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

Viestura Prospekts Oil Depot, Riga, Latvia.



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Sammendrag:

A former Soviet military fuel depot has been subject to site investigation to examine soil and groundwater contamination. 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 nearest surface water body within 35 years, even without taking into account sorption and biodegradation. The risk assessment also 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 groundwater resources 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 suffered from 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
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Grunnvannskvalitet	Grunnvann	Geofysikk

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1. INTRODUCTION

This report comprises a desk study, site investigation and risk assessment of a former Soviet military fuel storage depot at Viestura Prospekts, 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, are easily accessible and were expected to exhibit a range of contamination, both organic (e.g. Viestura) and inorganic (Valmieras). This report is an assessment of the contaminant situation at Viestura Prospekts.

2. SITE SIZE AND LOCATION

The site at Viestura Prospekts has a total area of ca. 20.5 Ha. A small part of the north of the site is currently in use by a private fuel management firm for daily operations including vehicle refuelling and repair. The remainder of the area is used by the firm for oil off-loading (from rail), pumping and storage, but is fenced off and declared a customs zone.

The site is located on the eastern side of Viestura Prospekts in the Meza Parks area of northern Riga (see Fig. 1).

3. TOPOGRAPHY

The topography of the site is illustrated in Fig. 2a. The site lies at between 5 and 12 m above sea level (a.s.l.). No clear regional gradient is apparent. The terrain is best described as hummocky. Some of these hummocks may be related to excavated materials during installation of the fuel bunkers, but the terrain in surrounding Meza Parks is similar, suggesting that most of the hummocks are natural. They may represent wind blown dunes in the sandy deposits of the Baltic Ice Lake, which constitute the underlying sediments.

The topography is dominated by the two fuel storage bunker complexes in the east of the site. These consist of groups of steel tanks encased in concrete bunkers. Low bunds of natural materials have been constructed around the bunkers. Within the bunds the ground is natural (i.e. sandy). While the bunds may have been effective at hindering spreading of surficial oil contamination, they would not have been effective at preventing ground and groundwater contamination.

4. LAND USE

The Viestura Prospekts site was in use from 1941 until 1992 as a fuel storage depot for the Soviet (later, Russian) Army (Figure 2a). Estimates of the total volume of fuel storage at the site vary from 4,400 m³ (GSL) to 13,200 m³ (Levins and Sicovs 1994 - Appendix 1). There exist both railhead, road tanker loading bay and pipeline to Riga port (following the course of Viestura Prospekts). It is believed that fuel arrived by rail and was distributed throughout the Soviet Union and Warsaw Pact lands by road and sea. At a similar, though larger and more strategically central, locality in Lithuania (Valciunai - see Paukstys et al. 1996), fuel also entered by rail. In the event of a critical situation, fuel could be freighted by road to a number of sub-depots and recipients.

It was initially believed that the hydrocarbon contamination at Viestura Prospekts was likely to be standard diesel. However, analyses (Appendix 6) performed at FFI indicate the observed oil contamination to be more comparable to jet fuel or paraffin than standard diesel. It is not known if other fuel types have been stored at Viestura Prospekts, although the presence of, for example, rocket fuel (as at Valciunai) is regarded as unlikely.

Following the withdrawal of the Russian/Soviet Army from the base in August 1992, the site has been in use by the company «Balt East-West». They essentially operate a fuel handling operation on a commercial basis, along similar lines but on a much smaller scale than the Soviet Army. The fuel is thus delivered by rail to the railhead and pumped via the pumphouse to the two bunker complexes. From here oil is either pumped via a pipeline north along Viestura Prospekts to Riga Port or is loaded into road tankers. «Balt East-West» occupies a small part of the site, near the entrance, for their daily operations. Around 50 m NE of borehole 3, a cluster of fuel pumps appears to be in use in this area. Slightly north of these pumps a small vehicle maintenance ramp is used for reparation of trucks.

The remainder of the site, including the railhead, is currently designated a "customs zone" and, although used by «Balt East-West» for bunker storage and for receipt of oil by rail, is not the focus of much human activity. This zone is within an inner wire fenced area. Inspection of selected smaller oil tanks (not the major bunkers) has revealed them to be empty, with the exception of one, semi-underground tank by the railway near borehole 13. This appears to be partially full of a diesel-like fuel.

The site is currently largely occupied by attractive mixed woodland (see below). The entire site has a robust perimeter fence of concrete segments topped with barbed wire, ca. 2 m high. The main gate from Viestura Prospekts is manned, by state police. The site is thus inaccessible for passers by, although a determined trespasser could gain access with few problems.

The western border of the site is formed by the Viestura Prospekts dual carriageway, a main road between the central and northern parts of Riga and heavily trafficked. On the western side of Viestura Prospekts is a residential area mainly comprising blocks of apartments. The remainder of the site perimeter borders onto Meza Parks, one of Riga's main park areas. The Park is largely occupied by mixed woodland with access tracks and paths and clearings for sports and cultural events.

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

- (i) Current use (i.e. fuel handling) Groundwater-related sub-scenarios include:
 - (a) that a borehole is drilled to the Devonian aquifer 500 m downgradient of the site for public supply
 - (b) that a domestic well in the Quaternary deposits is dug 200 m downgradient of the site for watering of Meza Parks.
 - (c) the impact of the contaminated groundwater on water quality in the River Daugava
- (ii) Conversion to parkland as part of Meza Parks (recreation)
- (iii) Conversion to other light industrial/commercial use
- (iv) Conversion to residential use

5. HABITAT

The Viestura Prospekts site is heavily vegetated and bears a considerable resemblance to the surrounding Meza Parks land. Mature trees are dominated by pine with some birch, rowan and a maple-like species. Medium level and shrub-like growth is sparse, possibly reflecting the fact that the land was managed by mowing or undergrowth-clearance during its military period. Immature pines, beeches (?), rowans and oaks are beginning to establish themselves. The organic soil layer is thin and the floor is populated by mosses, grasses, horsetails and a variety of herbaceous species (including wild strawberries, dandelions, clover, speedwell, vetch, buttercups, thistles, willowherb and white campions). Like many contaminated military sites which have been relatively undisturbed and off-limits to the public, the status of the flora appears "idyllic". The fauna of the site is unknown although a red-headed woodpecker and larger mammalian burrows have been observed.

The surrounding Meza Parks area is not dissimilar to the military site in terms of flora. The mixed woodland is dominated by pines, with mature oaks along access avenues. The park is publicly accessible and used for recreation - this is presumably reflected in a less "pristine" environment.

6. CONTAMINANT SOURCES AND VISUAL EVIDENCE OF CONTAMINATION

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

- (i) Leakage / spillage from the two main bunker complexes (Fig. 2a)
- (ii) Leakage from pipelines or pumphouse. The network of pipelines is shown in Figure 2a.
- (iii) Leakage from numerous smaller buried or half-buried oil storage tanks. These tend to be located along the railhead or along the road comprising the tanker loading bays.
- (iv) Spillage during filling of rail or road tankers.
- (v) Contamination associated with storage or filling activities in the currently active part of the site.

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

- (i) Hydrocarbon fuel this is believed to be dominantly diesel (possibly jet fuel / paraffin).
- (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). The presence of these is suspected to be of little importance due to the dominance of diesel/kerosene fuel.
- (iv) 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, non-oil contamination could be related to washing of vehicles, repair of vehicles and battery storage.

Regarding visual evidence of contamination, oil contamination of soils could be observed in the area of the railhead, the pumphouse, and the bunkers (especially near the western corner of the bund surrounding the southern bunker complex). The daily operational area of «Balt East-West» was not explicitly included in this study (whose objective was to focus on military contamination caused by the Soviet military). However, current activities at the site cannot be totally divorced from the former situation.

7. PREVIOUS CONTAMINATION INCIDENTS AND INVESTIGATIONS

No records are available which detail any former contamination incidents.

In 1994, the two firms "Urbsanas Centrs" and "Geo-Konsultants" undertook and reported a site investigation incorporating:

- (i) Topographical survey
- (ii) Geophysical survey (Georadar and Vertical Electric Sounding VES)
- (iii) Geochemical sampling of soil (20 cm depth) and subsoil (ca. 1.5 m depth)
- (iv) Drilling of eleven tubewells and sampling of groundwater.

The report of the investigation has been translated and is attached as Appendix 1.

The results of the investigation are summarised as follows:

- (i) the main lateral groundwater flow direction (on the basis of borehole and georadar evidence) is northwards. This conclusion has now been modified in the light of the most recent studies.
- (ii) VES methods permitted delineation of zones of low apparent resisitivity, indicating high groundwater mineralisation possibly caused by hydrocarbon contamination.
- (iii) hydrocarbon concentrations in soils varied between 20 and 950 mg/Kg. The greatest degree of concentration was observed in the vicinity of the bunkers, the railhead and the pumping station.
- (iv) hydrocarbon contamination was observed down to depths of several metres in the unsaturated zone on the basis of sediment samples from boreholes, the highest values being observed in boreholes 5 and 6 (see Figure 2b).
- (v) Dissolved hydrocarbon contamination of up to 1.35 mg/L was observed in groundwater from boreholes. The highest concentrations came from boreholes 5 and 6 in the vicinity of the northern bunker complex. No free product was observed, although this would not be expected as all the installed well filters were wholly below the water table.
- (vi) Degradation of oil products is believed to be indicated by elevated alkalinities (up to 677 mg/L HCO₃ or ca. 11 meq/L in borehole 2), high COD (up to 225 mg/L in borehole 2), low pH (down to 6.25 in borehole 2) and high NH₄ (up to 7.2 mg/L in borehole 2).

The presence of these indicators of indicators of biodegradation with only a moderate dissolved hydrocarbon content (0.35 mg/L) in borehole 2 may be indicative of older oil contamination in the vicinity of the pumping station, in contrast to boreholes 5 and 6 where the contamination may be newer.

The authors of the 1994 report suggest that the ammonium is a degradation product of oil. Two other explanations are also possible in the opinion of the current authors:

(i) that ammonium is the product of pre-existing nitrate in the aquifer which has been reduced in the presence of degrading oil.

(ii) that ammonium is derived by cation exchange on marine sediments for cations released by enhanced mineral weathering.

The wells installed in the 1994 investigations were incorporated into the sampling network of the current investigations (Figure 2b).

8. REGIONAL GEOLOGY AND HYDROGEOLOGY

The 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 a.s.l. 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 Prospekts and Valmieras iela sites) is just to the west of this «window» and connectivity is significantly poorer (see Table 4.1 and Fig. 4.1 in Gosk et al. 1996).

The Amata-Arukila aquifer sequence is underlain by the low-permeability clayey deposits of the Narva formation whose thickness exceeds 100 m.

