled profiles and was able to identify the water table. The water table level from the Georadar survey was then calibrated against real water level data from observation wells and was used to construct the water table map shown in Figure 5.

The groundwater map indicates a westerly groundwater gradient, towards the Daugava River.

11.4 Drilling of New Boreholes

5 monitoring wells were drilled at Valmieras iela in October 1996, namely wells 1-5. Well 1 was situated just inside the easternmost site gate to the Factory site and was intended to act as an up-gradient "background" control. Well 2 was sited near the tyre repair workshop and Work 5 just outside the former RBVZ repair shops. Wells 3 and 4 were sited in the scrapyard part of the site (Figure 3). All new wells were equipped with a 1.8 m long slotted section, emplaced straddling the water table, such that the wells could be used to detect LNAPL (light, non-aqueous phase liquid) contamination. Drilling details are provided in Appendix 9.

Boreholes were drilled using a simple rotary cylinder auger rig. No drilling fluid was employed, except limited amounts of clean water in difficult sections. No temporary casing was employed. Ready-constructed strings of uPVC pipe were inserted in the completed open hole. The uPVC pipe was constructed to ISO 3633, 75 mm diameter and in 1.8 m lengths welded together using a PVC adhesive (Casco Rørlim) based on 60-100% tetrahydrofuran and 5-10% cyclohexane. The slotted section was perforated with regularly spaced 2 cm diameter circular slots, wrapped around with a wire held and taped plastic mesh. The base of the casing string was sealed by a wooden branch stump. The annulus around the casing was backfilled with sand removed from the hole. To protect the well-head a length of mild steel pipe, up to 1 m long was inserted around the uPVC pipe, and sealed in with a lean cement mix.

Samples of drilling cuttings were taken from selected horizons of the new wells and placed in brown glass cylinders sealed with aluminium foil.

11.5 Geochemical Sampling

20 soil samples were taken of topsoil. Locations of sampling are shown on Fig. 3. Samples at each locality were comprised of a composite of 5 samples (taken at the centre of, and the four corners of, a 1 m edged square), at a depth of around 20-25 cm. The type of soil sampled was highly variable: in many cases it contained identifiable anthropogenic fragments. Two samples, numbers 13 and 14 were taken as background samples from the roadside grass verges adjacent to Vagonu iela. Samples 1-12 were taken from the "Factory Site", samples 15-20 from the "Scrapyard Site". Sample 7a comprised a sub-sample of a particularly oil-rich horizon in the vicinity of bulk sample 7, within the RBVZ repair sheds.

Samples for analysis of organics by FFI were placed in glass flasks, whereas samples for analysis by Latvia were placed in sealed plastic-bags.

Due to a misunderstanding, the samples were only subject, in Latvia, to analyses of heavy metals Zn, Cu, Pb, Cd and Hg and not for oil (Appendix 1). As soon as this misunderstanding became apparent, the samples were retaken (April 1997) as near as possible to the original sample localities and analysed for oil content (Appendix 2).

11.6 Groundwater Sampling

11.6.1 First Sampling Round

Groundwater sampling at Viestura Prospekts took place around 14 days after the completion of drilling. All five boreholes were sampled.

Before pumping commenced, rest water level was measured and the borehole checked, using a transparent bailer for any sign of free-phase oil.

Boreholes were pumped using a small ABS electric pump (Eickelkamp ™ submersible pump type Whale, 36*117mm), typically achieving a rate of ca. 4 l/min. The pump is designed as a

disposable pump but due to financial restraints on the Latvian Geological Survey, is used repeatedly to sample a number of boreholes. pH, temperature and conductivity were monitored using the Geological Survey of Latvias, field monitoring equipment in a closed throughflow cell. Sampling was not undertaken until stable reading had been obtained, a process usually requiring between 20 and 45 minutes per hole.

The Latvian Geological Survey took samples in a range of laboratory washed glass flasks, for different parameters to be analysed at the Latvian Hydrometeorological Agency laboratory in Riga.

GSL also took 100 ml filtered samples for ion chromatography (IC) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) at NGU. The samples were filtered at 0.45 µm using a nitrogen filtration line installed in the GSL sampling vehicle.

GSL also took 1 litre samples for FFI of selected wells' groundwaters in solvent-washed glass flasks, preserved with concentrated HNO₃ for gas chromatography analysis of hydrocarbons.

11.6.2 Second Sampling Round

The second sampling round at Valmieras iela took place on 19/6/97 and followed broadly the same procedure as the first, with the following exceptions.

NGUs Palintest Micro 900 meter was used to confirm Latvian pH measurements, without revealing any detectable discrepancy. The NGU thermistor consistently read 0.3-0.4°C higher than the Latvian. The Micro 900 meter was also used in the throughflow cell to determine Eh. In most cases it was possible to obtain a stable Eh reading.

NGU used an Aquamerck 1.11109 Field Alkalinity kit to determine alkalinity to an end point of pH=4.3 using a mixed indicator, by acid titration on 5 ml aliquots. An average of two determinations was calculated.

In the second sampling round, NGUs filtered samples were taken using a hand-held syringe and a Millipore $0,45~\mu m$ disposable filter.

FFI took 1 l acidified samples of water from all boreholes for hydrocarbon analysis.

12. ANALYSIS OF SAMPLES

12.1 Soil Samples

12.1.1 Latvian analyses

The soil samples, together with selected sediment samples taken during drilling, for analysis in Latvia were subject to the following analyses at the Latvian Hydrometeorological Agency laboratory in Riga:

- (i) Grain size analysis. The results are reproduced in Appendix.1.
- (ii) Analysis was undertaken of the metals Zn, Cu, Pb, Cd and Hg by atomic adsorption spectrophotometry. The results are reproduced in Appendix.1.
- (iii) The resampled sediments from April 1997 were extracted by acetone (method in Appendix 2) and analysed by infra red spectrophotometry for total hydrocarbon content. The results are reproduced in Appendix 2.

12.1.2 Samples analysed by FFI

A limited number of duplicate samples were taken for analysis by FFI. The sediments were ultrasonically extracted by a mixture of heptane and acetone and analysed for THC (Total Hydrocarbon Content) and PCB (Polychlorinated Biphenyls) by a Perkin Elmer Autosystem gas chromatograph, with a detection limit of 30 mg/Kg dry material for THC and 0.4 µg/Kg dry material for PCB (uncertainty 30%). Results are presented in Appendix 5. These samples were the original samples from September 1996 and hence may not be directly comparable with the re-sampled Latvian sediments from April 1997.

Furthermore, in June 1997, a further set of duplicate samples were collected from both Viestura Prospekts and Valmieras iela (Banks et al. 1998), and analysed by GC at FFI. Results are presented in Appendix 5.

12.1.3 Samples analysed by NGU

Two samples (borehole 3 at 5.5 m and borehole 4 at 3.1 m, taken during drilling) were run as control analyses by NGU. The samples were subject to grain size analysis by wet sieving. Results are presented in Appendix 9.

Another portion of the samples was extracted by autoclaving with 7N HNO₃ according to Norwegian Standard NS 4770. The extract was analysed:

- for around 30 elements by a Thermo Jarrell Ash ICP 61 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).
- for Cd and Pb by graphite oven atomic absorption spectrometry (AAS) using a Perkin Elmer Type SIMAA 6000
- for Hg by cold vapour technique AAS using a Perkin Elmer Type 403 (AA)/ Perkin Elmer 1 Mercury Hydride System (MHS)

A final portion of the sample was analysed for total carbon (TC), total sulphur (TS) and total organic carbon (TOC) by oven ignition using a Leco SC-444 oven.

Results are reported in Appendix 3.

12.2 Groundwater Analyses

12.2.1 Latvian samples

The Latvian water samples were delivered to the Latvian Hydrometeorological Agency laboratory in Riga. Aliquots of each sample were analysed for:

- Cr, Cd, Pb, Cu, Hg and Ni by atomic absorption techniques.
- Na, K, Ca, Mg
- SO₄=, Cl⁻, HCO₃
- amoniacal-N, nitrate-N, nitrite-N, mineral-N, organic-N and total-N
- colour
- mineral oil by infra-red spectrophotometry
- phenol, SSAS (surfactants), COD and BOD
- Phosphate-P

Methods are documented in Appendix 2. The results of these measurements, together with field measurements of pH and electrical conductivity, are presented in Appendices 1 and 2.

12.2.2 Samples analysed at FFI

A selection of samples were liquid-liquid extracted with dichloromethane and analysed at FFI for total hydrocarbon content (THC) by a Perkin Elmer Autosystem gas chromatograph, with a detection limit of 0.06 mg/L (uncertainty 10%). Results are presented in Appendix 5.

12.2.3 Samples analysed at NGU

Water samples arrived at NGU as filtered (0,45 μ m), unacidified samples in 100 ml polyethene screw top flasks.

On arrival the flasks were registered and a subjective assessment of colour made (a qualitative estimate of the iron content of the water, as iron began to precipitate out of the sample shortly after sampling). This is found in Appendix 4. The samples were stored in a dark cool-room at 4 °C.

Shortly after arrival, the flask was gently shaken and ca. 10 ml sample was decanted from the 100 ml flask for anion analysis by ion chromatography (IC) on a Dionex 2120i machine. Concentrations of Cl⁻, F⁻, Br⁻, NO₃⁻, NO₂⁻, PO₄³⁻ and SO₄⁻ were reported (Appendices 3 and 4).

The remaining 90 ml of sample was acidified in the original bottle using 7N HNO₃ to resolubilise precipiated and/or adsorbed metals (especially Fe). The sample was then run

• for around 30 elements by a Thermo Jarrell Ash ICP 61 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

- for Cd, As, Sn, Sb and Pb by graphite oven atomic absorption spectrometry (AAS) using a Perkin Elmer Type SIMAA 6000
- for Hg by cold vapour technique AAS using a Perkin Elmer Type 460 (AA)/ and a Perkin Elmer 20 mercury hydride system (MHS).

Original boron results in 1997 for ICP-AES were not reliable due to residual B-pollution in the system from a previous sample. The samples were re-run for B at a later date.

Be results by ICP-AES are regarded as unreliable due to interference with Fe at the very high Fe concentrations observed in the samples. This interference can be seen in the plots in Fig. 16.

Results are reported in Appendices 3 and 4.

12.3 Analytical Consistency

12.3.1 Water samples

NGU vs. Latvian inorganic analyses

An interlaboratory comparison of selected parameters was performed. The results are presented in cross-plots in Figures 6-7.

A comparison of NGUs 1996 results with Latvian results from 1996 (Figure 6) is very disappointing. Comparison was possible for Cl⁻, NO₃⁻, SO₄⁻, Na, Ca, Mg, K, Cd, Ni, Pb and P. Of these Cl⁻, SO₄⁻, Mg and Ca exhibited some degree of correlation. Results for K were of a completely different order of magnitude to NGU's results.

A comparison of NGU's 1997 results with Latvian results (Figure 7) for the same year is more promising than for 1996 but not satisfactory. Satisfactory correspondence was obtained for Ca, Mg alkalinity, SO₄ and Cl⁻. K results were still of a very different order of magnitude to those of NGU. A reason for the discrepancy for NO3 and SO4 may be that the water samples analysed at NGU were not stored according to good practise (refrigerator).

NGU Consistency from 1996 to 1997

NGU results for water analysis from 1996 and 1997 are compared in Figure 8. Satisfactory comparison is obtained for all elements run by IC and ICP-AES with the exception of P, Zn and the first B-measurement made in 1997 (due to contamination in the ICP-equipment - see above). The AA analyses are somewhat less consistent, especially for Cd and Pb, but the results are generally of the same order of magnitude.

Latvian Consistency from 1996 to 1997

A comparison of Latvian 1996 results with those of 1997 allows comparison of a range of parameters (Figure 9). Broadly, results for all parameters, except SSAS, show an acceptable degree of reproducibility. Particularly impressive is the reproducibility for phenol, Cu and Cd

(although this, in the absence of standard control samples) does not necessarily confirm the accuracy of the absolute values).

Oil - 1996 results

A comparison of Latvian THC (mineral oil) analyses with FFI's results for selected control samples from both Valmieras iela and Viestura Prospekts (Banks et al. 1998) is presented in Table 3 and Fig. 10. A comparison between the results for samples from 1996 reveals that the results from the two laboratories are all of the same order of magnitude and (in the case of Viestura Prospekts [Banks et al. 1998], if not Valmieras iela), all point towards specific wells having elevated concentrations (Viestura boreholes 6 and 14). Both FFI and Latvian analyses confirm low levels of THC in Viestura borehole 222a and a significant "background" in one of the cemetery boreholes. The results from Valmieras iela show poorer correspondence, although one is tempted to suggest that the Latvian results are more believable as borehole 3 was later shown to be the most contaminated, containing significant free-phase oil in 1997. It should also be remembered that the FFI samples have been subject to air transport and longer storage time than the Latvian samples.

Oil - 1997 results

In 1997, the concentrations of THC measured by FFI are considerably higher than those in the Latvian samples. For the new wells at Viestura (7a, 12-15) and at Valmieras, it is conceivable that this reflects the fact that a certain time lag exists for oil to drain out of the capillary zone and into the well. For the old wells, where the well-screen is below the water table, the large discrepancy is very difficult to explain. FFI later admitted to analytical error and submitted corrected values (App. 5).

	Latvian lab. 1994	Latvian lab. 1996	FFI 1996	Latvian Lab. 1997	FFI 1997
Viestura bh 1	420	180	< 60	200	15000
Viestura bh 2	350	270	445	340	
Viestura bh 3	100	120		300	5200
Viestura bh 6	1350	360	2622	250	
Viestura bh 7	450	280	224	The State Number of State of S	
Viestura bh 7a	450	1240	100	2500	16000
Viestura bh 8	50	90		70	630
Viestura bh 9	80	240	1	200	1100
Viestura bh 10	100	90	12 70 11	160	1400
Viestura bh 11	430	90	Tenes to	190	2300
Viestura bh 12		450	i maigle and	100	14000
Viestura bh 14		450	1054	170	12000
Viestura cemetry P2		130	320		TEXT AND
Viestura 222a		30	< 60	60	390
Valmieras bh 2		140	334	80	470
Valmieras bh 3	William Control	410	114	180	1600
Valmieras bh 4	The same of the	160	319	60	2100
Valmieras bh 5		230		40	1400

Table 3. Concentrations of mineral oil (THC) in water samples from Viestura Prospekts (Banks et al. 1998) and Valmieras iela in μ g/L as determined by the Latvian laboratory in 1994, 1996 and 1997, compared with determinations by FFI in 1997.

Latvian analyses of oil from 1996 and 1997 are of the same order of magnitude, and show a fair degree of reproducibility (Fig. 10)

In summary

Taking the Viestura Prospekts (Banks et al. 1998) and Valmieras iela data sets together, the Latvian 1996 analyses for some inorganic parameters appear unreliable. The consistency of NGUs inorganic analysis by IC and ICPAES indicates them to be reliable and these have been used for interpretation and risk assessment.

Ion balance errors in NGUs 1997 analyses have been calculated at between -1 and -11 % (Figure 11). These errors are worse than for Viestura Prospekts (Banks et al. 1998) but are within the bounds of acceptability for such a contaminated site, instilling further confidence in the validity of NGU's results for inorganic parameters by IC and ICPAES.