Table 1: A hydrogeological section of the Riga region (after Gosk et al. Table 4.1)

Currently, Riga City receives its potable water supply from the following sources:

- Surface water intakes on the River Daugava and Lake Jugla
- 2 wellfields based on artificial recharge from Lake Baltezers to a Quaternary aquifer at 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

Below a thin organic soil zone, occur fine-medium sand deposits of the Quaternary Baltic Ice Lake, with probably wind-blown dune sands forming hummocky areas of topography. The Baltic Ice Lake sediments appear to be rather homogeneous although it is reported (Appendix 1) that interlayering of fine and medium grained sands may occur. The thickness of the Baltic Ice Lake sand sequence is estimated at 21 m by the Latvian Geological Survey (or 30 - 40 m according to Appendix 1). 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 with gravel/pebble clasts (with possibly also some clayey / silty limnoglacial deposits). The thickness of this lower permeability Lower Quaternary sequence is reported by the Geological Survey of Latvia (Lacis pers. comm. 1997) as some 28 m, giving a total Quaternary thickness of some 49 m.

The Quaternary deposits overlie sedimentary rocks of the Upper Devonian Gauja Formation comprising sandstone with silty interlayers. This is an important aquifer for water supply in the Riga area.

10. HYDROGEOLOGY

The hydrogeology at the contaminated site essentially consists of two aquifer horizons, the Baltic Ice Lake sands and the Devonian Gauja Sandstone, separated by a ca. 28 m thick aquitard sequence of sandy silts and clays.

Rising head tests were performed in 5 boreholes on the Viestura site, yielding values of 1 - c. 8 m/d for hydraulic conductivity (Appendix 9). A sand sample from soil sample site 31 yielded an estimated value of 7.2 m/d based on grain size distribution (Appendix 10).

Further georadar profiles and water level determinations in new boreholes in 1996 indicate that the former hypothesis (Appendix 1) of a northerly water table gradient must be rejected in favour of a north-westerly gradient oriented towards the mouth of the River Daugava (Fig. 3).

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	М	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

A summary of the site investigations carried out at Viestura Prospekts prior to the commencement of the cooperative project is found in Appendix 1. At the start of the cooperative project, 11 observation wells had been drilled at the site. These generally had a 1 m slotted section. In all cases the slotted section had been installed below the water table: in no case did the slotted section straddle the water table. The existing wells were thus excellently designed to monitor dissolved contaminants, but gave no information on the presence of LNAPL (light, non-aqueous phase liquid) contaminants floating on the water table.

Pairs of monitoring wells had been installed; namely 2 & 11, 7 & 9 and 4 & 10, where slotted sections were installed at different depths. In each case, the well in italics was that with the deepest slotted section (1 m length, between ca. 8 and ca. 10 m bgl). Details of filter depths are found in Appendix 1.

11.2 Topographical Survey

A new topographical survey of the entire Viestura Prospekts site was carried out by the firm Geo-Konsultants. The result of this survey is shown in Fig. 2a.

11.3 Georadar Survey

A new Georadar survey was undertaken to supplement the previous survey (see Appendix 1, which also describes the methodology), 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 3.

The previous water table map had indicated a northerly groundwater table gradient. The newly constructed groundwater map indicates, however, a more logical NW groundwater gradient (i.e. some component of groundwater flow towards the Daugava).

11.4 Vertical Electrical Resistivity Sounding Survey (VES)

A supplementary VES survey was undertaken to supplement the previous survey (see Appendix 1, which also describes the methodology), by the firm Geo-Konsultants. Geo-Konsultants are of the opinion that the areas of low resistivity (high conductivity) on the resulting map (Fig. 4) indicate areas of oil contamination of groundwater. The rationale for this viewpoint is that the decomposition of the oil promotes reducing conditions (mobilisation of large amounts of Fe and Mn) and also releases CO_2 , which itself promotes weathering of carbonate and silicate phases, releasing further dissolved salts to groundwater. The map indicates two plumes of contamination, one starting from the southernmost of the two large oil bunkers and spreading NW (direction of groundwater gradient) under the northern oil bunker. The plume appears to migrate off-site in the direction of well 222a.

The second apparent plume starts on the western side of the railhead and extends also in a northwesterly direction.

11.5 Drilling of New Boreholes

4 new monitoring wells were drilled at Viestura Prospekts in September 1996, namely wells 12, 13, 14 and 15 (Fig. 2b). 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 contamination. Two of the wells were placed on the western side of each of the two oil bunkers, the other two in the vicinity of the railhead.

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.

Further, following sampling of the old well 7, the casing was drawn up such that the slotted section straddled the water table. This newly positioned well-screen was designated well 7a and resampled.

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

11.6 Geochemical Sampling

To supplement previous geochemical sampling of soils (see Appendix 1), 7 extra soil samples were taken, using the same methodology as previously, from 6 localities, namely 31-36 (see Figure 2b). 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 cm. The humic soil cover at the site appears to be poorly developed and thin, with a thickness of only around 5 cm. The samples were thus of sandy subsoil. Sample 31 was taken as a background sample from an apparently uncontaminated area (a duplicate of this sample was taken for grain-size and chemical analysis at NGU). Sample 32 was taken from very oil contaminated soil within the bund of the southernmost fuel bunker. A seventh sample, 32a, was taken comprising the most contaminated horizon from within the sampling holes of the bulk sample 32.

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

Due to a misunderstanding, the samples were only subject, in Latvia, to analyses of the heavy metals Zn, Cu, Pb, Cd and Hg and not for oil (Appendix 2). 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 3).

11.7 Groundwater Sampling

11.7.1 First Sampling Round

Groundwater sampling at Viestura Prospekts took place in the period from 26/09 to 20/10/96; the existing wells in the period before and during drilling, the new wells up to three weeks after drilling. All old and new boreholes were sampled. In addition, borehole 222a, part of the Riga City monitoring network and situated a short distance north of the study site was sampled. This well has a filter at 8.6-10.6 m deep (i.e. deeper than the monitoring wells within the site) and is thought to have been drilled in 1972.

In selected wells, bail tests were performed to estimate the hydraulic conductivity of the sediments. These consisted of removing 5-6 bailerfuls of water (of known volume = 0.65 l) from the hole and using an electrical dipper to monitor the recovery of water level.

Before pumping for sampling 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 TM 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 readings had been obtained, a process usually requiring between 20 and 45 minutes per hole.

The deeper borehole 222a was pumped using a larger-diameter Grundfos MP1 stainless steel sampling pump, which is able to displace larger quantities of water.

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.

NGU 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.

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

Additionally, NGU measured CO₂ concentrations in groundwaters using a Chemetrics Titrets K-1910 kits, which is able to determine CO₂ concentrations in the range 10 to 100 mg/L. NGU also used a field calibrated (using solutions of pH 4, 7 and 10) pH / temperature meter (Palintest Micro 900) on selected wells to verify Latvian measurements. The NGU thermistor measured consistently 0.3°C higher than the Latvian, and the pH meter measured around 0.20 pH units higher (although the NGU meter did, for some reason appear prone to drift).

To yield some indication of «background» water quality in the shallow aquifer, two wells at nearby cemeteries some 500-800 m SSW and SSE of the site were sampled (referred to as the SW and SE cemeteries - see Fig. 1). It is assumed that these hand-pumped wells, which are used to water graveside plants, tap the shallow aquifer (though it has been impossible to confirm this). The GSL believes these wells to be 10 - 20 m deep (i.e. deeper than the monitoring wells at Viestura Prospekts). It is also questionable, of course, as to whether these wells can be regarded as background. They are clearly unaffected by oil pollution at Viestura Prospekts, but may not be free of contamination from the graveyards themselves. NGU sampled the two cemetery wells on 3/10/96 although the Latvian samples of the same wells were only taken some few weeks later.

11.7.2 Second Sampling Round

The second sampling round at Viestura Prospekts took place between 16/6/97 and 18/6/97 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, this time without revealing any detectable discrepancy. The NGU thermistor consistently again 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 did not determine CO₂ in this sampling round, but did use 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 µm 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 for analysis in Latvia were subject to the following analyses at the Hydrometeorological Agency laboratory in Riga:

- (i) Grain size analysis. The results are reproduced in Appendix.2.
- (ii) Analysis was undertaken of the metals Zn, Cu, Pb, Cd and Hg by atomic adsorption spectrophotometry. The results are reproduced in Appendix.2.
- (iii) The re-sampled sediments from April 1997 were extracted by acetone (for method, see Appendix 3) and analysed by infra red spectrophotometry for total hydrocarbon content. The fact that only a small portion (if any) of each sample is greater than 2 mm grain size means that these results can be taken as approximately comparable to the oil content for the < 2 mm fraction. The results are reproduced in Appendix 3.

12.1.2 Samples analysed by FFI

A limited number of duplicate samples were taken for analysis by FFI in 1996. 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

 $0.4 \mu g/Kg$ dry material for PCB (uncertainty 30%). Results are presented in Appendix 6. 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 and Valmieras Prospekts, and analysed by GC at FFI. Results are presented in Appendix 6.

12.1.3 Samples analysed by NGU

One sample (soil sample 31 at 20 cm depth, taken in September 1996) was run as a duplicate analysis by at NGU. The sample was subject to grain size analysis by wet sieving. Results are presented in Appendix 4.

Another portion of the sample 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)

Regrettably, inspection of the NGU sample revealed that it appeared to have been «contaminated» by a small amount of humic topsoil, possibly rendering some of the analyses of limited value in characterising the aquifer material itself.

12.2 Groundwater Analyses

In Figures., sample prefixed by SW indicate shallow wells, those prefixt by DW indicate deep wells.

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 detailed in Appendix 3. The results of these measurements, together with field measurements of pH and electrical conductivity, are presented in Appendices 2 and 3.

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 6.

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 5. 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 4 and 5).

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).

Boron results in 1997 for ICP-AES were originally not cited 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 Figures 5 and 21.

Results are reported in Appendices 4 and 5.

12.3 Analytical Consistency

12.3.1 Water samples

NGU vs. Latvian inorganic analyses

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

A comparison of NGU's 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 and P. Of these only Ca exhibited an acceptable degree of correlation. Results for Na and 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 slightly more promising than for 1996 but not satisfactory. Satisfactory correspondence was obtained for Ca and alkalinity, while a better correlation was found for Mg & Cl than for 1996. 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 the first B-measurement in 1997 (due to contamination in the ICP-equipment - see above). The AA analyses are somewhat less consistent, especially for Cd, Pb and Sb, but (with the exception of Cd) the results are generally of the same order of magnitude.

Latvian consistency from 1994, 1996 and 1997

A comparison of the Latvian 1994 results with Latvian 1996 results (Figure 9) exhibits a poor degree of correlation for parameters such as Na, K, Mg, Cl⁻. The Latvian 1994 concentrations for Na are far more comparable to NGUs 1996/97 results. Field parameters (pH, EC) and parameters such as HCO₃⁻, NH₄-N, Ca and COD exhibit rather good reproducibility between 1994 and 1996 for the Latvian analyses. Mineral oil exhibits a poorer correlation, with lower concentrations in 1996, but this may be a real effect (biodegradation?, different pumping regime?).

A comparison of Latvian 1996 results with those of 1997 allows comparison of more parameters (Figure 10). Broadly, results for Ca, Mg, HCO₃⁻, dry residue, ammonium, nitrite, nitrate, total N, BOD, COD, phenol, SSAS, Cu, Pb, Cr, Hg and Ni show an acceptable degree of reproducibility. Na, K, SO₄⁻, Cl⁻ and Cd show poor reproducibility.

Oil - 1996 results

A comparison of Latvian THC (mineral oil) analyses with FFI's results for selected control samples is presented in Table 3 and Fig. 11. In general, a comparison between the results for samples from 1996 is encouraging, in as much as the results from the two laboratories are all of the same order of magnitude and (in the case of Viestura Prospekts, 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 borehole 222a and a significant "background" in one of the cemetery boreholes. The results from Valmieras iela (Banks et al 1998) 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 Latvian 1997 analyses and than previous (1996 analyses). For the new wells (7a, 12-15), it is conceivable that this reflects the fact that a certain time lag 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.

	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	MINERAL ELES	
Viestura bh 7a	450	1240	10-	2500	16000
Viestura bh 8	50	90		70	630
Viestura bh 9	80	240		200	1100
Viestura bh 10	100	90		160	1400
Viestura bh 11	430	90		190	2300
Viestura bh 12		450		100	14000
Viestura bh 14		450	1054	170	12000
Viestura cemetry P2		130	320		
Viestura 222a		30	< 60	60	390
Valmieras bh 2		140	334	80	470
Valmieras bh 3		410	114	180	1600
Valmieras bh 4		160	319	60	2100
Valmieras bh 5	hi-region during	230		40	1400

Table 3. Concentrations of mineral oil (THC) in water samples from Viestura Prospekts and Valmieras iela (Banks et al. 1998), 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. 11)

In summary

In summary, the Latvian analyses for many inorganic parameters (especially Na, K, Cl and SO_4) 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 -2.4 and -6.4 % (Figure 12), instilling further confidence in the validity of NGU's results for inorganic parameters by IC and ICPAES.

There is some suggestion that Latvian analyses for trace heavy metals are more reproducible than NGU's AA analyses. Analyses for cadmium have shown variation over several orders of magnitude and no laboratory has achieved an acceptable degree of reproducibility.

The consistency of Latvian COD, NO₂-N,, BOD, SSAS, phenol, N-total, NH₄-N and field measurements between 1996 and 1997, suggests that the Latvian analyses for these parameters 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 and Valmieras iela (Banks et al. 1998). 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. In fact FFI later confirmed that analytical error had occurred and corrected results are appended in Appendix 6.

	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		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 and Valmieras iela (Banks et al. 1998), 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 was recommended by NGU that the following data should be used:

- (i) NGU (1996/97) values for alkalinity and 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 (except Cd) in groundwater.
- (iii) Latvian (1997) values, in combination with 1994 results, for inorganic parameters and oil in sediments.

As trace heavy metals (Pb, Cd, Ni, Hg), arsenic and antimony have been difficult to reproduce satisfactorily in many cases (and especially for Cd), a worst-case risk assessment scenario should use the highest concentrations of these parameters determined.

13. RESULTS AND DISCUSSION

13.1 Geology and Hydrogeology

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 2 and 8.

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 sediments on the basis of d_{10} and d_{60} grain size. As the shallow soil samples (20-25 cm) were typically in sandy sediment, below the organic topsoil, they were also included in the data set in addition to samples from the drilled wells themselves.

Results of these estimates are presented in Appendix 10, but a summary is presented below in Table 6.

	K (m/s)	K (m/d)	n (%)	n _e (%)
Range	$0.7 - 2.3 \times 10^{-4}$	6 - 20	34 - 38	28 - 33
Arithemtic mean	1.3 x 10 ⁻⁴	11	37	31
Geometric mean	1.2 x 10 ⁻⁴	10	37	31
Median	1.2 x 10 ⁻⁴	10	37	32

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

Risng head slug tests were also carried out in boreholes 3, 4, 6, 8 and 10 in September 1996. Results were analysed by the Bouwer-Rice method for partially penetrating wells, using

Aquitest Software (Appendix 9), returning the following values for hydraulic conductivity (K):

Borehole	K m/d	K m/d
3	2	3 x 10 ⁻⁵
4	3	4 x 10 ⁻⁵
6	1	1 x 10 ⁻⁵
8	recovery too fa	st to measure (c. 8-9 m/d)
10	2	2 x 10 ⁻⁵

Table 7. Calculated values of apparent transmissivity and estimated values of hydraulic conductivity on the basis of rising head slug tests on boreholes at Viestura Prospekts, September 1996. The recovery in bore 8 was to fast to allow a good analysis of data (complete recovery in 30 s). Tentative calculations suggest a K value of at least 8 m/d.

Thus, in summary:

- Initially, the Latvian Geological Survey 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 6 20 m/d
- Estimates of K based on slug tests yield values of 1 maybe 8 9 m/d

13.2 Soil Contamination

Maps have been produced of almost every measured geochemical parameter and are presented in Appendix 8. 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. 13). In such diagrams the box represents the inetrquartile 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

The shallow (20-25 cm) and deep (1.5 m) subsoil sampling program in 1994 produced the map shown in Figures 14-17. These include samples taken from the sites of the monitoring wells (see Appendix 1).

The shallow soil samples taken in the extreme south of site are relatively unpolluted by oil compounds. The higher concentrations are near the centre of the site, around the pipelines, bunkers and pumphouse. The median oil concentration was 30.5 mg/Kg soil, reaching a maximum of 950 mg/Kg in borehole 2 by the pumphouse. 180 mg/Kg was found in sampling point 26.

The deep subsoil samples reveal a somewhat different pattern. In some cases, low concentrations occur in these deep samples where the shallow samples exhibited a high degree of contamination, and vice versa. The median oil concentration was 32 mg/Kg soil, reaching a maximum of 480 mg/Kg, again in sample 2, near the pumphouse.

Two samples of shallow (20-25 cm) soil from grass roadside verges outside the factory site at Valmieras iela (Banks et al. 1998) returned oil concentrations of 60 and 72 mg/Kg. The majority of the Viestura Prospekts site thus returned oil concentrations lower than what might be regarded as an urban background.

Figure 18 shows a map compiled from the 1994 and 1997 rounds of shallow subsoil sampling, combined. The median remains at 32 mg/Kg and the contaminated samples are dominantly in the central part of the site around the bunkers, pipelines, pumphouse and railhead. Sample 32a (320 mg/Kg) was a sample specifically taken from the most oil-contaminated horizon of the bulk sample at site 32 The maximum is at the site of borehole 2 (950 mg/Kg), by the pumphouse. 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).

13.2.2 Inorganic Parameters

Maps for metals analysed in soil samples are presented in Appendix 8. The Latvian laboratory measured Zn, Cu, Pb, Hg and Cd in the seven samples taken in 1996. Sample 31, by the southern fence of the site was intended as a background sample.

Zinc is typically 7 mg/Kg or below (background in sample 31 is 5 mg/Kg). In two samples, numbers 36 and 32, are elevated concentrations observed, of 15 and 35 mg/Kg. The Norwegian trigger value for zinc for the most sensitive land use is 150 mg/Kg.

Copper is typically 2 mg/Kg or below (background in sample 31 is 1 mg/Kg). In one sample, number 32, an elevated concentration of 6 mg/Kg is observed. The Norwegian trigger value for copper for the most sensitive land use is 100 mg/Kg.

Lead is typically 3 mg/Kg or below (background in sample 31 is 3 mg/Kg). In two samples, numbers 36 and 32, are elevated concentrations observed, of 8 and 15 mg/Kg. The Norwegian trigger value for lead for the most sensitive land use is 50 mg/Kg.

Cadmium is typically 0.05 mg/Kg or below (background in sample 31 is 0.05 mg/Kg). In one sample, sample 32, an elevated concentration of 0.13 mg/Kg is observed. The Norwegian trigger value for cadmium for the most sensitive land use is 1 mg/Kg.

Mercury is typically 0.02 mg/Kg or below (background in sample 31 is 0.01 mg/Kg). In one sample, sample 32, an elevated concentration of 0.07 mg/Kg is observed. The Norwegian trigger value for mercury for the most sensitive land use is 1 mg/Kg.

Under Norwegian practice, the concentrations of heavy metals in the soils would not be high enough to trigger the need for a specific quantitative risk analysis. However, concentrations of mineral oil in some parts of the site are enough to trigger such a need.

13.3 Groundwater 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. 13). 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

Free phase oil contamination was found in boreholes 12 and 13. No free phase oil was found in boreholes 7a, 14 or 15. In all other wells, the well-screen was situated below the water table and would therefore not be expected to register free phase contamination.

Thicknesses of free-phase oil are shown in Table 8. The thickness do 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. The thickness of the free oil layer was less in June 1997 then September 1996. This may reflect seasonal effects or may reflect a real thinning due to spreading and migration of the oil.

	September 1996	June 1997	
Well 12	ca. 40 cm	20 cm	
Well 13	ca. 80 cm	45 cm	

Table 8. Free oil thickness (cm) in monitoring wells 12 and 13.

13.3.2 Dissolved Oil Contamination

Figures 19a,b show dissolved oil contamination in groundwater according to the results of the 1996 sampling. The median concentration is 0.255 mg/L and the highest (1.24 mg/L) in well 7a. There is a clear vertical stratification of pollution in the aquifer, the newest wells, straddling the water table yielding the highest values (7a, 14, 15, free product in 12 and 13). Where pairs of wells exist (7,9; 4,10; 2,11), the highest concentrations are observed in the shallowest of the pair.

In well 222a, with a deep well screen, no significant contamination is observed. This does not mean, of course, that shallower groundwater at the site of well 222a is uncontaminated.

It would seem that significant dissolved hydrocarbon contamination of groundwater below the site is restricted to a ca. 2-3 m of the water table.

It is noteworthy that hydrocarbon contamination of 0.13 mg/L was found in the well at the SE cemetery. There are thus upstream sources of oil contamination and it cannot be automatically assumed that all oil contamination measured at the oil storage site is derived from there.