For trace heavy metals, it is proposed that the worst case, taken from both NGU and Latvian data sets are used for risk assessment purposes. In particular Cd has shown inconsistencies between NGU and Latvian analyses, although good internal reproducibility from 1996 to 1997 in Latvia.

The consistency of Latvian COD, BOD, NO₂, N-total, phenol, NH₄-N and field measurements between 1994 and 1996, suggests that the Latvian analyses for these and other organic parameters (oil) are acceptable.

Latvian values for oil analyses have been preferred over those produced by FFI in 1997 on the grounds of consistency between years. Ideally spiked control samples would be required to test the absolute accuracy of oil (and other) analyses.

12.3.2 Soil samples

Three soil samples were taken in 1996 as control samples to compare inorganic analytical results from Latvia and NGU. All three samples were of apparently clean sandy subsoil. Given that the samples were not strictly duplicates (Viestura 31 was sampled by a Latvian geochemist for the Latvian sample and by an FFI scientist for the NGU sample. The NGU sample was slightly contaminated by humic topsoil. The Valmieras samples come from differing depths), and that the laboratories used differing digestion techniques, the analytical correspondence is surprisingly good. There is some suggestion of a quantisation effect in the Latvian data, and the possibility that the laboratory has not given enough consideration to its detection limits (possibly tending to overestimates of concentrations in the low end of the analytical range).

		Viestura soil sample 31 (20 cm depth)		s borehole 3	Valmieras borehole 4	
	Latvia	NGU	Latvia 3 m depth	NGU 5.5m depth	Latvia 3 m depth	NGU 3.1 m depth
Zn	5	9.2	5	10.2	5	10.1
Cu	1	2.4	4	5.6	4	8.7
Pb	3	2.86	3	1.5	2	0.969
Cd	0.05	0.107	0.05	0.013	0.02	0.026
Hg	0.01	0.01	0.02	<0.01	0.01	< 0.01

Table 4. Comparison of Latvian and NGU analytical data from sediment samples taken in 1996 from Viestura Prospekts (Banks et al. 1998) and Valmieras iela. All concentrations in mg/Kg dry material.

Oil analyses of sediments/soils could be compared by using FFIs analysis of THC in selected soil samples collected in 1996, and Latvian and FFI results from samples recollected from (as near as possible) identical sites in April 1997 and June 1997, respectively.

Comparing FFI (1996) results with Latvian (1997) results: two of the sites (Viestura 32a and Valmieras 16) yield comparable results. Valmieras 9 did not yield comparable results, probably reflecting the fact that the new Latvian sampling of April 1997 missed a small «hot spot», or maybe the fact that the Latvian samples were taken by a geochemist (interested in obtaining representative bulk samples) while the FFI samples were taken by a weapons expert (interested in the most contaminated possible soil). The sample site were chosen by a geochemist and not by FFI. For the risk assessment it is important to discover were the source of the pollution are, and it is therefore necessary to take samples from the most contaminated possible soil.

A comparison of FFI (1997) results with previous results is rather disheartening. The latest FFI results indicate significantly higher oil concentrations than the other datasets. The most possible reason is that samples (both soil and water samples) taken in 1996 were stored in room temperature for about four months due to transportation problems between Latvia and Norway. Norwegian guidelines for sampling recommend a storage time of 24 hours at 4°C, when THC has been analysed in water samples. Due to the long storage time for samples taken in 1996, it is highly possible that most of the hydrocarbon content is lost due to leakage from the glass flask or to degradation in the hydrocarbons. The hydrocarbon pollution in the soil samples are strongly absorbed to particles and therefor the storage time is not so critical as for water samples. The pollution in soil can vary significantly between small distances and it is almost impossible to take exactly the same soil sample from year to year. With these to facts taken into consideration the analytical correspondence of THC in soil analysed by FFI are reasonable. (Se Appendix 5).

	FFI analysis Sampled Sept. 1996	Latvian analysis 1997 Sampled April 1997	FFI analysis Sampled June 1997
Viestura site 32a	424	320	6000 4800
Valmieras site 7		250	1200
Valmieras site 7A*	14508		
Valmieras site 8	PSE SHOOL VALUE	128	6000
Valmieras site 9	8489	84	8400
Valmieras site 16	121	190	710

^{• =} sample of the most oil-polluted area in the vicinity of site 7. This sample is thus not directly comparable to the bulk Latvian sample from site 7.

Table 5. Comparison of FFI analytical data from sediment samples taken in 1996 from Viestura Prospekts (Banks et al. 1998) and Valmieras iela, compared with Latvian data from samples taken in April 1997. All concentrations in mg/Kg dry material.

12.3.3 Choice of parameters for risk assessment

For the purposes of risk assessment, it is recommended by NGU that the following data are used:

- (i) NGU (1996/97) values for alkalinity, inorganic components by IC and ICPAES in groundwater
- (ii) Latvian (1996/97) values for organic components, N-components and field parameters (T, EC, pH) and possibly trace heavy metals in groundwater.
- (iii) Latvian (1997) values for inorganic parameters and oil in sediments.

As some trace heavy metals have been difficult to reproduce satisfactorily in many cases, a worst-case risk assessment scenario should ideally use the highest concentrations of these parameters determined.

13. RESULTS AND DISCUSSION

13.1 Geology and Hydrogeology

The drilling logs for the new boreholes are presented in Appendix 9

In borehole 1 (the supposed "background well"), the bore entered a medium sand which contained recognisable anthropogenic fragments. By 2 m depth, the drillhole had entered apparently clean sands. An oily smell was encountered at around 5-7 m (i.e. under the water table). At around 10 m the hole encountered a compact reddish brown silt, possibly representing the base of the Baltic Ice Lake Sands aquifer or maybe representing merely a silty interlayer.

Borehole 2 was drilled in a grassy bed near the tyre repair shop. The hole entered natural clean sands below topsoil and no obvious sign of contamination was encountered during drilling.

Borehole 3 was drilled on the scrapyard site. Ca. 2.4 m of anthropogenically influenced soil /made ground was penetrated before reaching natural sands. The anthropogenic soil exhibited oily smells around 2 m. The smell persisted down into the sands, while between around 3.5 m and 6 m, very strong oil contamination of the sediments was both observed visually and smelled.

Borehole 4 was drilled at the scrapyard site. Ca. 0.3 m of asphalt and concrete was penetrated before entering soil and sand with anthropogenic fragments and an oily smell down to ca. 2.7 m. The borehole then entered natural sand deposits and only a slight or no oil smell was observed.

Borehole 5 was drilled on the "Factory Site" near the former RBVZ sheds. 20 cm concrete were penetrated before entering a sandy soil with anthropogenic fragments to around 2.5 m. The remainder of the hole was drilled in natural sands. Slight oily smells were noted during several parts of the drilling.

The drilled wells were drilled almost exclusively in uniform fine-medium sand with median grain size of the order of 0.15 - 0.25 mm. Results of grain size analyses are presented in Appendices 1 and 9.

The Bayer relationship (after Langguth & Voigt 1980) and explained in Odling et al. (1994) was employed to estimate the hydraulic conductivity, porosity and effective porosity of the sediment samples taken during drilling on the basis of d_{10} and d_{60} grain size. As the shallow soil samples (20-25 cm) were typically in anthropogenic soils and made ground, they are not used for hydraulic conductivity estimation.

Results of these estimates are presented in Appendix.9, but a summary is presented below in Table 6.

	K (m/s)	K (m/d)	n (%)	n _e (%)
Range	1.7 - 12 x 10 ⁻⁵	1 - 10	32 - 37	22 - 31
Arithemtic mean	6 x 10 ⁻⁵	5	35	27
Geometric mean	5 x 10 ⁻⁵	4	35	27
Median	6 x 10 ⁻⁵	5	35	28

Table 6. Estimated values of hydraulic conductivity (K), porosity (n) and effective porosity (n_e) using the Bayer Method (Langguth & Voigt 1980).

During pumping for sampling in June 1997, pumping rates were noted, in addition to rest and pumping water levels. The time of pump switch-off was noted and the recovery of water level in the well was also observed using an electric dip-meter. These simple recovery tests were analysed using the Theis/Jacob recovery method, using Waterloo Hydrogeologic's Aquifer Test software. Analyses returned the following values for apparent transmissivity (T_a). Apparent transmissivity can be converted to hydraulic conductivity (K) by

 $K = T_a / D_e$

where D_e is the effective aquifer thickness, which is somewhere between the real aquifer thickness (several 10's of m) and the length of the saturated well-screen (1 m). As the tests were very short-term, a value in the range 1 - 2 m is probably realistic. Recovery test analyses are found in Appendix 8, and the calculated T_a and estimated K values are presented in Table 7.

Borehole	$T_a (m^2/s)$	$K m/d (D_e = 1 m)$	$K m/d (D_e = 2 m)$
1	1.4 x 10 ⁻⁵	1.2	0.6
2	5.7 x 10 ⁻⁵	4.9	2.5
3	Not observed du	e to thick oil layer	Liver State of the
4	1.8 x 10 ⁻⁵	1.6	0.8
5	1.5 x 10 ⁻⁵	1.3	0.6

Table 7. Calculated values of apparent transmissivity and estimated values of hydraulic conductivity on the basis of recovery tests on boreholes at Valmieras iela, June 1997.

Thus, in summary:

- Initially, the Latvian Geological Surevy estimated a K value of 8 10 m/d for the sands on the basis of experience
- Estimates of K based on grain size yield values of 1 10 m/d
- Estimates of K based on recovery tests yield values of ca. 1 5 m/d

13.2 Soil Contamination

Maps have been produced of almost every measured geochemical parameter and are presented in Appendix 7. These maps are produced in the geochemical data analysis program DAS, which is itself based on non-parametric, statistical methods of exploratory data analysis (Tukey 1977). The symbols for most of the diagrams are based on the Boxplot method of presentation (see Fig. 12). In such diagrams the box represents the interquartile range, containing the central 50 % of the data, with a horizontal line marking the median. The whiskers represent the extra quartile range of data, with boxes or crosses marking extreme outlying data.

13.2.1 Organic parameters

Fig. 13 shows a map of the oil contamination (Latvian analyses) observed in shallow soil (20 - 25 cm) samples taken in April 1997. The median concentration is 66 mg/Kg, with a range from 24 to 250 mg/Kg.

Two samples (numbers 13 and 14)of shallow (20-25 cm) soil from grass roadside verges outside the factory site at Valmieras iela returned oil concentrations of 60 and 72 mg/Kg.

Approximately half the samples from the Valmieras iela site thus returned oil concentrations lower than what might be regarded as an urban background. Two main contaminated areas are observed: (i) around the active scrapyard (maximum 190 mg/Kg in sample 16) and (ii) in the west of the Factory Site (RBVZ sheds) with a maximum of 250 mg/Kg in sample 7. PCB were not found in the samples analysed at FFI.

The Norwegian trigger value for mineral oil for the most sensitive land use is 100 mg/Kg (SFT 1995), above which a site-specific risk assessment is required.

13.2.2 Inorganic Parameters

The Latvian laboratory measured Zn, Cu, Pb, Hg and Cd in the 20 samples taken in 1996, and in samples from 1 m depth and 3 m depth taken from boreholes 3, 4 and 5 during drilling. Samples 13 and 14 from the roadside verge are taken as background samples. Results are presented in the form of maps in Appendix 7.

Zinc exhibits a wide range of values. Background in samples 13 and 14 is 60 and 98 mg/Kg, respectively. The median concentration is ca. 150 mg/Kg. The lowest concentrations are observed in the sediment samples from 3 m deep (as low as 5 mg/Kg), although two of the samples from 1 m depth exhibit levels above the median, indicating that zinc contamination occurs to some depth in the anthropogenically affected soil. The highest observed value is in sample 16 at the scrapyard at 563 mg/Kg. At least two main hot spot areas are observed: (i) around the active scrapyard and (ii) in the west of the Factory Site (RBVZ sheds), where 417 mg/Kg is observed in sample 8. The Norwegian trigger value for zinc for the most sensitive land use is 150 mg/Kg.

Copper also exhibits a wide range of values. Background in samples 13 and 14 is 13 and 25 mg/Kg, respectively. The median concentration is ca. 54 mg/Kg. The lowest concentrations are observed in the sediment samples from 3 m deep (as low as 4 mg/Kg), although two of the samples from 1 m depth exhibit levels above the median, indicating that copper contamination occurs to some depth in the anthropogenically affected soil. The highest observed value is in sample 16 at the scrapyard at 225 mg/Kg. At least two main hot spot areas are observed: (i) around the active scrapyard and (ii) near the petrol pump area, where 173 mg/Kg is observed in sample 12. The Norwegian trigger value for copper for the most sensitive land use is 100 mg/Kg.

Lead also exhibits a wide range of values. Background in samples 13 and 14 is 24 and 29 mg/Kg, respectively. The median concentration is ca. 157 mg/Kg. The lowest concentrations are observed in the sediment samples from 3 m deep (as low as 2 mg/Kg), although all three of the samples from 1 m depth exhibit levels above the median, indicating that lead contamination occurs to some depth in the anthropogenically affected soil. The highest observed value is in sample 19 at the scrapyard at 3300 mg/Kg. At least two main hot spot areas are observed: (i) around the active scrapyard and (ii) in the west of the "Factory Site", where 2190 mg/Kg lead is observed in sample 1. The Norwegian trigger value for lead for the most sensitive land use is 50 mg/Kg.

Cadmium also exhibits a wide range of values. Background in samples 13 and 14 is 0.15 and 0.14 mg/Kg, respectively. The median concentration is 0.64 mg/Kg. The lowest concentrations are observed in the sediment samples from 3 m deep (as low as 0.02 mg/Kg), although all three of the samples from 1 m depth exhibit levels at or above the median, indicating that cadmium contamination occurs to some depth in the anthropogenically affected soil. The highest observed value is in sample 8 in the RBVZ sheds at 11 mg/Kg. At least two main hot spot areas are observed: (i) around the active scrapyard (up to 1.57 mg/Kg in sample 16) and (ii) near in the west of the Factory Site. The Norwegian trigger value for cadmium for the most sensitive land use is 1 mg/Kg.

Mercury also exhibits a wide range of values. Background in samples 13 and 14 is 0.09 and 0.05 mg/Kg, respectively. The median concentration is ca. 0.09 mg/Kg. The lowest concentrations are observed in the sediment samples from 3 m deep (as low as 0.01 mg/Kg), although all three of the samples from 1 m depth exhibit levels at or above the median, indicating that mercury contamination occurs to some depth in the anthropogenically affected soil. The highest observed value is in sample 19 at the scrapyard at 0.62 mg/Kg. At least two main hot spot areas are observed: (i) around the active scrapyard and (ii) in the west of the "Factory site", where 0.53 mg/Kg is observed in sample 2. The Norwegian trigger value for mercury for the most sensitive land use is 1 mg/Kg.

Under Norwegian practice, the concentrations of oil, Zn, Cu, Cd and Pb in the soils would be high enough to trigger the need for a specific quantitative risk analysis. Concentrations of mercury would not be high enough to trigger a site-specific risk analysis.

13.3 Groundwater Contamination

Maps have been produced of almost every measured geochemical parameter and are presented in Appendix 6. These maps are produced in the geochemical data analysis program DAS, which is itself based on non-parametric, statistical methods of exploratory data analysis (Tukey 1977). The symbols for most of the diagrams are based on the Boxplot method of presentation (see Fig. 12). In such diagrams the box represents the interquartile range, containing the central 50 % of the data, with a horizontal line marking the median. The whiskers represent the extra quartile range of data, with boxes or crosses marking extreme outlying data.

13.3.1 Free Phase Oil Contamination and Halogenated Hydrocarbons

Free phase oil contamination was not found conclusively in any borehole during the 1996 sampling round. In 1997, around 60 cm rather dirty oil was found in borehole 3. The thickness does not represent the thickness of the oil phase in the aquifer. Abdul et al. (1989) suggest that the boreholes overestimate the true thickness of the LNAPL phase by a factor of approximately 4.

A sample of this oil was taken to Norway for analysis at SINTEF Kjemi (Oslo). It is known that any contamination by chlorinated solvents will tend to preferentially concentrate in the LNAPL phase (relative to water). The analysis failed to detect a range of halogenated solvents

in the sample, indicating a lack of halogenated hydrocarbon contamination at the scrapyard site. (Appendix 5).

A water sample from well 2 was also submitted for halogenated hydrocarbon analysis and also failed to yield detectable concentrations. (Appendix 5).

13.3.2 Dissolved Oil Contamination

Figure 14 shows dissolved oil contamination in groundwater according to the results of the 1996 sampling. The median concentration is 0.16 mg/L and the highest (0.41 mg/L) in well 3. Well 1 (the supposed background well) returns a concentration of 0.08 mg/L. The situation in 1997 (Appendix 6) is not dissimilar, but here the median was 0.08 mg/l and the maximum 0.18 mg/l.

Figures 15a-c show some indication of a weak correlation between oil and iron (redox-controlled) and between oil and total mineralisation (weathering enhanced by CO₂ generated by biodegradation), although this is by no means as strong as at Viestura Prospekts (Banks et al. 1997, 1998). Figure 16 indicates that total iron is a good indicator of redox conditions in groundwater: high iron contents in groundwater in wells 3, 4 and 5 coincide with low nitrate and sulphate and high manganese, indicating reducing conditions (presumably related to organic contamination). The high alkalinity in these wells also indicates CO₂ generated by oil degradation reacting with mineral phases to release bicarbonate ions.

13.3.3 Inorganic Species

A range of heavy metals have been analysed. None of the maps in Appendix 6 suggest that these occur in concentrations violating commonly accepted drinking water norms. For example, lead does not exceed 0.93 μ g/l (NGU 1997 data) or <1.5 μ g/l (Latvian 1997 data), cadmium does not exceed <0.02 μ g/l (NGU 1997 data) or 1.3 μ g/l (Latvian 1997 data), while copper does not exceed <5 μ g/l (NGU 1997 data) or 3 μ g/l (Latvian 1997 data).

Barium occurs at 322 μ g/l in well 3 (Norwegian guideline value = 100 μ g/l), due to the reduction of sulphate enhancing the (probably natural) barium solubility (barite solubility control - see Figure 16).

Interestingly, nitrate occurs at > 50 mg/l in well 1 (i.e. in exceedence of the drinking water maximum). As well 1 is regarded as a background well, this value is regarded as an "urban background", unrelated to contamination at the site.

14. MODELLING OF CONTAMINANT TRANSPORT

In order to determine the direction of contaminant transport and time needed to reach the nearest water body from the Valmieras iela site, calculations have been made using a numerical model taking into account advection only: i.e. processes of sorption and

degradation were not taken into account. At the Valmieras iela site, no time-series contamination monitoring was carried out. The modelling exercise thus allows us to simulate the evolution of the dissolved contaminant plume with time; i.e. the direction of contaminant transport and the transport time of components not subject to sorption. The movement of components subject to sorption and biodegradation (e.g. oils) is much slower, such that one can say that the "worst" case has been modelled.

The movement of a water particle by advection with groundwater flow is described by the system of equations (1) as follows:

$$\begin{cases} \frac{dx}{dt} = -\frac{k}{n} \frac{\delta h}{\delta x}; \\ \frac{dy}{dt} = -\frac{k}{n} \frac{\delta h}{\delta y}. \end{cases}$$
(1)

where (x, y) are the coordinates of the water particle, t - time, k - hydraulic conductivity, n - effective porosity, h - groundwater head.

The integration of equations (1) and the interpolation of basic data (permeability, transmissivity etc.) were carried out by the Geological Survey of Latvia using the software package PKGR (Grikevich & Buzayev, 1995). The calculations were made for a total area of $7 \text{ km} \times 12.5 \text{ km}$. The chosen area incorporates both the Viestura Prospekts (Banks et al. 1998) and Valmieras iela objects as contamination sources. The area was discretised as a rectangular mesh, consisting of 6,250 (50×125) blocks.

For the interpolation of the groundwater head maps (Fig. 17), data from 1,807 geotechnical boreholes have been used; these data were retrieved from a database at the State Geological Survey of Latvia. In the interpolation algorithm, watercourses and surface water bodies, as well as the zero water level, were taken into account.

For the interpolation of the maps of hydraulic conductivity (Fig. 18), data from 5,119 measurements from 831 boreholes were used. The hydraulic conductivities were calculated based on grain-size data. In cases where several values were determined from a number of levels from the same borehole, the following formula was used to yield a k value representative for the borehole:

$$k = \frac{\sum k_i m_i}{\sum m_i}; \tag{2}$$

where k_i , m_i are, respectively, the hydraulic conductivity and the thickness of the i^{th} -level (stratum).

For the whole area, the effective porosity of the sand was considered to be approximately equal to that of the minimum value in the Quaternary sand, i.e. n=0.1.

For the purposes of the particle tracking modelling, the perimeter of the contaminated area (i.e. Valmieras iela) was divided into 50 points, situated at equal distances from one another.

The coordinates of these points were assumed as initial conditions for the equation system (1). Modelling was performed by setting the particles in motion along flow lines based on the groundwater head map (Fig. 17), with transport velocity controlled by the hydraulic conductivity distribution in Fig. 18. The calculated direction of contaminant transport is shown in Fig. 19.

The isochrones, characterizing the speed of contaminant movement, are shown in Fig. 20. The isochrones correspond to intervals of 5, 10, 20, 30 and 40 years.

As regards the Valmieras iela site, contamination derived therefrom is predicted to arrive at the River Daugava no earlier than after 39 years have elapsed.

Taking into consideration the fact that the modelled areas are contaminated predominantly, by oil products, which concentrate in the upper part of the top aquifer, contaminant migration to the lower (Devonian) aquifers is improbable. There is, however, a possibility of contaminants reaching the underlying aquifers which are extensively used for water supply.

In order to produce and calibrate a more reliable migration model, it is necessary to establish a monitoring network, both in the contaminated Quaternary aquifer and the underlying aquifer. This would allow an evaluation of the vertical and horizontal transport velocity of contaminants.

It should also be pointed out that this modelling exercise does not attempt to simulate the migration of LNAPL phase oil. Specific numerical models are available for this task, which should be given priority before a future decision is made on the fate of the site. It should also be noted that the following risk assessment does not specifically include consideration of the LNAPL phase oil at the site.

15. RISK ASSESSMENT

15.1 Introduction

This chapter describes the risk assessment of the Valmieras iela study site using the methodology described by Grundy & Quint (1998). The assessments presented here have been undertaken at the Tier 1 and Tier 2 levels as described in this methodology. It is important to note that certain simplifying assumptions have been made in the course of undertaking the assessments presented here - these are detailed in the text as appropriate. The results should be viewed in this light.

15.2 Land Uses Considered in the Risk Assessment

The future land use for the site is currently not known. For the purpose of illustration, the following scenarios have been considered in the risk assessment:

(i) Current use.

- (ii) Redevelopment for commercial (office) usage.
- (iii) Redevelopment for residential use with and without gardens
- (iv) Abandonment with open access to the public

With respect to the assessment of groundwater risk from contamination, four sub-scenarios have been considered:

- (a) The on-site Devonian borehole is re-used for process and drinking water supply for the factory.
- (b) A borehole is drilled to the Devonian aquifer 500m down-gradient of the site for public supply.
- (c) A domestic well in the Quaternary deposits is dug 200m down-gradient of the site for watering a garden.
- (d) Assessment of the impact of contaminated groundwater on water quality in the River Daugava.

15.3 Human Health Risk Assessment

The methodology and algorithms used for performing the human helath risk assessment are those documented in Grundy & Quint (1998).

15.3.1 Data Assessment

The investigation data provided by NGU was assessed to identify contaminants of potential concern, i.e. those which exceed Tier 1 screening criteria. The screening criteria used in the assessment of soil and groundwater contamination were the Norwegian Guidelines for assessment of contaminated land set by the state pollution control authority SFT (1995). Any contaminants exceeding the screening criteria on one or more occasions were included as contaminants of potential concern in the risk assessment

It is understood from NGU that no previous contamination investigations have been carried out. The investigation carried out for NGU included taking 20 samples of topsoil at a depth of around 20 - 25 cm. Two samples were taken from roadside grass verges at the site to represent background. Samples were analysed for heavy metals (zinc, copper, lead, cadmium and mercury) and also total hydrocarbon (oil) content.

15.4 Contaminants of Potential Concern

The contaminants of potential concern for the site are shown in Table 8. These include the following heavy metals which were found to exceed the Norwegian Trigger Values for the most sensitive land use: cadmium, copper, lead and zinc. Oil, most probably diesel, was also found to exceed the screening criteria for soil, and free-phase oil was found in Borehole 3. The highest oil concentration was found in the RBVZ Sheds (Russio-Balt Vagon Zavod - coach factory). The guidance from the Norwegian State Pollution Control Authority (SFT

1995) indicates that a site-specific risk assessment should be carried out where a contaminant concentration exceeds the trigger value.

15.5 Conceptual Site Model (CSM)

The conceptual site model was developed to include four land use scenarios as described previously:

- (i) Current use.
- (ii) Redevelopment for commercial (office) usage.
- (iii) Residential use with and without gardens.
- (iv) Abandonment with open access to the public.

15.5.1 Current Use

Table 9 shows the pathways and receptors considered for the scenario where the site continued in its present use. The receptors considered include on-site employees, off-site employees and nearby residents, both adults and children. All pathways were considered for on-site employees in the risk assessment. For the off-site employees and residents the dust inhalation pathway was considered. Also the potential for inhalation of groundwater vapours were considered for the off-site employee. It is important to note that exposure to floating product has not been considered quantitatively.

The exposure assumptions used for the scenario of continuing current use are shown in Table 10. These include soil ingestion rates for the various receptor groups which assume that a child (nearby resident) will ingest 200 mg/day of soil, i.e. worst case assumptions. The exposure frequency is also worst case and assumes that the child will spend 350 out of 365 days at the site.

Table 11 shows the assumptions used for the site characteristics. Risk-based clean-up levels (RBCLs) derived for the site (where significant levels of risk have been calculated) are shown in Table 12 for the case of the on-site employee. These indicate that there is no requirement to deal with the observed heavy metal contamination since it is not posing a significant risk to human health under the assumed worst case conditions. Similarly the TPH concentrations in soil and groundwater do not pose a significant risk to human health on the basis of the assumed worst case conditions. Remediation is therefore not required if the site continues in its present use.

Table 13 shows the results of the health risk assessment for off-site employees on the basis of the site continuing in its current use. The table indicates that the contaminant concentrations present do not pose a significant risk for this scenario.

The results of the risk assessment modelling also found no significant risk to human health for off-site residents (adults and children) under the assumption that the site continues in its current use (see Table 14).

15.5.2 Redevelopment for Commercial Use

Table 15 shows the pathways considered for the scenario of site redevelopment for commercial (office) use. Indoor inhalation of vapours associated with hydrocarbon contamination in deep soil (>0.5m below ground level) and groundwater were considered in the assessment of risks to human health for on-site employees.

Table 16 shows the human exposure assumptions used in the model for on-site employees. These assume that the employee spends 90% of the time indoors during the working day. It is also conservatively assumed that employees spend 43 years of their life working at this particular site.

The findings of this risk assessment, which has concentrated on indoor vapour inhalation, indicate that the health risk to on-site employees is insignificant for proposed future redevelopment for commercial use (see Table 17).

15.5.3 Redevelopment for Residential Use with Gardens

The pathways considered for adults and children living on-site for the proposed scenario of site redevelopment for residential use with gardens are summarised in Table 18, and Table 19 shows the exposure assumptions made for these residents. The exposure parameters assume ingestion of potentially contaminated drinking water and home-grown produce.

The risk-based clean-up levels derived for the site are shown in Table 20. These indicate that either Tier 3 risk assessment or remediation is required to address TPH, cadmium and lead contamination in the soil. The site could not be redeveloped for residential use without either some form of remedial treatment for this contamination or a Tier 3 risk assessment, since at Tier 2 the site in its present state is deemed to pose a significant risk to human health. Remedial action may include clean-up to the RBCLs specified in Table 20.

15.5.4 Redevelopment for Residential Use without Gardens

Table 21 shows the pathways considered for future residents, both adults and children, for the scenario of site redevelopment for residential use without gardens. The pathways considered include vapour inhalation, ingestion of and dermal contact with contaminated tap water.

Table 22 shows the relevant human exposure assumptions used in the risk assessment. The risk-based clean-up levels derived for the site, where applicable, are shown in Table 23. These indicate that TPH in shallow soil and groundwater poses an unacceptable risk to health and that either remediation (which could be site clean-up to the RBCLs specified) or a Tier 3 risk assessment is required prior to the site being redeveloped for residential use where no gardens are proposed.

15.5.5 Abandonment of the Site with Unlimited Public Access

The pathways considered for this scenario are shown in Table 24. These include ingestion of and dermal contact with soil for any member of the public visiting the site. Exposure to outdoor dust and inhalation of vapours from shallow soil, deep soil, and groundwater is also considered. The human exposure assumptions (Table 25) include the assumption that an adult spends 104 out of 365 days at the site, and a child 180 out of 365 days at the site.

The risk-based clean-up levels, where significant risks exist, are shown in Table 26. These indicate that the TPH and lead concentrations in soil could constitute a health risk to a child regularly playing on the site, and hence a Tier 3 risk assessment or remedial action is recommended. For this scenario an alternative remedial option to clean-up to the RBCLs specified (removal of the contamination source) would be to securely fence off the site to ensure that children do not have access (removal of the pathway).

Table 8a. Contaminants of potential concern.

	Soil Concer	trations (mg/kg)	Groundwater mg/l		Groundwater mg/l Simulated		
	-		On site	<u> </u>	Off-site	·	
Chemical	Shallow	Deep	Observed	From on-site GW	From on-site soil	Off-site	
C10-C16 (TPH)	250	250	2.06	1.60E+00	3.22E-01	1.60E+00	
Copper	225	225	0.006	2.48E-05	4.20E-06	2.48E-05	
Zinc	563	563	0.0935	4.14E-05	4.17E-04	4.17E-04	
Cadmium	11.11	11.11			1.74E-05	1.74E-05	
Lead	3300	3300	0.002	1.07E-06	1.55E-03	1.55E-03	

Table 8b. Contaminants of potential concern.

Valmieras iela Site

Contaminant	Observed Soil	Norwegian Soil	Observed	Target	Ref.
	Concentration	Trigger	Groundwater	Concentration	
	(mg/kg)	Concentration	Concentration	in Groundwater	
		(mg/kg)	(μg/l)	(μg/l)	
Arsenic	-	20	5.3	10	W
Boron	-	na	178.3	300	N
Cadmium	11.11	1	•	5	N
Copper	225	100	5.6	300	N
Lead	3300	50	2.4	20	N
NIckel	-	30	21.9	50	N
Zinc	563	150	93.5	300	N
TPH (C10- C16)/DRO	250	100	2060*	10	N
,	1	,		1	

Note: "-" values either below the detection limit (groundwater) or not detected (soil)

Groundwater target concentrations are either Norwegian (N) or WHO (W).