13.3.3. Redox parameters and mineral content as indicators of hydrocarbon contamination

When oil biodegrades, it produces CO_2 and consumes oxygen, and eventually other electron acceptors (Fe₂O₃, NO₃, SO₄⁼). This process may have two consequences:

- (i) increased weathering of carbonates and silicates by CO₂, to release alkalinity, and the major cations Na, Ca and Mg. This leads to an increase in the water's mineral content and its electrical conductivity. This may be the explanation for the low-resistivity plumes on the VES profile in Fig. 4.
- (ii) oxidation of hydrocarbons leads to reducing groundwater conditions and promotes sulphate reduction, nitrate reduction and iron mobilisation as ferrous iron.

Figures 20 a-c, plotting iron against oil content, electrical conductivity and sum of anions, indicates a clear positive correlation amongst several of these parameters. Bearing in mind the difficulty (and cost) in reproducible sampling and analysis of organic parameters such as hydrocarbons, the inorganic parameters may be a more reliable indicator of organic contamination for routine monitoring.

Indeed, the plots in Figure 21 demonstrate that Fe is a more reliable redox indicator than, for example Eh. There is a clear correlation between Fe and alkalinity and a negative correlation between iron and sulphate and between iron and nitrate (nitrate only being present in the most oxidised, least contaminated samples, from well 222a). Interestingly Fe also shows some correlation with V. This may purely reflect mobilisation of both components from the aquifer matrix under contaminated conditions, but it may also reflect the possible derivation of vanadium from the Russian oil.

Further discussion and interpretation of groundwater chemical data can be found in the paper by Banks et al. (1997), presented to a NATO conference in Vilnius in October 1997, and reproduced in this report as Appendix 11.

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 Viestura Prospekts 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 Viestura Prospekts 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 and Valmieras iela (Banks et al. 1998) 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. 22), 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. 23), 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. Viestura Prospekts) 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. 22), with transport velocity controlled by the hydraulic conductivity distribution in Fig. 23. The calculated direction of contaminant transport is shown in Fig. 24.

The isochrones, characterizing the speed of contaminant movement, are shown in Fig. 25. The isochrones correspond to intervals of 5, 10, 20, 30 and 40 years.

As regards the former Soviet oil base at Viestura Prospekts, the contaminants from it do not appear to reach the Sarkandaugava water body before 35 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 Viestura Prospekts 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 / Conversion to parkland as part of Meza Parks.

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

- (a) A borehole is drilled to the Devonian aquifer 500m down-gradient of the site for public supply.
- (b) A domestic well in the Quaternary deposits is dug 200m down-gradient of the site for watering a garden / Meza Parks.
- (c) 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 health 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

This previous investigation carried out and reported in 1994 found hydrocarbon contamination in soils in the range 20 to 950 mg/kg. The hydrocarbon contamination was found to depths of several metres in the unsaturated zone on the basis of sediment samples from boreholes. The worst contamination was observed in the vicinity of the bunkers, the railhead and the pumping station.

15.4 Contaminants of Potential Concern

The contaminants of potential concern for the site are shown in Tables 9a,b. The only contaminant found to exceed the screening criteria was a hydrocarbon fuel most likely to be jet fuel or paraffin. The highest hydrocarbon concentrations were found in the vicinity of the bunkers, the railhead and the pumping station. Dissolved oil contamination was observed in many of the on-site boreholes and free phase oil was found in two boreholes. The maximum

dissolved total petroleum hydrocarbon (TPH) concentration was thus, for the purposes of the risk assessment, assumed to be equal to the approximate solubility of the oil: i.e. 2.5 mg/l.

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

The pathways considered for the site assuming it remains in its current use are shown in Table 10. The risks to on-site employees via all pathways are considered whilst the risks to off-site employees include the following pathways; dust inhalation and inhalation of vapours from contaminated groundwater. Dust inhalation is the only pathway considered for off-site residents (adults and children).

The human exposure and site assumptions used are listed in Tables 11 and 12 respectively. The assumptions used are identical to those used for the Valmieras iela site (Banks et al. 1998) for the continuation of current use scenario.

The risk-based clean-up level tables for receptors at the Viestura Prospekts site (Tables 13, 14 and 15) indicate that there are no significant risks to human health for the receptors identified assuming the site continues in its current use.

15.5.2 Redevelopment for Commercial Use

The pathways considered for on-site employees exposed to hydrocarbon contamination are identical to those for Valmieras iela (Banks et al. 1998), namely indoor inhalation of vapours from soil and groundwater (Table 16).

Table 17 shows the human exposure assumptions used in the risk assessment. These are identical to those used in the risk assessment of the Valmieras site commercial use scenario (Banks et al. 1998). The risk-based clean-up level table for the site (Table 18) indicates that the observed hydrocarbon contamination would not present a significant risk to human health if the site were to be redeveloped for commercial (office) use.

15.5.3 Redevelopment for Residential Use with Gardens

The pathways considered for adult and child residents, assuming a future residential use, are shown in Table 19 and are identical to those modelled in the Valmieras iela site risk assessment for the same end-use (Banks et al. 1998).

The human exposure assumptions used are listed in Table 20 and again are identical to those used in the Valmieras iela risk assessment for the same residential scenario (Banks et al. 1998).

Table 21 shows the risk-based clean-up levels derived for the site. These indicate that there is a requirement for further risk assessment at Tier 3, or for some form of remedial treatment (including site clean-up to the RBCLs given) before the site could be redeveloped for residential use, i.e. that the observed soil hydrocarbon concentrations pose a significant risk to human health.

15.5.4 Redevelopment for Residential Use Without Gardens

Table 22 shows the pathways assessed for adult and child resident receptors. Soil ingestion, dermal contact with soil, dust inhalation and vegetable ingestion are not included as they are not relevant to this scenario. The human exposure assumptions used are listed in Table 23.

The risk-based clean-up levels for the site are shown in Table 24. These indicate that TPH (Total Petroleum Hydrocarbons) in soil and groundwater presents an unacceptable risk to human health and Tier 3 risk assessment or remediation (which may be clean-up to the RBCLs) is required to address this contamination before redevelopment of the site for this end-use goes ahead.

15.5.5 Abandonment of the Site with Unlimited Public Access

The pathways considered for this scenario are shown in Table 25. All listed pathways with the exception of indoor dust inhalation and indoor vapour inhalation are considered. The exposure assumptions used are shown in Table 26. The risk-based clean-up levels derived for the site are shown in Table 27. Significant risks may be associated with exposure of adults and children to TPH contamination in shallow soil. As with the Valmieras site (Banks et al. 1998), either Tier 3 risk assessment or remedial action (which may include clean-up to the RBCL specified) is required, with one remedial option being restriction or control of access to the abandoned site.

Table 9a. Contaminants of Potential Concern.

	Soil (r	ng/kg)	Groundwater (mg/l)	er Groundwater (mg/l) Simulated		lated
Chemical			On-site	Off-site		
!	Shallow	Deep	Observed	From on-site groundwater	From on-site soil	Maximum off-site
TPH	950	480	2.5*	0.655	0.0736	0.655

^{* =} Estimated TPH solubility

Table 9b. Contaminants of potential concern.

Viestura Prospekts 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	13.14	10	W
Cadmium	0,013	1	12.5	5	N
Cobalt	-	na	40	4.9	
Lead	15	50	16.78	20	N
Nickel	-	30	1.8	50	N
Vanadium	-	na	10.2	24.5	
Zinc	35	150	1128.7	300	N
TPH (C10-	950	100	2500*	10	N
C16)/DRO			l		

Note: "-" values below trigger

concentrations na: not applicable

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

* solubility

Table 10. Potential exposure pathways for current use or redevelopment for commercial use

tation	On-Site Employee	Off-site Employee	Adult Resident	
			Addit Resident	Child Resident
sw	60	60	60	15
EF (230	230	350	350
ED	43	43	24	6
L	25550	25550	25550	25550
M _o	0.07	0.07	0.07	0.07
F _{sd}	100%	100%	100%	100%
t _o ·	42%	42%	100%	100%
	20	20	20	15 0.07
F _i	100%	100%	100%	100%
Bi	20	20	20	15
od	50%	. 50%	10%	10%
Fid	50%	50%	90%	90%
	EF ED L PM _o F _{id} t _o Bo	EF 230 ED 43 L 25550 PM ₀ 0.07 F _{sd} 100% t ₀ 42% Bo 20 PM ₁ 0.07 F _i 100% Bi 20 Fod 50%	EF 230 230 ED 43 43 L 25550 25550 PM _o 0.07 0.07 F _{sd} 100% 100% t _o 42% 42% Bo 20 20 PM ₁ 0.07 0.07 F _i 100% 100% Bi 20 20 Fod 50% 50%	EF 230 230 350 ED 43 43 24 L 25550 25550 25550 PM _o 0.07 0.07 F _{td} 100% 100% 100% t _o 42% 42% 100% Bo 20 20 20 PM ₁ 0.07 0.07 F _i 100% 100% 100% Bi 20 20 20 Fod 50% 50% 10%

Table 11. Current use. Human exposure assumptions.

	On-site	7	Off-site			
	Commercial	Employee	Res	ident		
Pathway	Employee	Adult	Adult	Child		
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	J		
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	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?		0	
Significant risk levels			
Non-carcinogenic risk (HI)		1	$\neg \neg$
Carcinogenic risk	1 in	10,000	

1: Pathway exists

0: No pathway

Table 12. Site characteristics - assumptions.

	.:	
Parameter	Notation	On-site
Capillary fringe thickness (cm)	h _{eap}	5
Vadose zone thickness (cm)	h.	445
Depth to groundwater (cm)	L_{rw}	450
Depth to product (cm)	L _p	450
Building exchange rate (1/sec)	ER.	0.00083
Building volume/area ratio (cm)	L_{b}	300
Building foundation/wall thickness (cm)	L _{track}	15
Areal fraction of cracks	η	1 %
Air content of foundations/wall cracks	$\theta_{\mathtt{acrack}}$	26%
Total soil porosity	θ_{T}	20%
Water content of foundations/wall cracks	θ_{werack}	12%
Air content of capillary fringe	θ_{acap}	23.0%
Water content of capillary fringe	θ_{weap}	2.0%
Air content of vadose zone	θ_{as}	42 %
Water content of vadose zone	θ_{us}	6%
Soil bulk density	ρ_{s}	1.6
Fraction organic carbon	F _{oc}	2.00%
Depth to subsurface shallow soil sources (cm)	L,	10
Depth to subsurface deep soil sources (cm)	L,	50
Wind Speed (cm/sec)	U,ir	225
Ambient Air Mixing Zone Height (cm)	δair	200
Area of Site (cm²)	A.	25000000
Width of Source Area Parallel to Wind Direction (cm)	w	5000
Henry's Law constant (unitless)	Н	Chemical-specific
Organic carbon-water partition coefficient 1	K _{oc}	Chemical-specific
Air diffusion coefficient (cm²/sec) t	D^{air}	Chemical-specific
Water diffusion coefficient (cm²/sec) 1	D_{Max}	Chemical-specific

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

Chemical	Shallow Soil	Deep Soil	Groundwater
	RBCLs	RBCLs	RBCLs
	(mg/kg)	(mg/kg)	(mg/l)
C10-C16 (TPH)	IR	IR	IR

IR = Insignificant Risk, Clean-up levels not required

Table 14. 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

IR = Insignificant Risk, Clean-up levels not required

Table 15. 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)	IR	IR	IR

IR = Insignificant Risk, Clean-up levels not required

Table 16. 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 17. 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	0	1
Climate Factor (not active)	Z	1
Outdoor Dust Concentration (mg/m³)	PM_{o}	0.07
% Soil Particles in Dust	F_{sd}	100%
Fraction of time spent on site	to	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 18. Commercial development. On-site employee risk-based clean-up levels.

Chemical	Deep Soil RBCLs (mg/kg)	Groundwater RBCLs (mg/l)
C10-C16 (TPH)	IR	IR

Table 19. Potential exposure pathways for residential with gardens.

	On-	-site			
	Open Space				
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			
		_			

$\overline{}$		 		_
IC.	ee product		Λ	1 1 · D
ILI	ee product		U	I.F
_				
				^

^{1:} Pathway exists
0: No pathway

Significant risk levels

Non-carcinogenic risk (HI)

Carcinogenic risk

1 i 10000

Table 20. Residential with gardens. Human exposure assumptions.

		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 .	360	360
Exposure duration (years/lifetime)	ED	24	6
Lifetime (days)	L	25550	25550
Skin surface (cm²)	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_1	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	t
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 spent outdoor	Fod	50%	50%

		ADULT			CHILD			Final	
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 mg/kg	Groundwater RBCLs mgll
C10-C16 (TPH)	1.83E+02	IR	1.62E-01	5.99E+01	2.75E+02	1.68E-01	5.99E+01	2.75E+02	1.62E-01

Table 22. Potential exposure pathways for residential without gardens.

	On-	-site
Pathway	Adult	Child
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
Significant risk levels		
Non-carcinogenic risk (HI)		1
Carcinogenic risk	1 in	10000

1: Pathway exists

0: No pathway

Table 23. Residential without gardens. Human exposure assumptions.

		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)	Ĺ	25550	25550	
Oral Bioavailability	О	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		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 RBCLs (mg/l)	Shallow soil RBCLs mg/kg	Deep soil RBCLs mg/kg	Groundwater RBCLs mgll	
C10-C16 (TPH)	1.95E+02	IR	2.13E-01	6.51E+01	2.75E+02	5.48E-01	6.51E+01	2.75E+02	2.13E-01	

Table 25. 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)	1	1			
Deep soil vapours (indoors)	0	0			
Deep soil vapours (outdoors)	1	1			
GW vapours (indoors)	0	0			
GW vapours (outdoors)	1	i			
Free product vapours (indoors)	0	0			
Free product vapours (outdoors)	0	0			

Free product		0
Significant risk levels		
Non-carcinogenic risk (HI)		1
Carcinogenic risk	1 in	10000

1: Pathway exists

0: No pathway

Table 26. Open space. On-site child and adult. Human exposure.

		O-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 (cm²)	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_1	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		Final			
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 mg/kg	Groundwater RBCLs mg/l
C10-C16 (TPH)	6.79E+02	IR	IR	1.29E+02	IR	İR	1.29E+02	IR	ĬŔ

Table 28. Parameters used for groundwater modelling at the Viestura Prospekts site.

Parameter	Value		
Hydraulic conductivity (m/day) (shallow/deep)	1	3	
Hydraulic gradient	0.0023		
Fraction of organic carbon	0.01		
Length of source parallel to groundwater flow (m)	340		
Source width (m)	255		
Source thickness (m)	3		
Infiltration rate (m/yr)	0.06		
Thickness of aquifer (m) (shallow/deep)	20	80	
Mixing zone depth (m) (shallow/deep)	20	38	
Porosity % (shallow/deep)	31	15	
Aquifer dilution factor (shallow/deep)	1.8	6.4	
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 Viestura Prospekts site for four future land use scenarios. It is important to note that a quantitative assessment of free product migration and 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 it continues in its current use. Similarly no significant health risks are anticipated if the site is redeveloped for commercial (office) use.

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

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.

The risk assessment of the scenario involving the site being abandoned with unlimited public access also found unacceptable health risks for adults and children. 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 Tables 9a and 9b. 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 jet fuel range (C_{10} - C_{16} hydrocarbons) 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 lenses and that it is equal to the solubility of the oil product. At Viestura Prospekts, where the LNAPL appears to be similar to jet fuel, the maximum concentration is set to 2.5 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 28. All soil and groundwater contaminants reported are from the shallow Quaternary aquifer. It was assumed that the entire unsaturated zone was contaminated for modelling purposes. Therefore a source thickness of 3.0m 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

200m Compliance Point:

Groundwater concentrations were simulated from soil and groundwater contamination at the Viestura site for a 200m compliance point. This compliance point represents a domestic well in the shallow Quaternary aquifer. The results are summarised below:

Arsenic : 9 x 10⁻³ μg/l;
 Cadmium : 9 x 10⁻³ μg/l;
 Cobalt : 2.8 x 10⁻² μg/l;
 Zinc : 7.82 x 10⁻¹ μg/l;
 TPH : 1.9 x 10⁻¹ μg/l from soil

plus 1.73 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 Viestura 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 (following simulated migration through the aquitard) were used as input values for subsequent simulation of lateral migration of the groundwater concentrations down-gradient within the Devonian aquifer. The results can be summarised as follows:

• Zinc : $4.6 \times 10^{-3} \mu g/l$; • TPH : $1.4 \times 10^{-1} \mu g/l$.

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 Viestura Prospekts, 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 TPH (diesel range organics) in soil and groundwater RBCLs are shown in Table 21.

Residential without gardens

Significant risks could be associated with exposure to TPH (diesel range organics) in soil and groundwater RBCLs are shown in Table 24.

Abandonment with unlimited access to the public

Significant risk could be associated with exposure to TPH (diesel range organics) in soil RBCLs are shown in Table 27.

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

Contamination of groundwater due to hydrocarbon spillages, far from being merely the province of the organic chemist, offers much food for thought for the inorganic hydrochemist. This is not a new observation, but has been tackled in detail by the work of Mary-Jo Baedecker and her colleagues (Cozzarelli et al. 1990, Bennett et al. 1993, Eganhouse et al. 1993, Baedecker et al. 1993). This study provides clear indications that oil contamination in groundwater may be positively correlated with total ion content, alkalinity, electrical conductivity and iron, and negatively correlated with redox indicators such as sulphate and nitrate. These species thus offer low cost alternatives to hydrocarbon analyses for monitoring of oil contamination. Organic analyses are expensive, crave extremely high standards of purity in sampling techniques and are often less reproducible than inorganic analyses due to problems with entrainment of emulsified oil phase. Such inorganic parameters may also allow some assessment to be made of the contamination's degradation status.

Secondly, the correlation of oil concentrations with electrical conductivity appears to allow contamination plume migration to be identified with geophysical techniques such as VES.

Thirdly, it has been shown that the distribution of oil contamination in the aquifer at Viestura Prospekts is highly vertically stratified and confined to within the upper few metres below the water table. This has important implications for design of monitoring networks.

The message is clear: contamination specialists should avoid a philosophy which involves peppering a site with monitoring boreholes and analysing sampled waters merely for the contaminants under question.

Rather, the use of geophysics can assist in reducing the number of necessary observation boreholes, and in locating them most efficiently. A monitoring network should not just aim to achieve maximum areal coverage, but to obtain information on the three-dimensional distribution of contaminants. Analytical programs should place more emphasis on characterising major ionic chemistry. Such a philosophy may save money on costly organic chemical analyses.

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 nearest surface water body within 35 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 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. Note however, that the significance of the migration of the LNAPL plume has not been fully adressed.

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.

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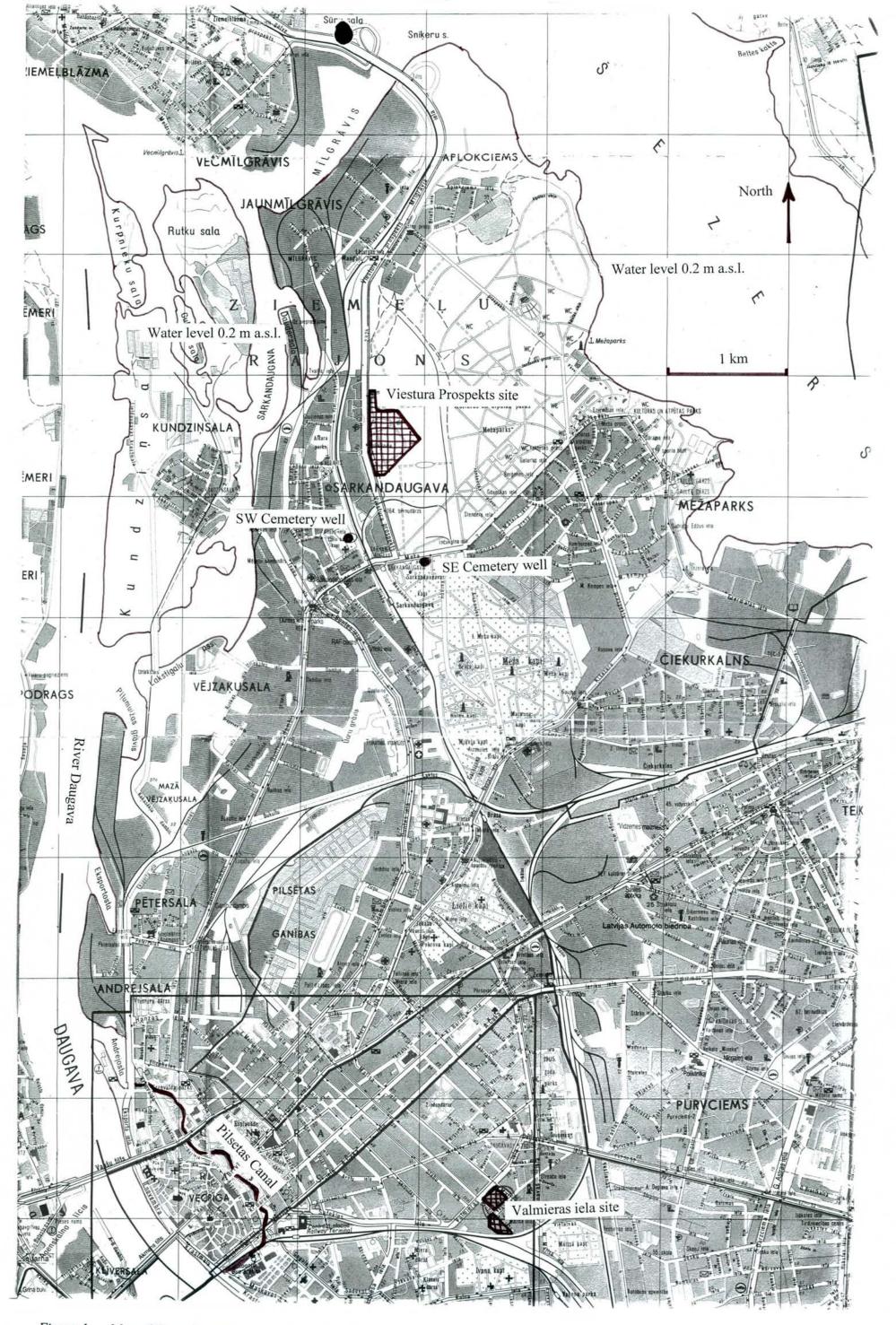


Figure 1. Map of Riga, showing the location of the Viestura Prospekts and Valmieras iela sites.