* solubility

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	On-site		Off-site			
	Commercial	Employee	Resident			
Pathway	Employee	Adult	Adult Chi			
Soil ingestion	1	0	0 .	0		
Soil dermal contact	1	0	0	0		
Indoor dust inhalation	1	1	1	1		
Outdoor dust inhalation	1	1	1	1		
Shallow soil vapours (indoors)	1	0	0	0		
Shallow soil vapours (outdoors)	1	0	0	. 0		
Deep soil vapours (indoors)	1	0	0	0		
Deep soil vapours (outdoors)	1	0	0	0		
GW vapours (indoors)	1	1 1	0	0		
GW vapours (outdoors)	1	1	0	0		
Free product vapours (indoors)	0	0	0	0		
Free product vapours (outdoors)	0	0	0	0		

Free product?		- 1	0	

1:	Pathway exists
0:	No pathway

Significant risk levels			
Non-carcinogenic risk (HI)		1	
Carcinogenic risk	1 in	10,000	

Table 10. Current use. Human exposure assumptions.

				Off-site	
Parameter	Notation	On-Site Employee	Off-site Employee	Adult Resident	Child Resident
Body weight (kg) Exposure frequency (days/year)	BW EF	60 230	60 230	60 350	15 350
Exposure duration (years/lifetime) Lifetime (days)	ED	43 25550	43 25550	24 25550	6 25550
Outdoor Dust Concentration (mg/m³)	PM _o	0.07	0.07	0.07	0.07
% Soil Particles in Dust Fraction of time spent on site	F _{sd} t _o	100% 42%	100% 42%	100% 100%	100% 100%
Outdoor inhalation rate (m³/day) Indoor Dust Concentration (mg/m³)	Bo PM _I	20 0.07	20 0.07	20 0.07	15 0.07
Fraction of outdoor dust which is indoors (%) Indoor Inhalation Rate (m³/day)	F _i Bi	100%	100% 20	100% 20	100% 15
Fraction of time spent outdoors	Fod	50%	50%	10%	10%
Fraction of time spent indoors	Fid	50%	50%	90%	90%

Table 11. Site characteristics - assumptions.

Parameter	Notation	On-site
Capillary fringe thickness (cm)	h_{cap}	5
Vadose zone thickness (cm)	h_{ullet}	445
Depth to groundwater (cm)	L_{gw}	450
Depth to product (cm)	\mathbf{L}_{p}	450
Building exchange rate (1/sec)	ER	0.00083
Building volume/area ratio (cm)	L_b	300
Building foundation/wall thickness (cm)	\mathbf{L}_{crack}	15
Areal fraction of cracks	η	1 %
Air content of foundations/wall cracks	θ_{acrack}	26%
Total soil porosity	θ_{T}	20%
Water content of foundations/wall cracks	θ_{wcrack}	12%
Air content of capillary fringe	θ_{acap}	23.0%
Water content of capillary fringe	θ_{wcap}	2.0%
Air content of vadose zone	θ_{as}	42%
Water content of vadose zone	θ_{ws}	6%
Soil bulk density	ρ_{s}	1.6
Fraction organic carbon	$\mathbf{F}_{\mathbf{oc}}$	2.00%
Depth to subsurface shallow soil sources (cm)	L_{s}	10
Depth to subsurface deep soil sources (cm)	L_{s}	50
Wind Speed (cm/sec)	$\mathbf{U}_{\mathtt{air}}$	225
Ambient Air Mixing Zone Height (cm)	$\delta_{ m air}$	200
Area of Site (cm²)	Α	25000000
Width of Source Area Parallel to Wind Direction (cm)	w	5000
Henry's Law constant (unitless) 1	Н	Chemical-specific
Organic carbon-water partition coefficient ¹	K_{oc}	Chemical-specific
Air diffusion coefficient (cm ² /sec) ¹	\mathbf{D}^{air}	Chemical-specific
Water diffusion coefficient (cm²/sec) 1	$\mathbf{D}^{\mathbf{wat}}$	Chemical-specific

Table 12. Current use. On-site employee risk-based clean-up levels.

Chemical	Shallow Soil RBCLs (mg/kg)	Deep Soil RBCLs (mg/kg)	Groundwater RBCLs (mg/l)
Potential Contaminants			
C10-C16 (TPH)	IR	IR	IR
Copper	"IR	-	-
Zinc	IR	-	-
Cadmium	IR	-	-
Lead	IR	<u>-</u>	

IR: Insignificant Risk. Cleanup levels not required

Table 13. Current use. Off-site employee risk-based clean-up levels.

Chemical	Shallow Soil RBCLs (mg/kg)	Groundwater RBCLs (mg/l)
C10-C16 (TPH)	IR	IR
Copper	IR	-
Zinc	IR	-
Cadmium	IR	-
Lead	IR	<u>-</u>

IR = Insignificant Risk, Clean-up levels not required

Table 14. Current use. Off-site resident. Risk-based clean-up levels.

Chemical	ADULT Shallow Soil RBCLs (mg/kg)	CHILD Shallow Soil RBCLs (mg/kg)	FINAL Shallow soil RBCLs mg/kg
C10-C16 (TPH) Copper Zinc Cadmium Lead	IR IR IR IR IR	IR IR IR IR	IR IR IR IR IR

Table 15. Potential exposure pathways. Redevelopment for commercial use (offices).

	On-site
	Commercial
Pathway	Employee
Soil ingestion	0
Soil dermal contact	0
Indoor dust inhalation	0
Outdoor dust inhalation	0
Shallow soil vapours (indoors)	0
Shallow soil vapours (outdoors)	0
Deep soil vapours (indoors)	1
Deep soil vapours (outdoors)	0
GW vapours (indoors)	1
GW vapours (outdoors)	0
Free product vapours (indoors)	0
Free product vapours (outdoors)	0

Free product?		0	
Significant risk levels			
Non-carcinogenic risk (HI)		1	
Carcinogenic risk	1 in	10,000	

1: Pathway exists

0: No pathway

Table 16. Commercial development. On-site employee. Human exposure assumptions.

Parameter	Notation	On-Site Employee
Soil ingestion rate (mg/day)	IR	40
Body weight (kg)	BW	60
Exposure frequency (days/year)	EF	230
Exposure duration (years/lifetime)	ED	43
Lifetime (days)	L	25550
Skin surface (cm²)	SA	16467
Soil adherence (mg/cm²)	SL	1
Fraction of Skin exposed	F_s	20%
Oral Bioavailability	O	1
Outdoor Dust Concentration (mg/m³)	PM_o	0.07
% Soil Particles in Dust	F_{sd}	100%
Fraction of time spent on site	t _o	42%
Outdoor inhalation rate (m³/day)	Во	20
Indoor Dust Concentration (mg/m³)	PM_{I}	0.07
Fraction of outdoor dust which is indoors (%)	F_{i}	100%
Indoor Inhalation Rate (m³/day)	Bi	20
Fraction spent outdoor	Fod	10%
Fraction spent indoor	Fid	90%

Table 17. Commercial development. On-site employee risk-based clean-up levels.

Chemical	Deep Soil RBCLs (mg/kg)	Groundwater RBCLs (mg/l)
Potential Contaminants		
C10-C16 (TPH)	IR	IR
Copper	-	-
Zinc	-	-
Cadmium	-	_
Lead		<u>-</u>

IR: Insignificant Risk - cleanup levels not required

Table 18. Potential exposure pathways for residential with gardens.

	On-site			
Pathway	Adult	Child		
Soil ingestion	1	1		
Soil dermal contact	1	1		
Indoor dust inhalation	1	1		
Outdoor dust inhalation	1	1		
Vegetable ingestion	· 1	1		
Shallow soil vapours (indoors)	1	1		
Shallow soil vapours (outdoors)	1	1		
Deep soil vapours (indoors)	1	1		
Deep soil vapours (outdoors)	1	1		
GW vapours (indoors)	1	1		
GW vapours (outdoors)	1	1		
Free product vapours (indoors)	0	0		
Free product vapours (outdoors)	0	0		
Tap water ingestion	1	1		
Tap water vapours (indoors)	1	1		
Tap water dermal contact	1	1		

Free product		0	1: Pathway exists
	-		0: No pathway
Significant risk levels			
Non-carcinogenic risk (HI)		1	
Carcinogenic risk	1 in	10000	

Table 19. Residential with gardens. Human exposure assumptions.

		On-	-site
Parameter	Notation	Adult Resident	Child Resident
Soil ingestion rate (mg/day)	IR	100	200
Body weight (kg)	BW	60	15
Exposure frequency (days/year)	EF	360	360
Exposure duration (years/lifetime)	ED	24	6
Lifetime (days)	L	25550	25550
Skin surface (cm ²)	SA	16467	6381
Soil adherence (mg/cm²)	SL	1	1
Fraction of Skin exposed	F_s	30%	48%
Oral Bioavailability	O	1	1
Outdoor Dust Concentration (mg/m³)	PM_o	0.07	0.07
% Soil Particles in Dust	F_{sd}	100%	100%
Fraction of time spent on site	t _o	100%	100%
Outdoor inhalation rate (m³/day)	Во	20	15
Indoor Dust Concentration (mg/m³)	PM_I	0.07	0.07
Fraction of outdoor dust which is indoors (%)	F_{i}	100%	100%
Indoor Inhalation Rate (m³/day)	Bi	20	15
Drinking Water Ingestion Rate (I/day)	DW	2	1
Root vegetable ingestion rate (mg/day)	V_R	0.239	0.239
Home-grown fraction of root vegetables	HG_R	0.05	0.05
Non-root vegetable ingestion rate (mg/day)	V_{NR}	0.209	0.209
Home-grown fraction of non-root vegetables	HG_{NR}	0.05	0.05
Fraction of time spent outdoor	Fod	50%	50%
-			

		ADULT			CHILD				
Chemical	Shallow Soil RBCLs (mg/kg)	Deep Soil SSTLs (mg/kg)	Groundwater SSTLs (mg/l)	Shallow Soil RBCLs (mg/kg)	Deep Soil RBCLs (mg/kg)	Groundwater SSTLs (mg/l)	Shallow soil RBCLs mg/kg	Deep soil RBCLs mg/kg	Groundwater RBCLs mgll
C10-C16 (TPH) Copper Zinc Cadmium Lead	1.82E+02 IR IR IR 4.56E+02	IR - - -	2.12E-01 IR IR IR	5.99E+01 IR IR 1.10E+01 9.73E+01	IR - - - -	5.31E-01 IR IR IR	5.99E+01 IR IR 1.10E+01 9.73E+01	IR	2.12E-01 IR IR IR

IR: Insignificant risk - cleanup level not required

Table 21. Potential exposure pathways for residential without gardens.

	On-	site
Pathway	Adult	Child
C-11 :	0	0
Soil ingestion	0	0
Soil dermal contact	0	0
Indoor dust inhalation	0	0
Outdoor dust inhalation	0	0
Vegetable ingestion	0	0
Shallow soil vapours (indoors)	1	1
Shallow soil vapours (outdoors)	1	1
Deep soil vapours (indoors)	1	1
Deep soil vapours (outdoors)	1	1
GW vapours (indoors)	1	1
GW vapours (outdoors)	1	1
Free product vapours (indoors)	0	0
Free product vapours (outdoors)	0	0
Tap water ingestion	1	1
Tap water vapours (indoors)	1	1
Tap water dermal contact	1	1

Free product	0	1: Pathway exists
	_	0: No pathway
Significant risk levels		

Significant risk levels		
Non-carcinogenic risk	1	
Carcinogenic risk	1 in	10000

Table 22. Residential without gardens. Human exposure assumptions.

	1	On-site		
Parameter	Notation	Adult Resident	Child Resident	
Body weight (kg)	BW	60	15	
Exposure frequency (days/year)	EF	360	360	
Exposure duration (years/lifetime)	ED	24	6	
Lifetime (days)	L	25550	25550	
Oral Bioavailability	0	1	1	
Fraction of time spent on site	t _o	100%	100%	
Outdoor inhalation rate (m³/day)	Во	20	15	
Indoor Inhalation Rate (m³/day)	Bi	20	15	
Drinking Water Ingestion Rate (I/day)	DW	2	1	
Fraction of time spent outdoor	Fod	25%	25%	

		ADULT			CHILD			FINAL	
Chemical	Shallow Soil RBCLs (mg/kg)	Deep Soil SSTLs (mg/kg)	Groundwater RBCLs (mg/l)	Shallow Soil RBCLs (mg/kg)	Deep Soil RBCLs (mg/kg)	Groundwater SSTLs (mg/l)	Shallow soil RBCLs mg/kg	Deep soil RBCLs mg/kg	Groundwater RBCLs mgll
C10-C16 (TPH) Copper	1.95E+02	IR -	2.13E-01 IR	6.51E+01	IR -	5.47E-01 IR	6.51E+01	IR	2.13E-01 IR
Zinc Cadmium	-	- -	IR	-	-	IR			IR
Lead	-	-	IR	-	-	IR			IR

Table 24. Potential exposure pathways for open space (unlimited access for public).

		On-site			
		Open Space			
Pathway		Adult	Child		
Soil ingestion		1	1		
Soil dermal contact		1	1		
Indoor dust inhalation		0	0		
Outdoor dust inhalation		1	1		
Shallow soil vapours (indoors)		0	0		
Shallow soil vapours (outdoors)	ĺ	1	1		
Deep soil vapours (indoors)		0	0		
Deep soil vapours (outdoors)		1	1		
GW vapours (indoors)	Ì	0	0		
GW vapours (outdoors)		1	1		
Free product vapours (indoors)		0	0		
Free product vapours (outdoors)		0	0		
Free product?		0	1: Pathway exists		
		··	0: No pathway		
Significant risk levels			<u> </u>		
Non-carcinogenic risk (HI)		1			
Carcinogenic risk 1	in 1	.0000			

Table 25. Open space. On-site child and adult. Human exposure.

		On-site		
Parameter	Notation	Adult Resident	Child Resident	
Soil ingestion rate (mg/day)	.IR	40	200	
Body weight (kg)	BW	60	15	
Exposure frequency (days/year)	EF	104	180	
Exposure duration (years/lifetime)	ED	24	6	
Lifetime (days)	L	25550	25550	
Skin surface (cm ²)	SA	16467	6381	
Soil adherence (mg/cm²)	SL	1	1	
Fraction of Skin exposed	F_s	30%	48%	
Oral Bioavailability	0	1	1	
Outdoor Dust Concentration (mg/m³)	PM_o	0.07	0.07	
% Soil Particles in Dust	F_{sd}	100%	100%	
Fraction of time spent on site	t _o	100%	100%	
Outdoor inhalation rate (m³/day)	Во	20	15	
Indoor Dust Concentration (mg/m³)	PM_{I}	0.07	0.07	
Fraction of outdoor dust which is indoors (%)	F_i	100%	100%	
Indoor Inhalation Rate (m³/day)	Bi	20	15	
Fraction spent outdoor	Fod	25%	25%	

		ADULT			CHILD				
Chemical	Shallow Soil RBCLs (mg/kg)	Deep Soil RBCLs (mg/kg)	Groundwater RBCLs (mg/l)	Shallow Soil RBCLs (mg/kg)	Deep Soil RBCLs (mg/kg)	Groundwater RBCls (mg/l)	Shallow soil RBCLs mg/kg	Deep Soil RBCLs	Groundwater RBCLs mg/l
CIO CIA (TDU)	IR	IR	IR	1.29E+02	IR	IR	1.29E+02	IR	IR
C10-C16 (TPH) Copper	IR	ık	, IK	IR	-	•	IR	-	-
Zinc	IR	_	_	IR	-	-	IR	-	-
Cadmium	IR	-	-	IR	- .	•	IR	-	-
Lead	IR	-	-	4.61E+02	-	•	4.61E+02	-	-

IR = Insignificant Risk, Clean-up levels not required

Table 27. Parameters used for groundwater modelling at the Valmieras iela site.