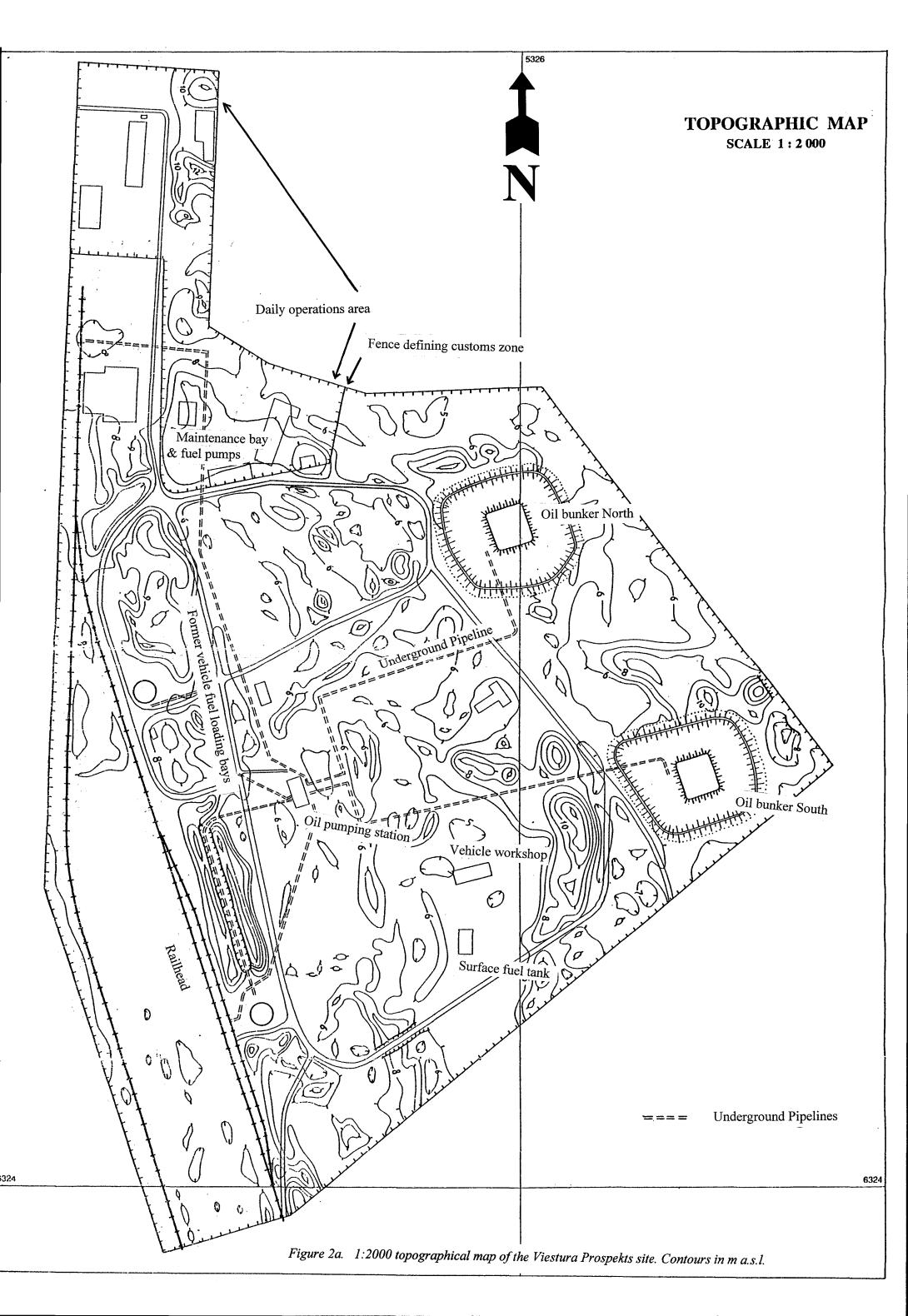


Figure 2b. 1:2000 topographical map of the Viestura Prospekts site with borehole and sampling positions. Contours in m a.s.l.

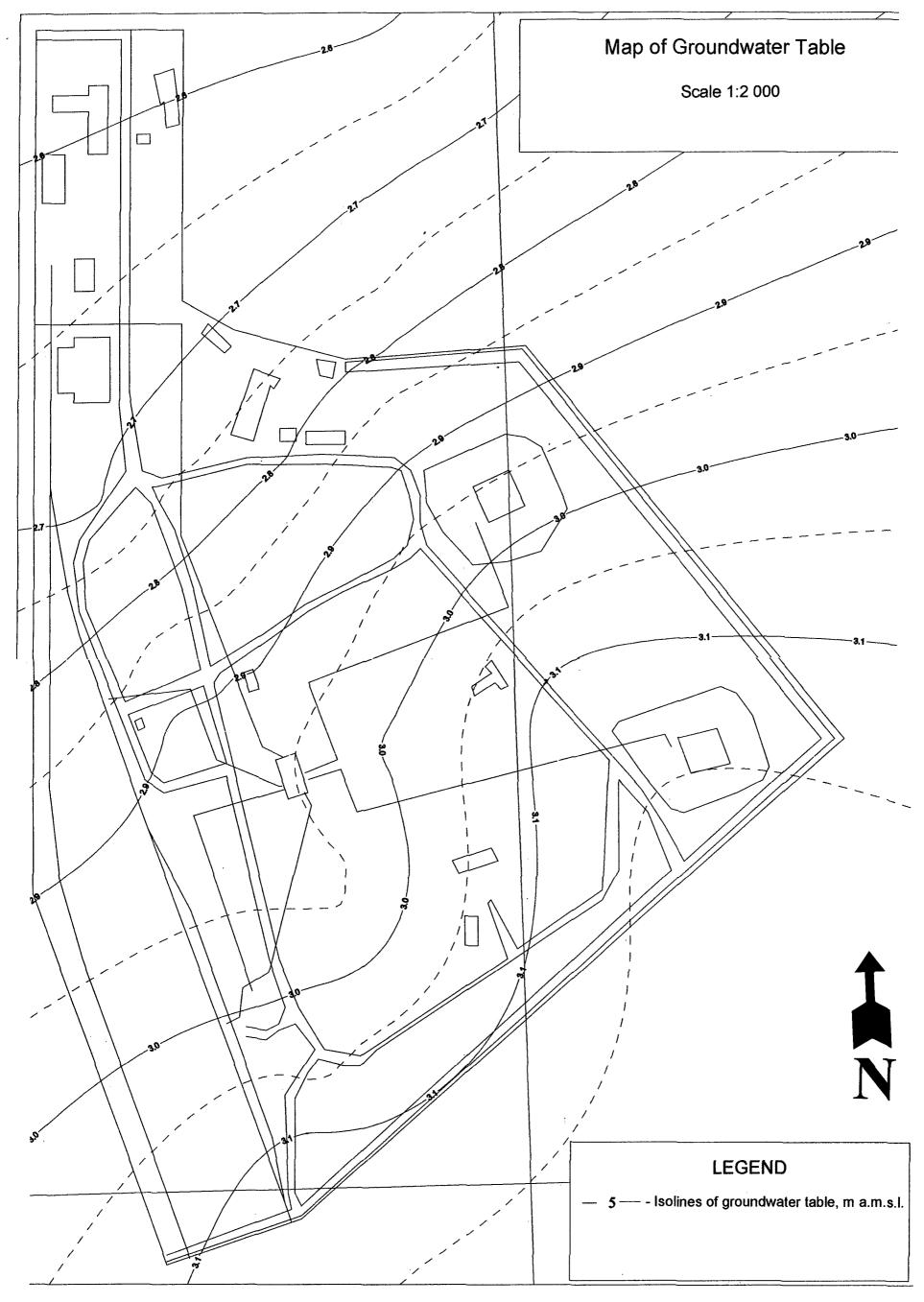


Figure 3. Map of water table at Viestura Prospekts site, based on 1996 Georadar survey calibrated against real measurements in observation boreholes.

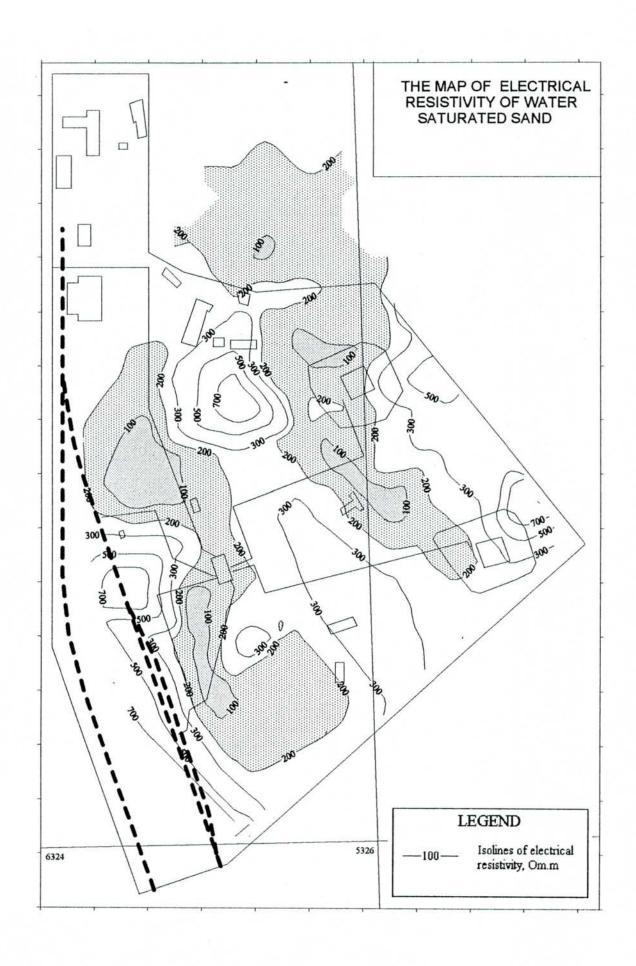


Figure 5. Interference between Be and Fe in groundwater by ICPAES at NGU at the Viestura Prospekts site.

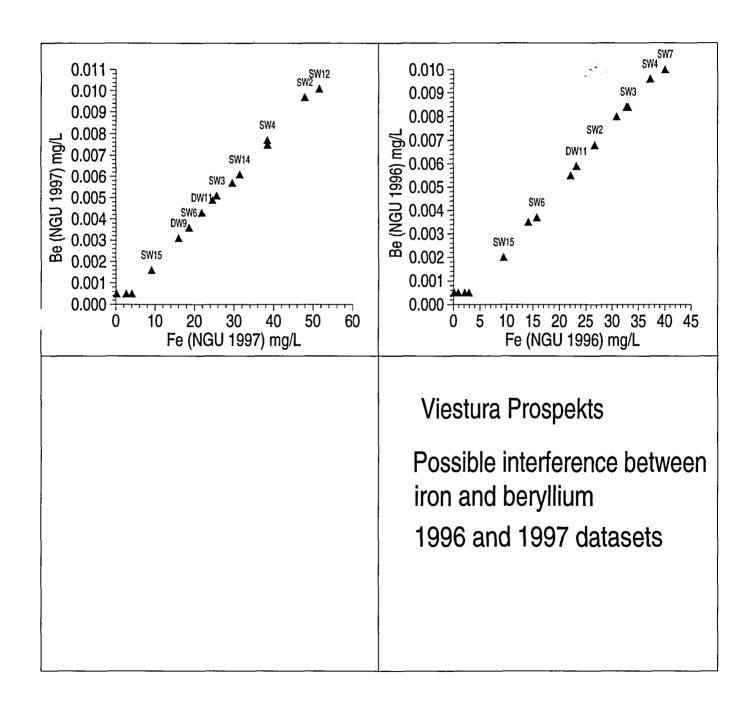


Figure 6. Comparison between NGU analyses and Latvian analyses of groundwater from Viestura Prospekts for 10 selected parameters in 1996. All values below detection limit have been plotted at 0.5 x detection limit.

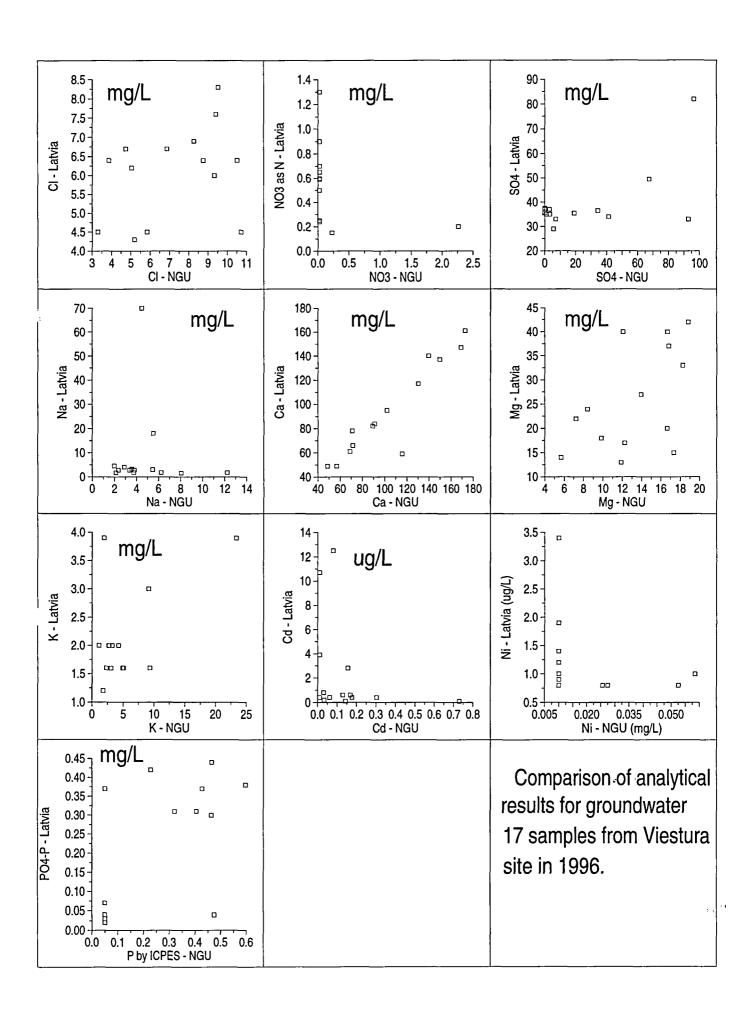


Figure 7. Comparison between NGU analyses and Latvian analyses of groundwater from Viestura Prospekts for 16 selected parameters in 1997. All values below detection limit have been plotted at 0.5 x detection limit.

Viestura Prospekts 1997

Comparison of NGU and Latvian groundwater analyses

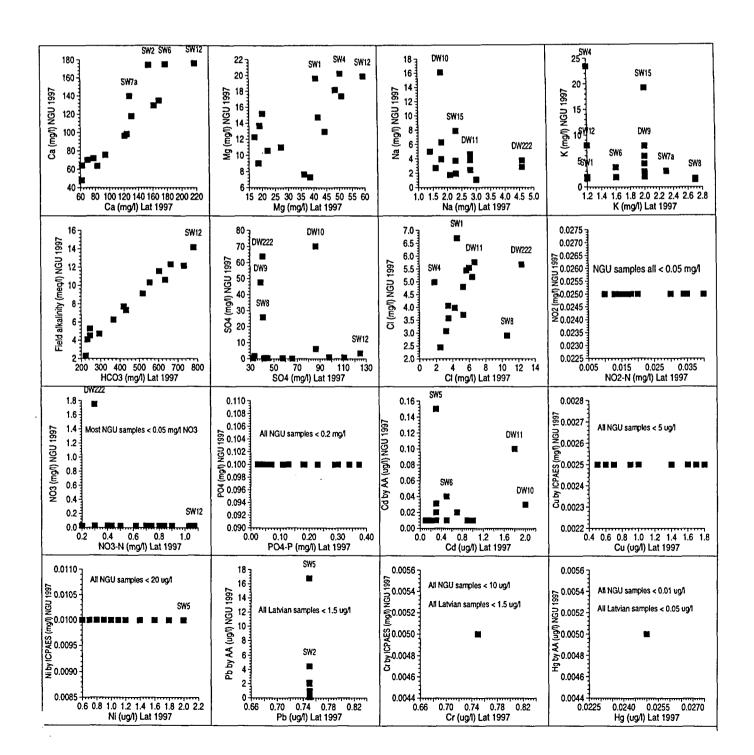


Figure 8. Comparison between NGU's 1996 and NGU's 1997 of groundwater from Viestura Prospekts for 24 selected parameters. All values below detection limit have been plotted at 0.5 x detection limit.

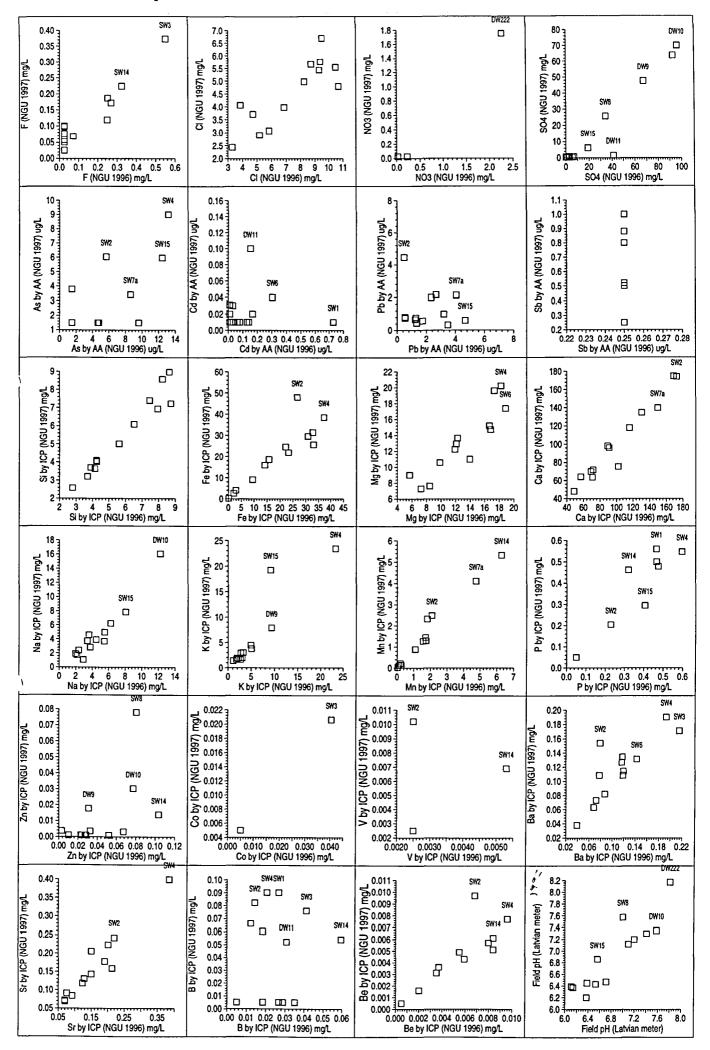


Figure 9. Comparison between Latvian 1994 analyses and Latvian 1996 analyses of groundwater from Viestura Prospekts for 12 selected parameters. All values below detection limit have been plotted at 0.5 x detection limit.