Parameter	Va	lue
Hydraulic conductivity (m/day) (shallow/deep)	1	0.86
Hydraulic gradient	0.0	034
Fraction of organic carbon	0.	01
Length of source parallel to groundwater flow (m)	2.	55
Source width (m)	39	90
Source thickness (m)		7
Infiltration rate (m/yr)	0.0	015
Thickness of aquifer (m) (shallow/deep)	7	30
Mixing zone depth (m)	7	27
Effective porosity % (shallow/deep)	27	1
Aquifer dilution factor (shallow/deep)	3	74
Dry bulk density (g/cm³)	1.	65
Distance to compliance point (m)	200	500
Longitudinal dispersivity (m)	20	50

15.6 Conclusions of Health Risk Assessment

The human health risk assessment considered the potential health risks associated with the observed contamination at the Valmieras iela site for four future land use scenarios. *It is important to note that a quantitative assessment of free product vapours has not been undertaken.* The first scenario assumed that the site continued in its current use. It was found that no significant risks to human health arise from the observed contamination assuming that the site continues in its current use. Similarly no significant health risks are anticipated if either of the sites are redeveloped for commercial (office) use.

The risk assessment for the scenario involving proposed redevelopment of the sites for residential use (with gardens) found unacceptable risks to human health associated with the presence of TPH in soil and groundwater, and cadmium and lead in soil.

The risk assessment of the scenario of redevelopment for residential use without gardens also found significant risks to human health associated with the presence of soil and groundwater TPH contamination.

For both the proposed residential scenarios it would be necessary to carry out further risk assessment at Tier 3 or some form of remedial treatment (which may be clean-up to the RBCL specified) to ensure that the site does not present unacceptable risks to human health for future residents. Alternatively, a different end-use should be considered for such sites.

The risk assessment of the scenario involving sites being abandoned with unlimited public access also found unacceptable health risks for children from oil and lead in soils. As discussed previously, appropriate options for remedial action in this scenario may include secure fencing-off of the site or patrol by security guards.

All of the above conclusions are based on the observed contaminant concentrations found in recent ground investigations. If conditions were to change at the site in the future then it may be necessary to carry out further risk assessment work based on the findings of further investigations.

15.7 Sensitivity Analysis

The results of the human health risk assessment associated with contaminants in soil and groundwater could be enhanced by providing sensitivity analysis of certain input parameters. Sensitivity analysis is performed for those parameters associated with an inherent degree of uncertainty and for parameters with an underlying variability.

A sensitivity analysis should include the major input parameters used to estimate human health risk. The following parameters have considerable influence in the final results of risk assessment:

- depth to contamination,
- organic carbon content,
- porosity (air, water),
- vegetable consumption,
- body weight,
- inhalation rate,
- soil ingestion,
- exposure assumptions.

15.8 Groundwater Risk Assessment

The methodology and algorithms used for performing the groundwater risk assessment are those documented in Grundy & Quint (1998). Essentially three relatively simple analytical models are used to simulate (i) leaching of contaminant from soil to pore water, (ii) mixing of pore water into the aquifer and (iii) transport of groundwater in aquifer taking into account advection, dispersion and retardation functions.

15.8.1 Contaminants of Potential Concern

Contaminants of potential concern are listed in Table 8b. These tables present all contaminants in both soil and groundwater that are used in the groundwater risk assessment. All soil contaminant concentrations were observed in shallow soil at a depth of 20 - 25 cm. These data were screened against Norwegian trigger values for the most sensitive land use. Total Petroleum Hydrocarbon (TPH) was assumed to be within the diesel range for Valmieras iela for the purposes of the risk assessment modelling.

In order to assign a maximum concentration of dissolved hydrocarbon (TPH) at source, it has been assumed that the maximum concentration occurs underneath the LNAPL lens at the site and that it is equal to the solubility of the oil product. At Valmieras iela, where the LNAPL is diesel-like, the maximum concentration is set to 2.06 mg/l. In the absence of any detailed product identification data, the mole fraction of each component compound in groundwater has not been calculated.

15.8.2 Conceptual Site Model (CSM)

The hydrogeology of the Riga area is described in detail in the report prepared by the Geological Survey of Denmark and Greenland (1996/52), 'Groundwater as a Source of Drinking Water for Riga City' (Gosk et al. 1996). The two aquifers (Quaternary Baltic Ice Lake Sediments and Devonian) have been treated as separate horizons with limited vertical flow through the aquitard. The parameters used for the groundwater risk assessment are presented in Table 27. All soil and groundwater contaminants reported are from the shallow Quaternary aquifer and the made ground. The soil samples at the Valmieras site were all taken from the shallow unsaturated soil at depths of 20 to 25 cm below ground level. It is understood that no further sampling was attempted at greater depths. It was assumed that the

entire unsaturated zone was contaminated for modelling purposes. Therefore a source thickness of 7.0m was chosen. Although it is assumed that the Devonian aquifer is initially uncontaminated, limited vertical flow through the less permeable Quaternary deposits is expected to occur and will therefore permit transport of dissolved contaminants into the Devonian. The potential contaminant migration pathways for soil and groundwater contaminants have been identified as follows:

- partitioning of soil contaminants into the aqueous phase through the infiltration of rainfall in the unsaturated zone and subsequent mixing and dilution of the contaminants in the shallow aquifer;
- Potentially rapid vertical migration of dissolved phase contamination within the shallow aquifer down-gradient;
- Slower vertical migration of dissolved phase contamination through the less permeable Quaternary aquitard into the deeper Devonian aquifer, and subsequent mixing, dilution and transport with attenuation down-gradient.

15.8.3 Results of Groundwater Risk Assessment

On-Site Deep Borehole:

All data for contamination in soil and groundwater for this site were from shallow Quaternary deposits. These data were used to simulate concentrations in the deeper Devonian aquifer and represent the water in the deep borehole. It was assumed that limited vertical flow occurs through the aquitard and therefore dispersion and attenuation occurs (in the clays).

The results can be summarised in table 28.

Table 28. Groundwater risk modelling for deep on-site Devonian borehole

Chemical	Drinking water standard or equivalent (µg/l)	Simulated concentration in the deep aquifer borehole below site (µg/l)	Compliance Point Waters Hazard Index (WHI)	Risk-based clean-up level (RBCL) for water (µg/l)
Arsenic	10	0.032	<1	na
Boron	300	1.08	<1	na
Cadmium	5	0.17	<1	na
Copper	300	0.007	<1	na
Lead	20	59.7	3	15*
Nickel	50	0.133	<1	na
Zinc	300	2.20	<1	na
TPH(C ₁₀ -C ₁₆)/DRO	10	12.0	1.2	23

n a - RBCL not applicable: maximum concentration simulated within RBCL value.

DRO - Diesel Range Organics

The results presented in Table 28 illustrate that the concentration of lead in the deep aquifer could potentially reach values above the target drinking water standard of $20~\mu g/l$. The source of lead contamination is 3,300 mg/kg in the unsaturated zone at a depth of 20 cm. The concentration of lead in the soil that would produce leachate and groundwater concentrations that are acceptable was estimated to be 15 mg/kg. This concentration is known as the risk-based clean-up level (RBCL). TPH in groundwater could also pose a significant risk to the deep on-site borehole - the RBCL is 23 μ g/l for on-site groundwater.

200m Compliance Point:

Groundwater concentrations were simulated from soil and groundwater contamination at the Valmieras iela site for a 200m compliance point. This compliance point represents a domestic well in the shallow Quaternary aquifer. The results can be summarised as follows:

^{* -} Simulated concentration is from soil contamination. RBCL is for soil (mg/kg).

Table 29. Simulated concentrations in groundwater in a well 200 m down-gradient from the contaminated site in the Quaternary aquifer.

• Parameter	Simulated concentration
Arsenic	3.74 x 10 ⁻³ μg/l from groundwater contamination.
Boron	1.26 x 10 ⁻¹ μg/l from groundwater contamination.
Cadmium	2.75 x 10 ⁻³ μg/l from soil contamination.
Copper	6.24 x 10 ⁻⁴ µg/l from soil and 3.69 x 10 ⁻³ µg/l from groundwater contamination.
• Lead	2.45 x 10 ⁻¹ μg/l from soil and 1.69 x 10 ⁻³ μg/l from groundwater contamination.
Nickel	1.54 x 10 ⁻² μg/l from groundwater contamination.
• Zinc	3.97 x 10 ⁻² µg/l from soil and 6.57 x 10 ⁻² µg/l from groundwater contamination.
Total Petroleum Hydrocarbon (TPH) (Diesel Range Organics)	1.97 x 10 ⁻² μg/l from soil and 1.27 x 10 ⁻¹ μg/l from groundwater contamination.

All simulated concentrations are below the target water values and there are no risks to users of the well for domestic purposes.

500m Compliance Point:

Groundwater concentrations were simulated from soil and groundwater contamination at the Valmieras iela site for a 500m compliance point. This compliance point represents a public supply borehole in the deep Devonian aquifer. The groundwater concentrations in the Devonian aquifer simulated for the on-site borehole (see above) were used as input values for simulating the groundwater concentrations down-gradient within the same aquifer. The results can be summarised as follows as concentrations at the target borehole:

•	Arsenic	:	$7.74 \times 10^{-6} \mu g/l;$
•	Boron	:	$2.59 \times 10^{-4} \mu\text{g/l};$
•	Cadmium	:	$6.24 \times 10^{-5} \mu\text{g/l};$
•	Copper	:	$2.49 \times 10^{-6} \mu\text{g/l};$
•	Lead	:	$5.12 \times 10^{-3} \mu g/l;$
•	Zinc	:	$8.27 \times 10^{-4} \mu\text{g/l};$
•	TPH	:	$4.16 \times 10^{-4} \mu\text{g/l}$.

All simulated concentrations are below the target water values and there are no risks to users of the well for domestic purposes.

Impact on River Daugava

It is considered that the observed soil and groundwater contamination will have no detrimental impact on the river. This assessment is based on:

- (i) the lack of any target level exceedence in the Quaternary well at only 200 m distance
- (ii) dilution and attenuation effects during transport to the river
- (iii) the huge dilution potential of the River Daugava.

15.9 Conclusions of Risk Assessment

A summary of the risk assessment conclusions is provided below. This focuses on the existence of significant levels of risk at the site, under the range of end-uses considered. It is important to note that the risk assessment has been undertaken at the Tier 2 level and is subject to certain limitations as discussed in the text and by Grundy & Quint (1998). Where significant levels of risk have been identified, several options are possible:

- 1. one option is to remediate the source of the contamination such that concentrations left insitu will no longer pose a risk. Alternatively, risk may be reduced by addressing migration/exposure pathways or initiating land-use restrictions. If direct source-orientated options are selected then the Risk-Based Clean-Up Levels (RBCLs) provide numerical criteria that can be used to determine the scope of remediation that is required.
- 2. Alternatively, a more sophisticated (Tier 3) risk assessment could be undertaken. It is likely that this will focus on key issues only and be characterised by a reduction in some of the conservatism that is a feature of the assessment presented here. This risk assessment may thus be able to recommend a more focussed, but less costly, action plan than can be recommended on the basis of only a tier 2 assessment.

Specifically, at Valmieras iela, the existing risk assessment concluded the following:

Continued Use

No significant risks to human health are posed by contaminants at the site.

Redevelopment for commercial use

No significant risks to human health are posed by contaminants at the site.

Residential with gardens

Significant risks could be associated with exposure to petroleum hydrocarbons, TPH (diesel range organics) in soil an groundwater, cadmium and lead in soil. Risk Based Clean-up Levels (RBCLs) are shown in Table 20.

Residential without gardens

Significant risks could be associated with exposure to petroleum hydrocarbons, TPH (diesel range organics) in soil and groundwater. RBCLs are shown in Table 23.

Abandonment with unlimited access to the public
Significant risks could be associated with exposure to TPH (diesel range organics) in soil.
RBCLs are shown in Table 26

The risk assessment assumes that the LNAPL oil phase is a stationary source of dissolved contaminants to groundwater. No attempt has been made to estimate human exposure or to model the possible migration of the LNAPL phase itself. It is very important that a supplementary risk assessment / modelling of this possibility should be undertaken before any final decision is taken on the remediation/non-remediation of the free phase oil layer at both sites.

16. CONCLUSION

Site investigations have indicated that groundwater at the Valmieras iela site is contaminated by hydrocarbons, free phase LNAPL oil being found in one of the boreholes (borehole 3 beneath the scrapyard). Soils at the site are contaminated by oil and heavy metals, including the metals Pb, Cu, Zn and Cd.

Risk assessment techniques have been applied to make a so-called "Tier 2" assessment of risk to human health and risk to water resources from the site. The assessment has concluded that contamination from the site will not reach the River Daugava within 39 years, even without taking into account sorption and biodegradation.

The risk assessment concludes that the site can remain in its current usage or be redeveloped for commercial purposes without any risk to human health. The assessment predicts no unacceptable risk to off-site groundwater resources (well in Quaternary aquifer at 200 m distance or bore in Devonian at 500 m distance) or to the River Daugava from the site. If it planned to re-instate the use of the existing on-site borehole to the Devonian aquifer, it may be susceptible to contamination by lead and hydrocarbons. A more detailed risk assessment (Tier 3) of this possibility is required (or alternatively, clean-up of the site for these parameters to specified standards).

If the site is redeveloped for residential use or for open public access, an unacceptable human health risk may be present. If such redevelopment is proposed, either (a) a "Tier 3" risk assessment should be carried out to make a more refined, less conservative assessment of risk or (b) cleanup of selected areas should be carried out to cited risk-based clean-up levels.

The investigation has had three main shortcomings:

(i) Lack of reproducibility of analytical data. Recommendation: that all national laboratories used for contamination assessments should take part in internationally recognised accreditation schemes and international ring tests. Sampling should include adequate provision for spiked samples and blanks.

- (ii) Lack of sensitivity analysis for modelling of groundwater contaminant transport and risk assessment. Recommendation: no model results or risk assessments should be accepted as the basis for decision-making unless accompanied by a quantitative sensitivity analysis or, at the very least, (i) some quantification of likely margins of error in the results or (ii) a full justification of the conservatism of the approach.
- (iii) Lack of modelling or risk assessment of evolution of LNAPL plume or risk therefrom. Recommendation: As LNAPL plumes frequently represent the greatest concentrations of contaminants at many former military bases, transport and risk models simulating LNAPL evolution should be assessed and implemented as a matter of urgency.

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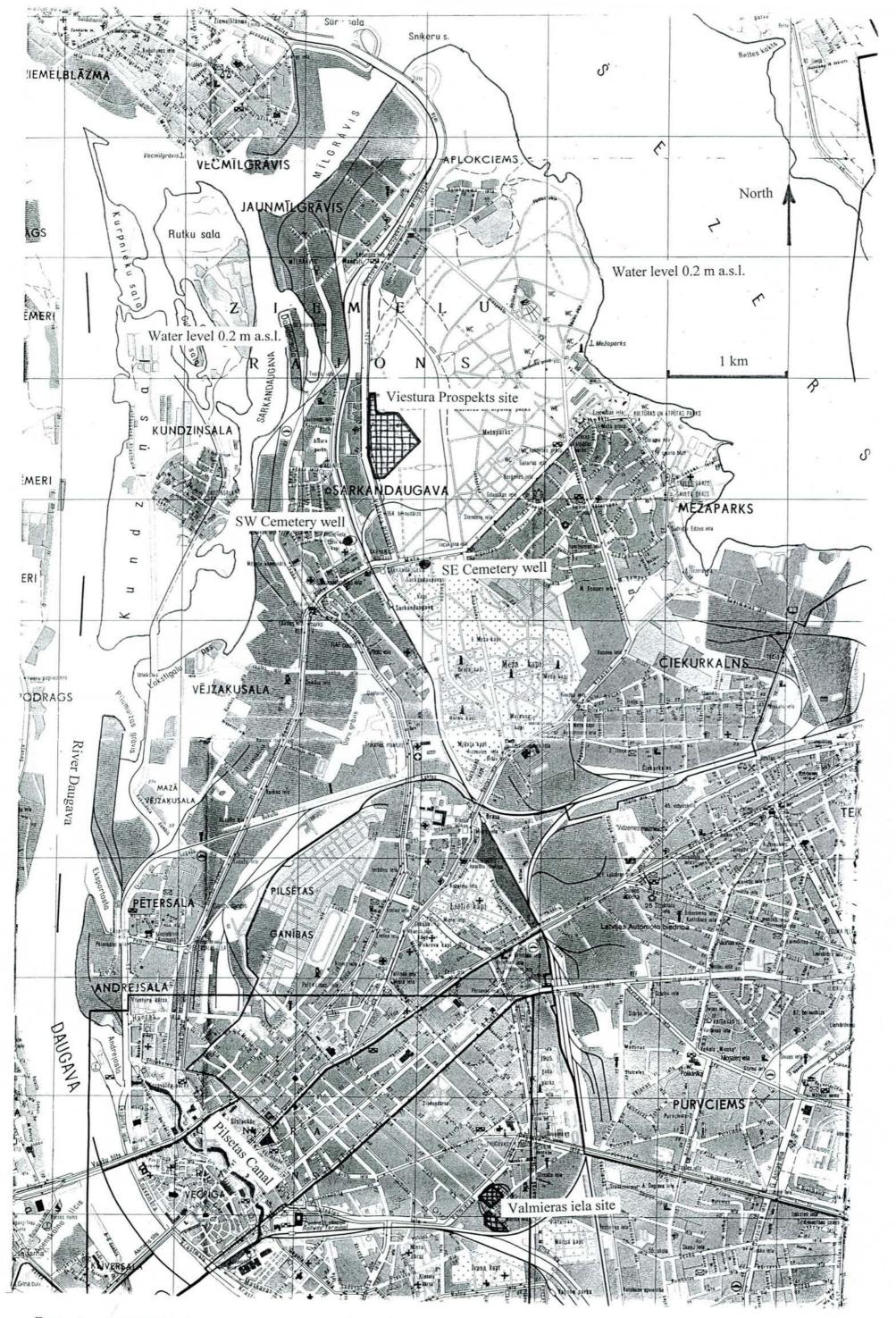


Figure 1. Map of Riga, showing the location of the Viestura Prospekts and Valmieras iela sites.

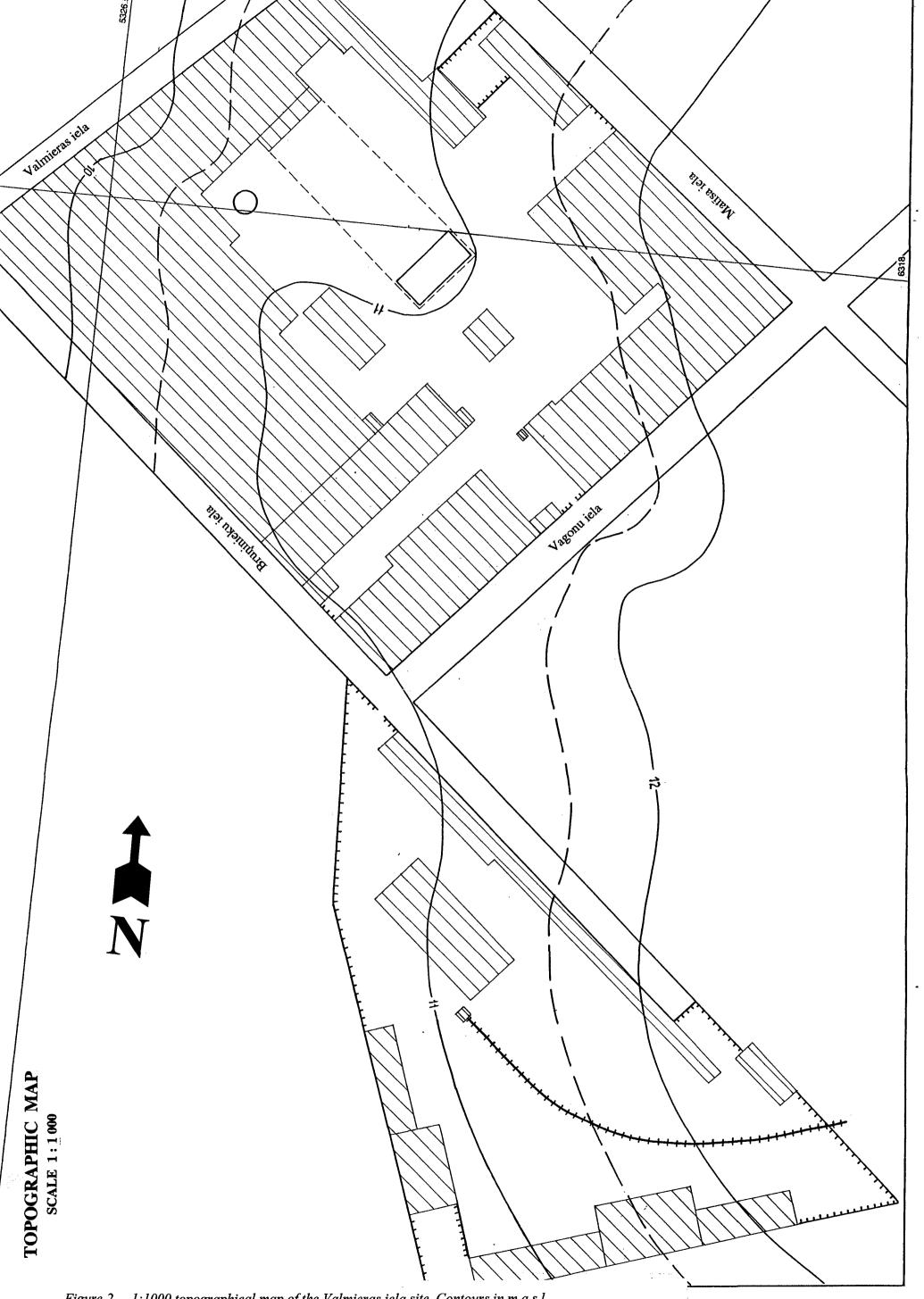
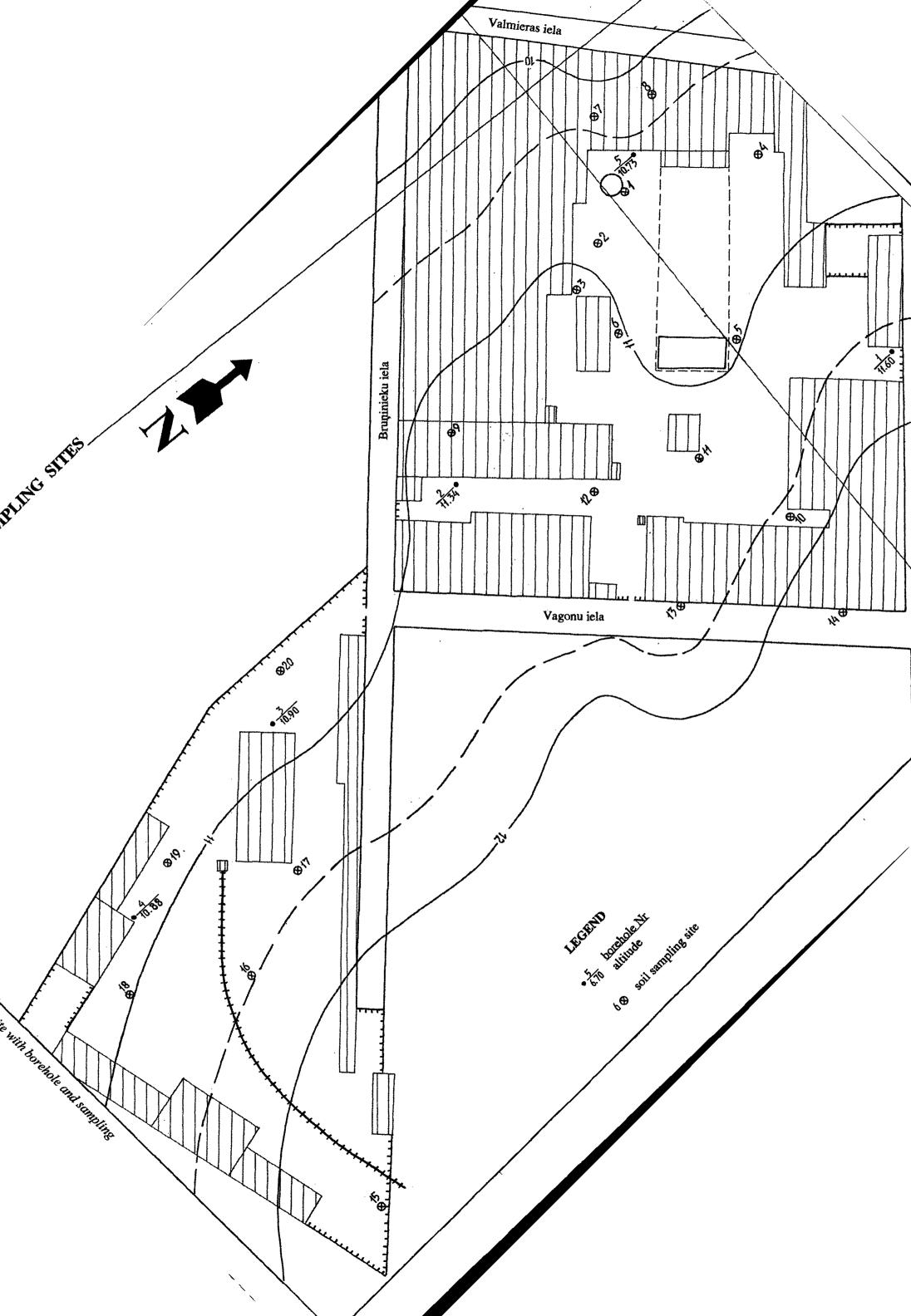


Figure 2. 1:1000 topographical map of the Valmieras iela site. Contours in m a.s.l.



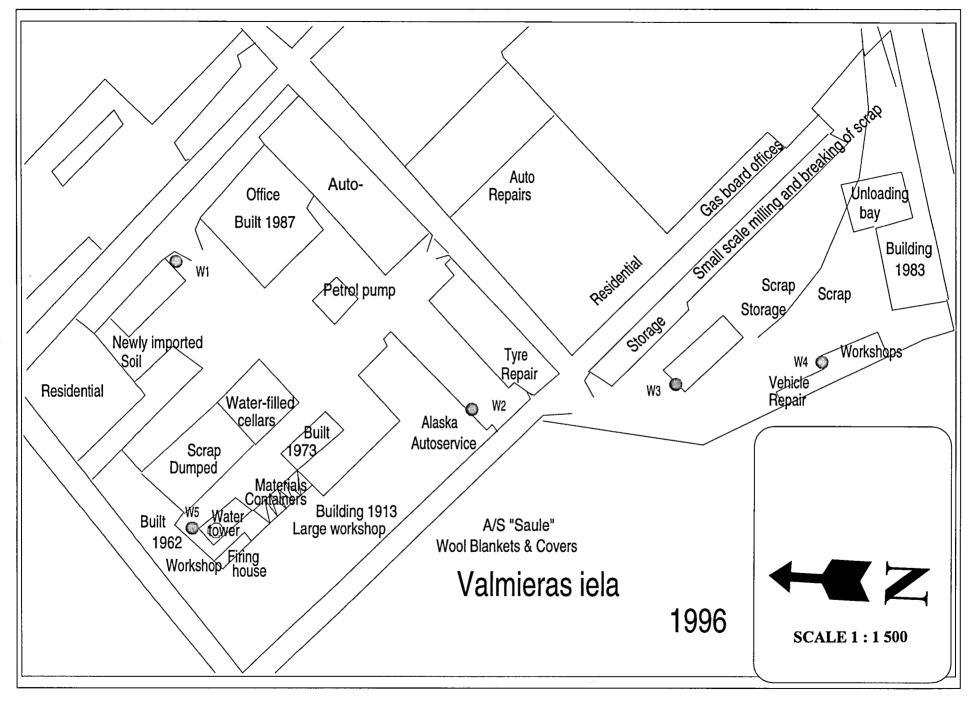


Figure 6. Comparison between NGU analyses and Latvian analyses of groundwater from Valmieras iela for 11 selected parameters in 1996. All values below detection limit have been plotted at 0.5 x detection limit.

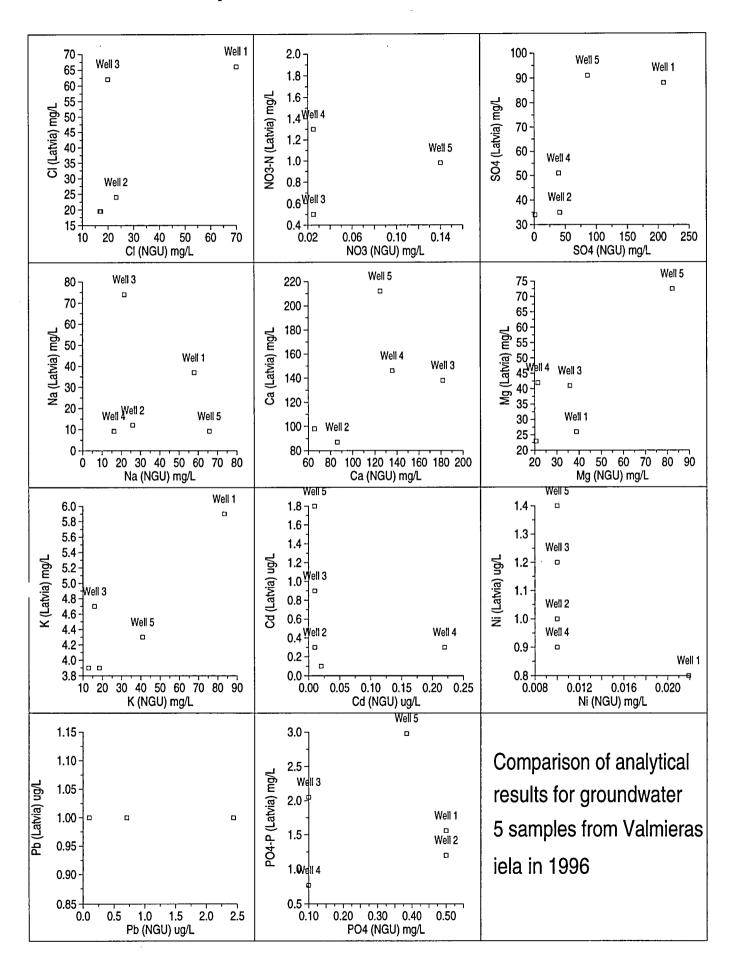


Figure 7. Comparison between NGU analyses and Latvian analyses of groundwater from Valmieras iela for 16 selected parameters in 1997. All values below detection limit have been plotted at 0.5 x detection limit.

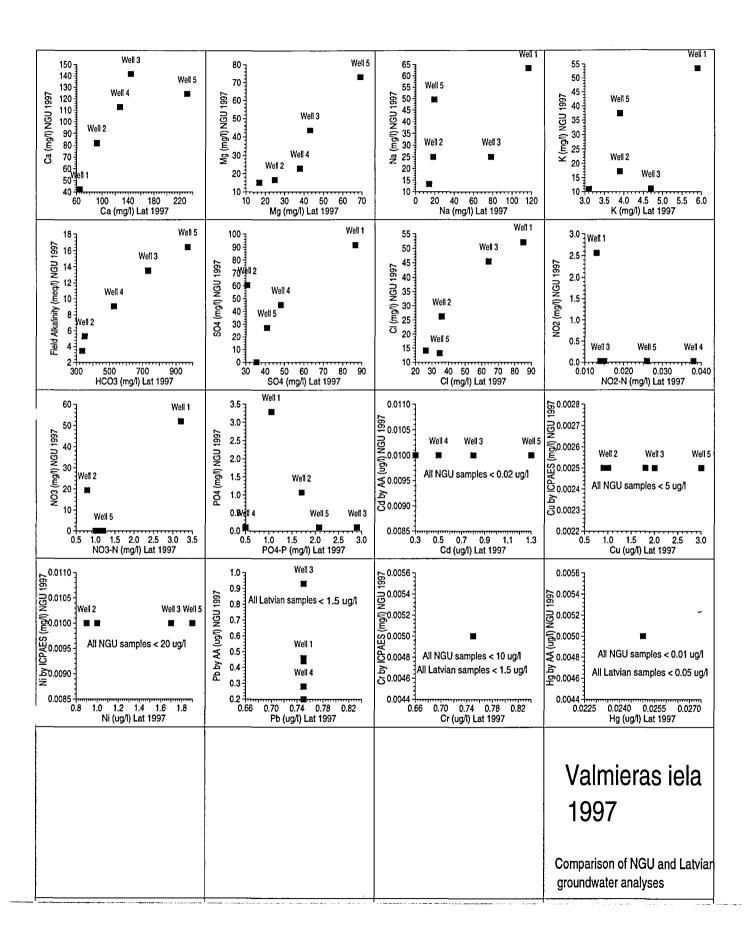


Figure 8. Comparison between NGU's 1996 and NGU's 1997 of groundwater from Valmieras iela for 24 selected parameters. All values below detection limit have been plotted at 0.5 x detection limit.

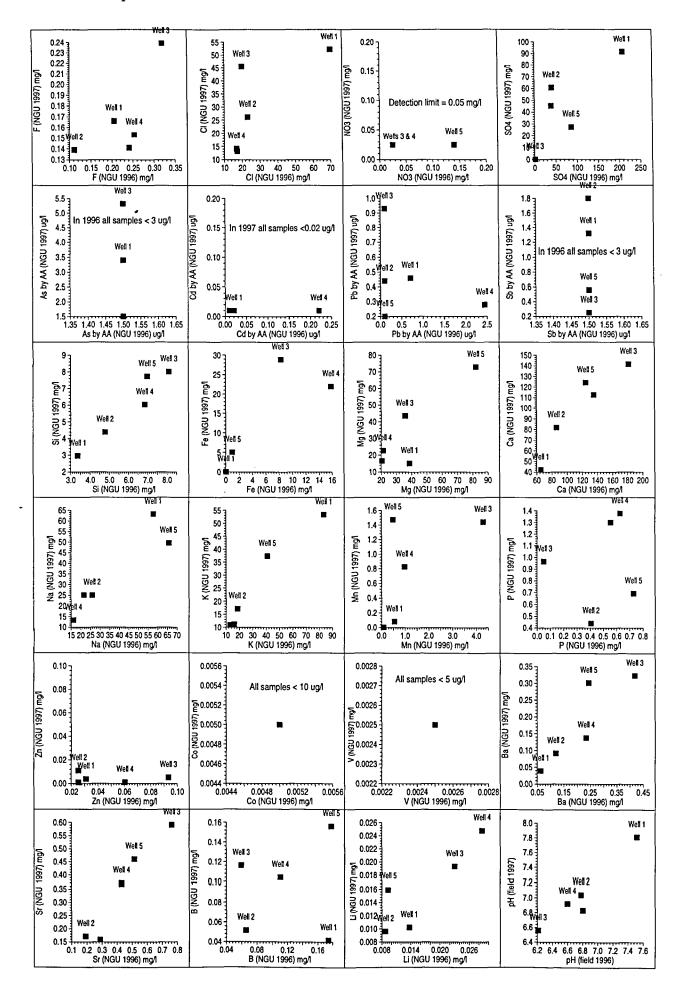


Figure 9. Comparison between Latvian 1996 analyses and Latvian 1997 analyses of groundwater from Valmieras iela for 22 selected parameters. All values below detection limit have been plotted at 0.5 x detection limit.

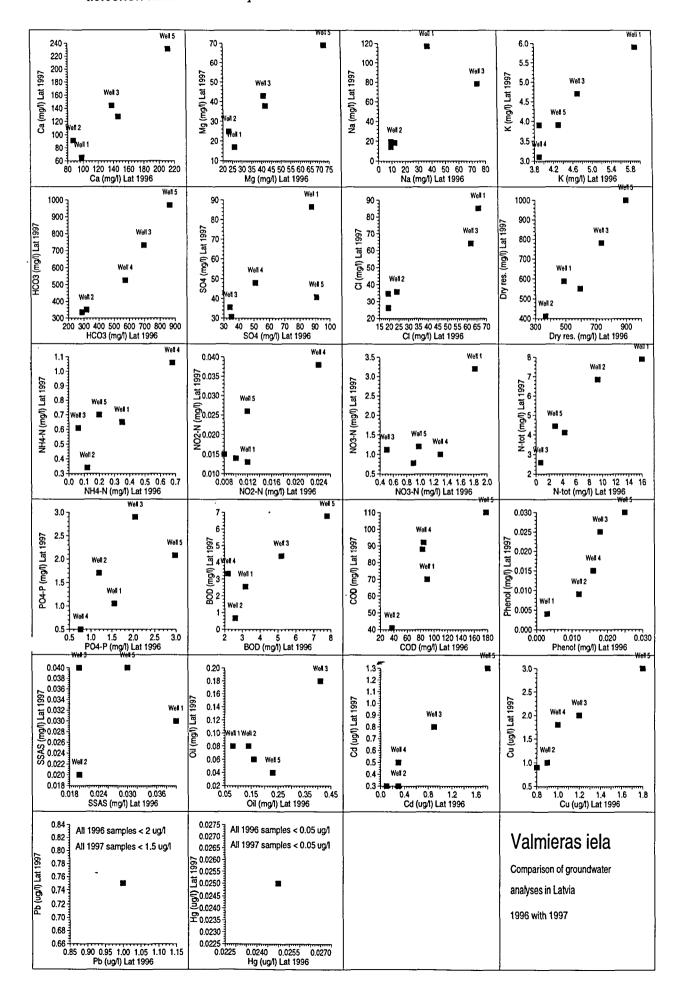


Figure 10. Comparison between 1996 and 1997 analyses from Latvia and from FFI for oil in groundwater from Valmieras iela. All values below detection limit have been plotted at 0.5 x detection limit.

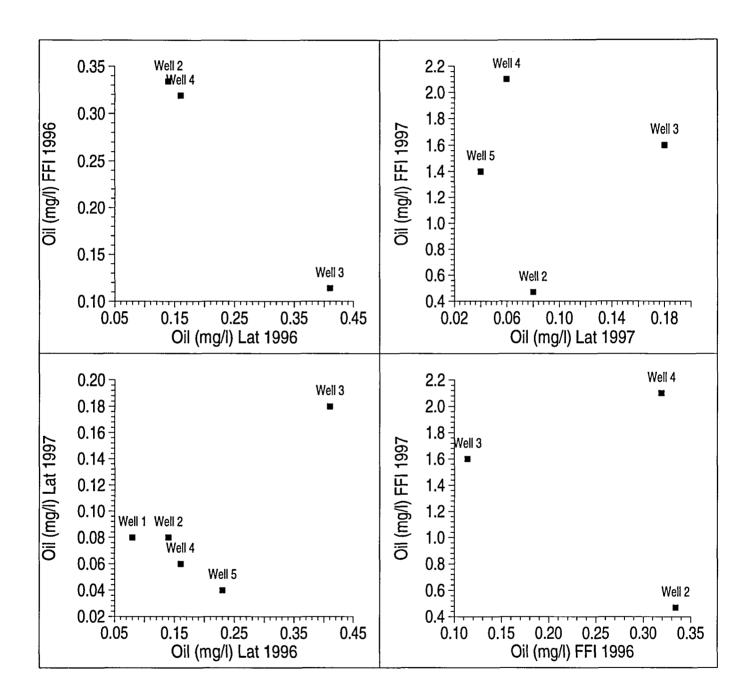
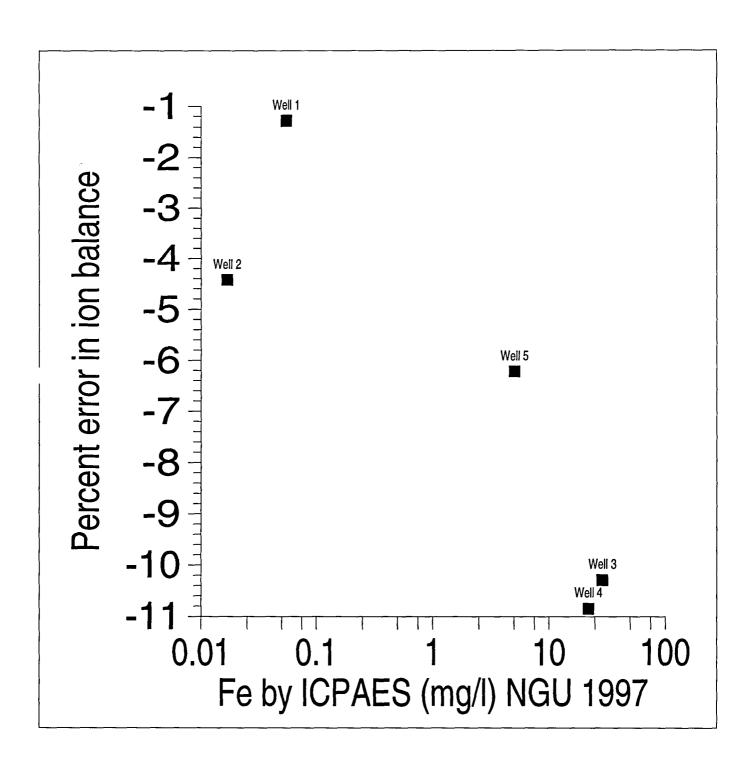


Figure 11. Plot of ion balance error = (sum cations - sum anions)/(sum cations + sum anions) x 100% versus iron for Valmieras iela groundwaters in 1997. Using field alkalinity, Cl⁻, SO₄⁼ and NO₃⁻ by IC and Fe, Mn, Na, K, Ca and Mg by ICPAES, analysed by NGU. All parameters in meq/l.



Explanation of the BOXPLOT 83 ppm **MAXIMUM** MAX. to UH: ca. 25 % upper whisker (UW) upper hinge (UH) 3.6 UH to MED: ca. 25 % **MEDIAN** 28 MED to LH: lower hinge (LH) 24 ca. 25 % LH to MIN: ca. 25 % of the data lower whisker (LW) 0.7 **MINIMUM** 0.5 (N=316)**Definitions:** hinge spread (HS) = UH - LHupper whisker = $UH + 1.5 \times HS$ lower whisker = $LH - 1.5 \times HS$ the whiskers are drawn at the last actual data point

Figure 13. Map of oil contamination in soils at the Valmieras iela site.

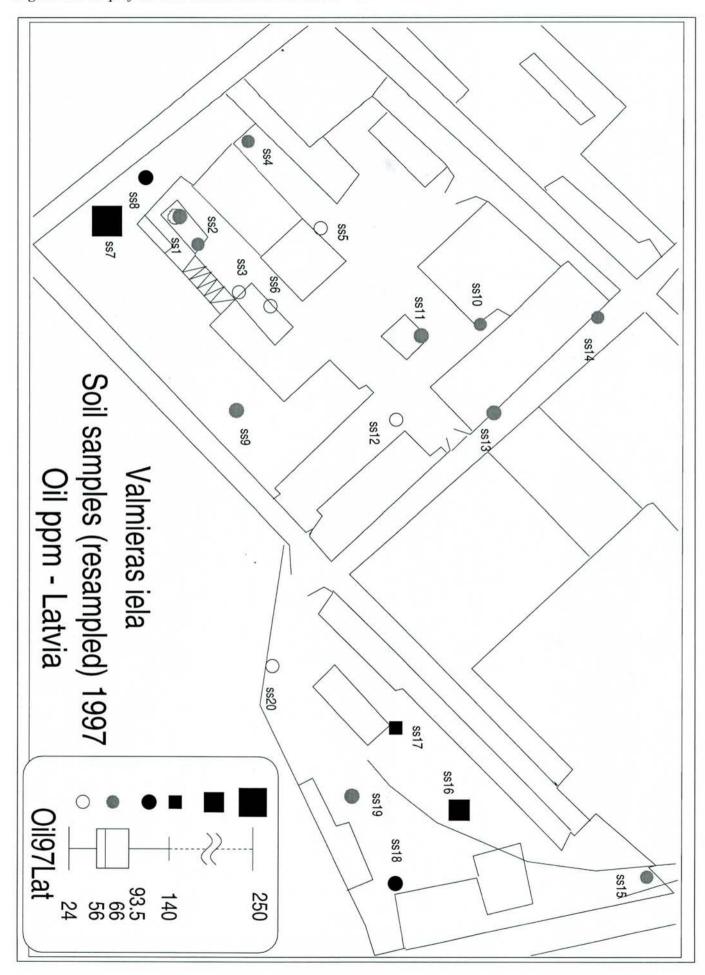


Figure 14. Map of dissolved hydrocarbon contamination in groundwater at the Valmieras iela site.

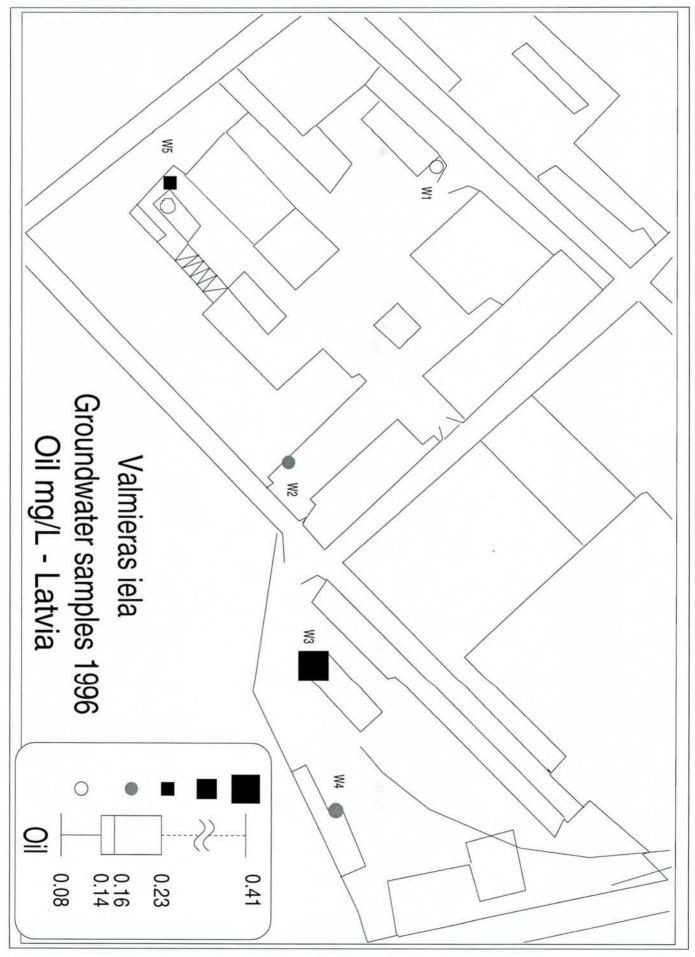


Figure 15a. Correlations between iron and conductivity / total anion content. Note use of both log. and linear scales.

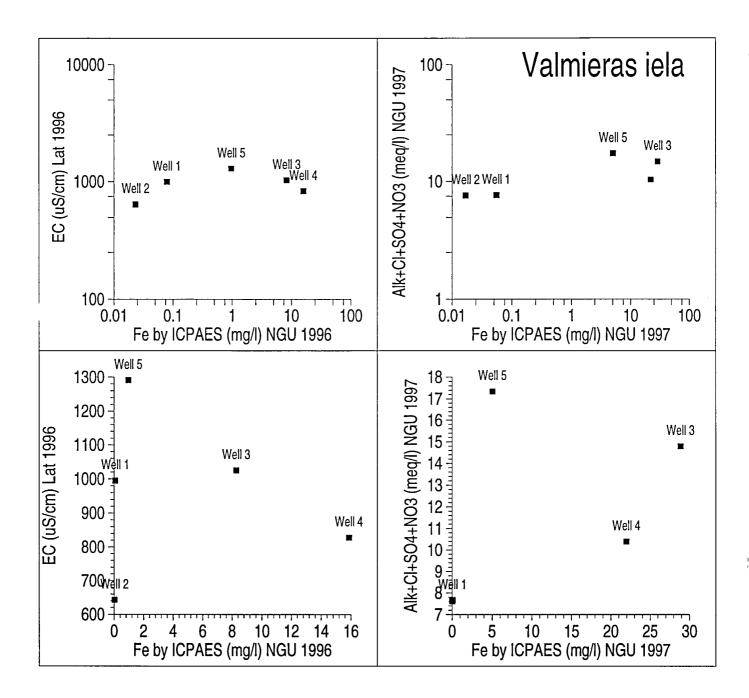


Figure 15b. Correlations between oil and iron / conductivity for 1996. Note use of both log. and linear scales.

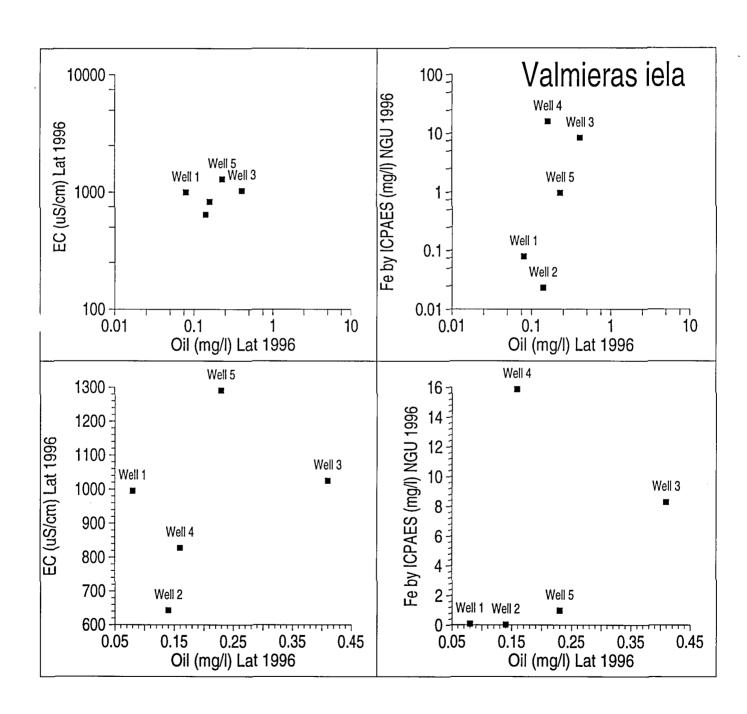


Figure 15c. Correlations between oil and iron / total anion content for 1997. Note use of both log. and linear scales.

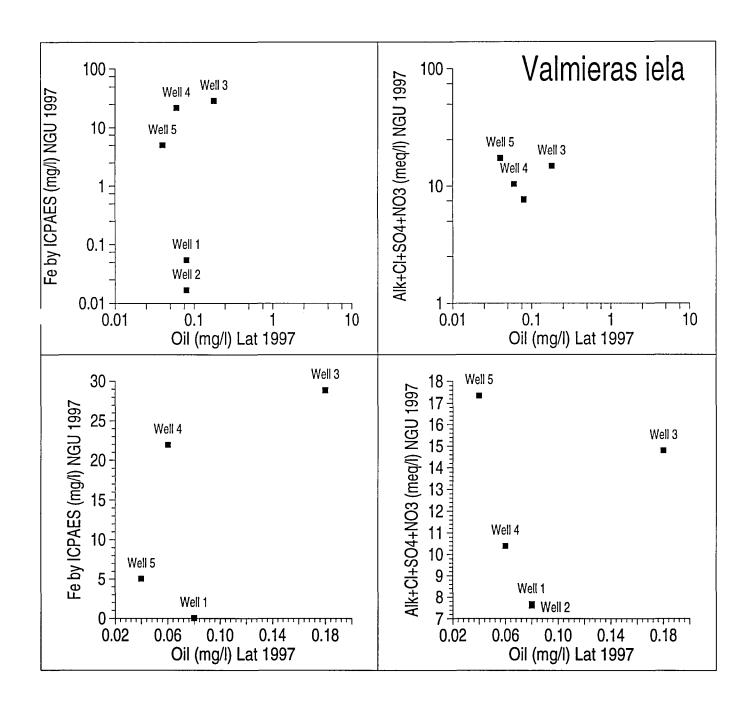
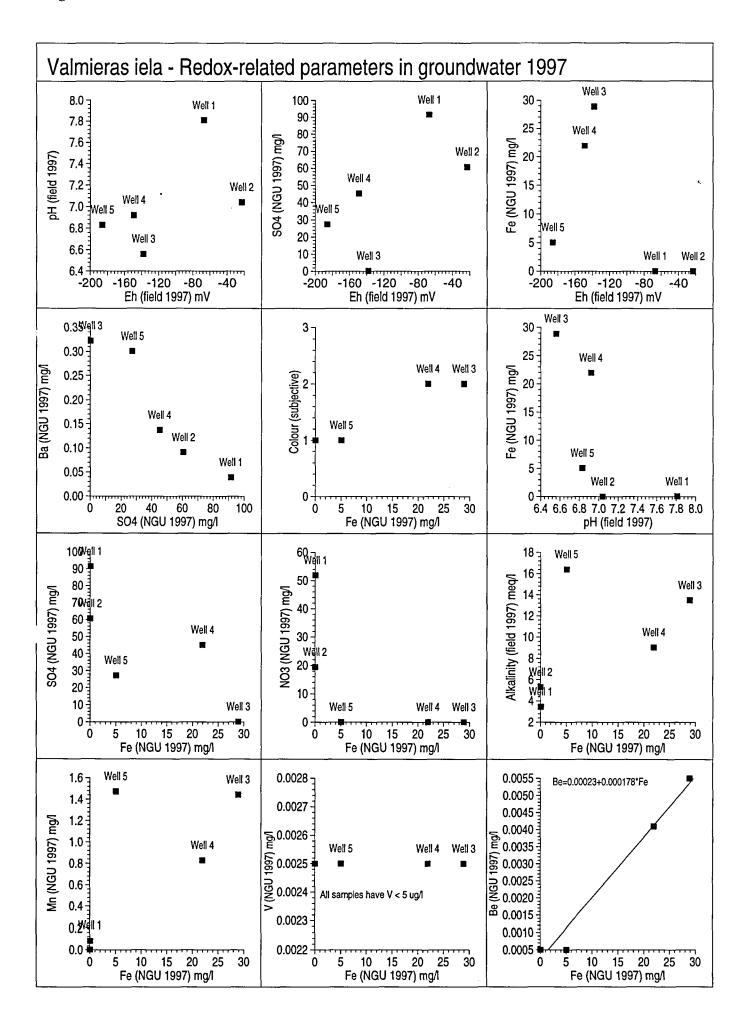


Figure 16. Redox-related parameters in groundwater, 1997. Note interference between Be and Fe.



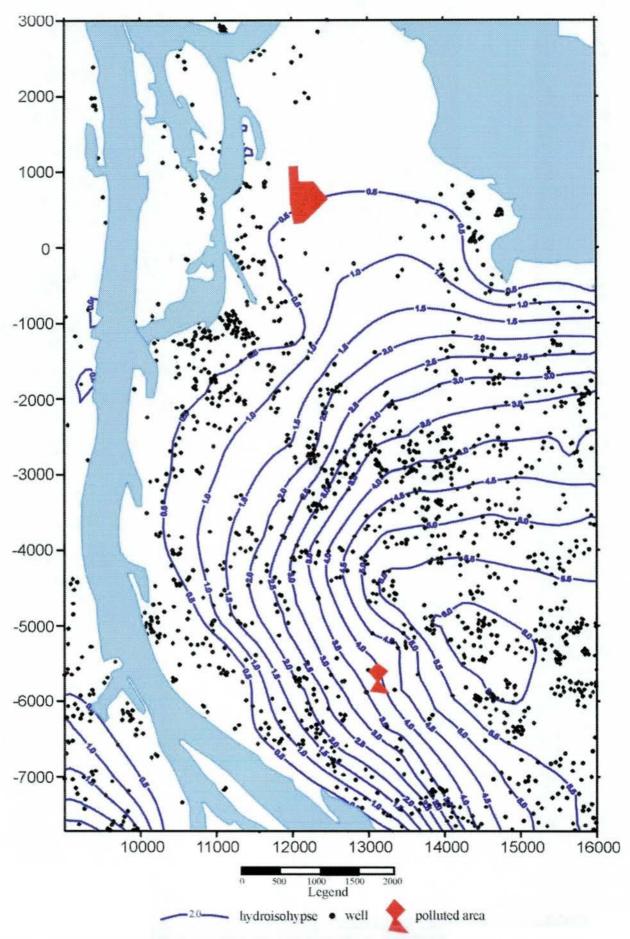
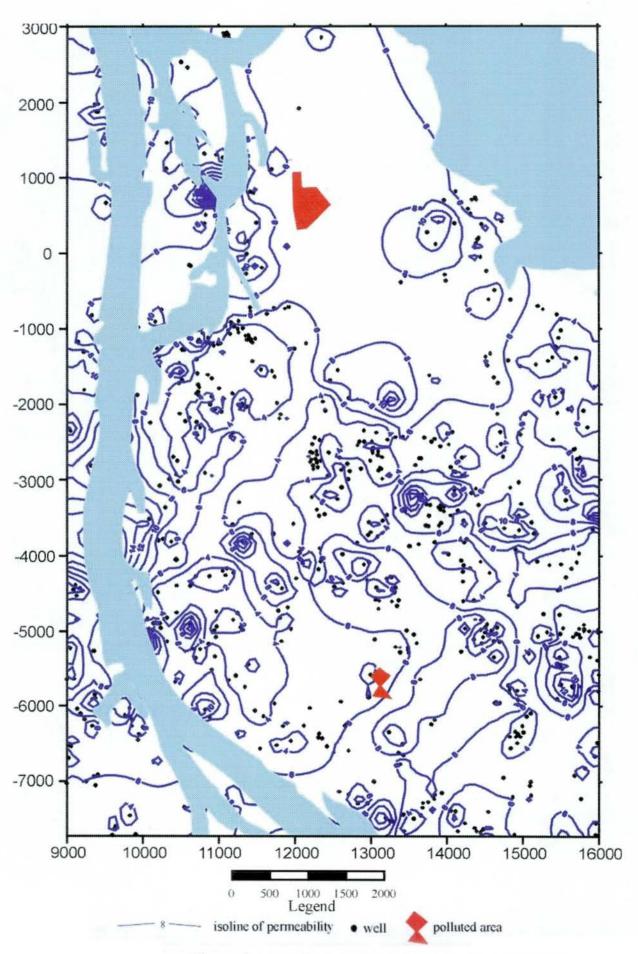


Figure 17. Modelled area of Riga, showing distribution of groundwater head in the shallow Quaternary aquifer (m a.s.l.).



rigure 18. Modelled area of Riga, showing distribution of hydraulic conductivity in the shallow Quaternary aquifer. Units m/day

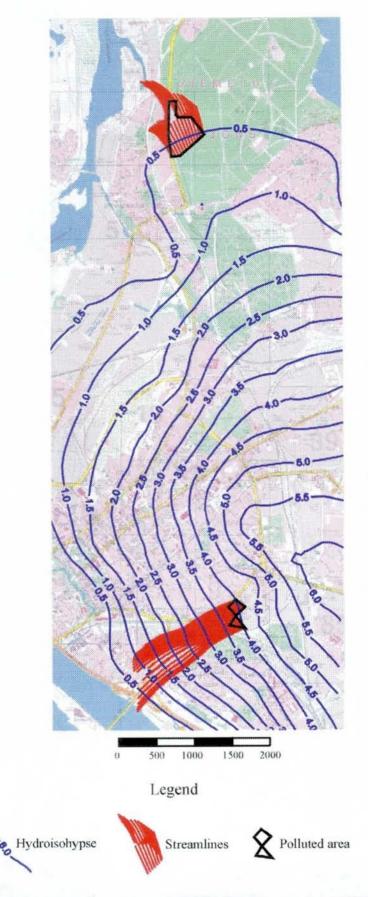


Figure 19. Modelled area of Riga, showing calculated directions of contaminant transport from the Viestura Prospekts and Valmieras iela sites.



Figure 20. Modelled migration of contamination from the Viestura Prospekts and Valmieras iela sites after elapsed time intervals of 5, 10, 20, 30 and 40 years.