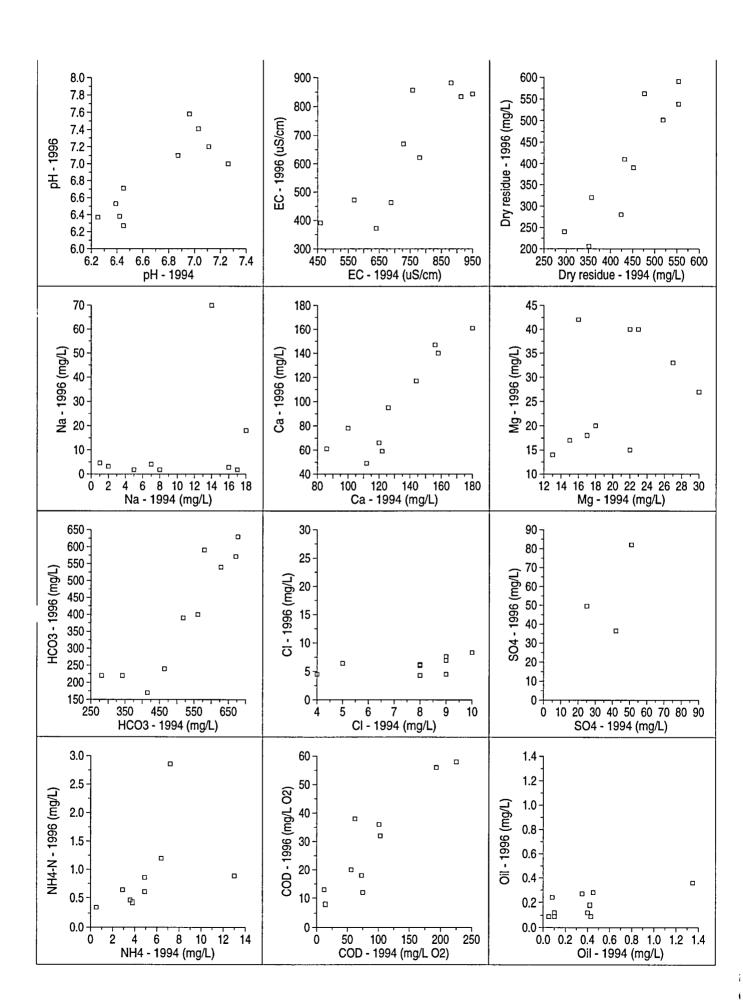


Figure 10. Comparison between Latvian 1996 analyses and Latvian 1997 analyses of groundwater from Viestura Prospekts for 23 selected parameters. All values below detection limit have been plotted at 0.5 x detection limit.

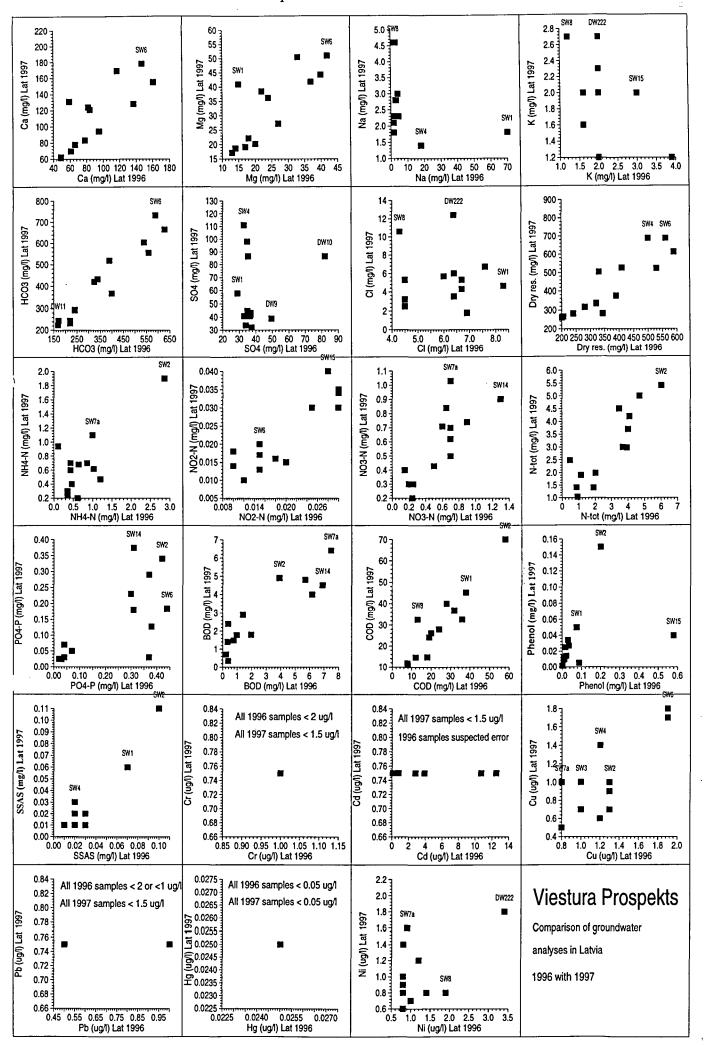


Figure 11. Comparison between 1996 and 1997 analyses from Latvia and from FFI for oil in groundwater from Viestura Prospekts. All values below detection limit have been plotted at 0.5 x detection limit.

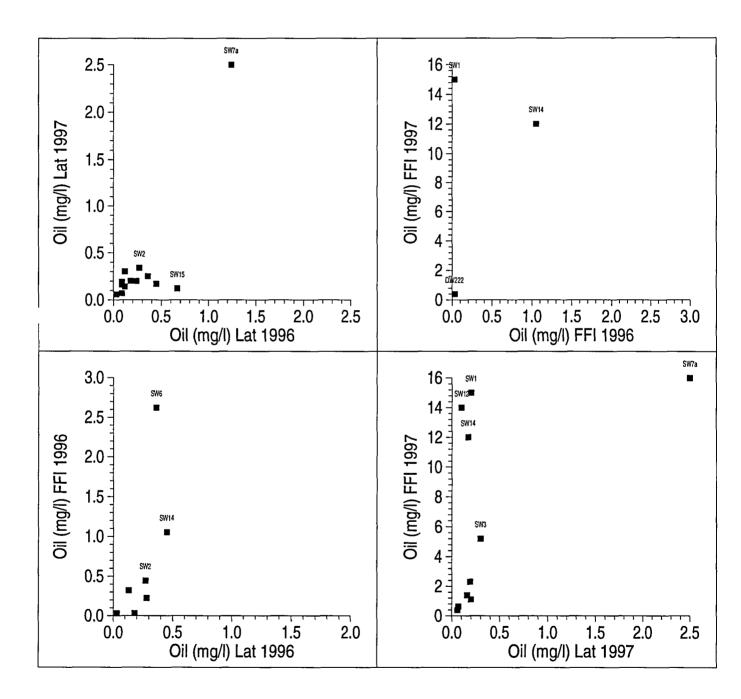


Figure 12. Plot of ion balance error = (sum cations - sum anions)/(sum cations + sum anions) x 100% versus iron for Viestura Prospekts groundwaters in 1997. Using field alkalinity, Cl-, SO₄= and NO₃- by IC and Fe, Mn, Na, K, Ca and Mg by ICPAES, analysed by NGU. All parameters in meq/l.

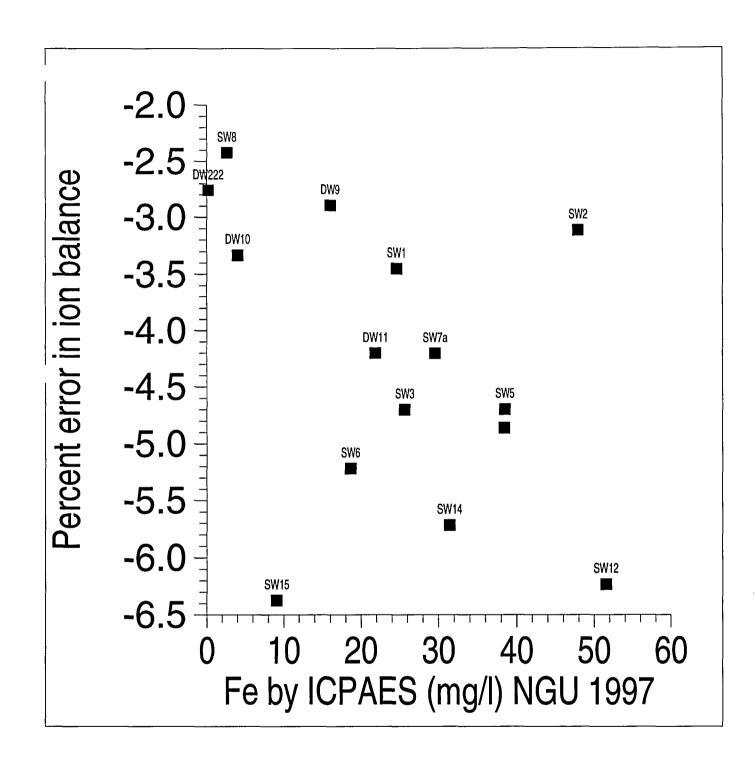


Figure 13. Explanation of the boxplot method of data presentation.

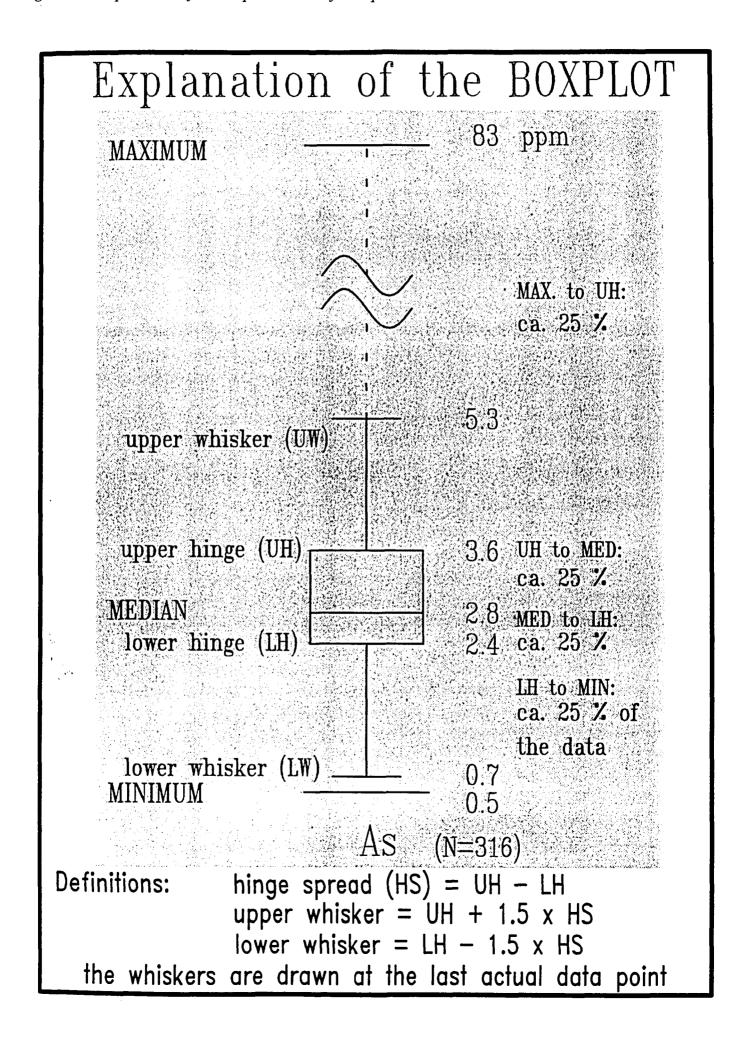


Figure 14. Oil concentrations in shallow soils as measured in 1994. Latvian data. Classes based on boxplot.

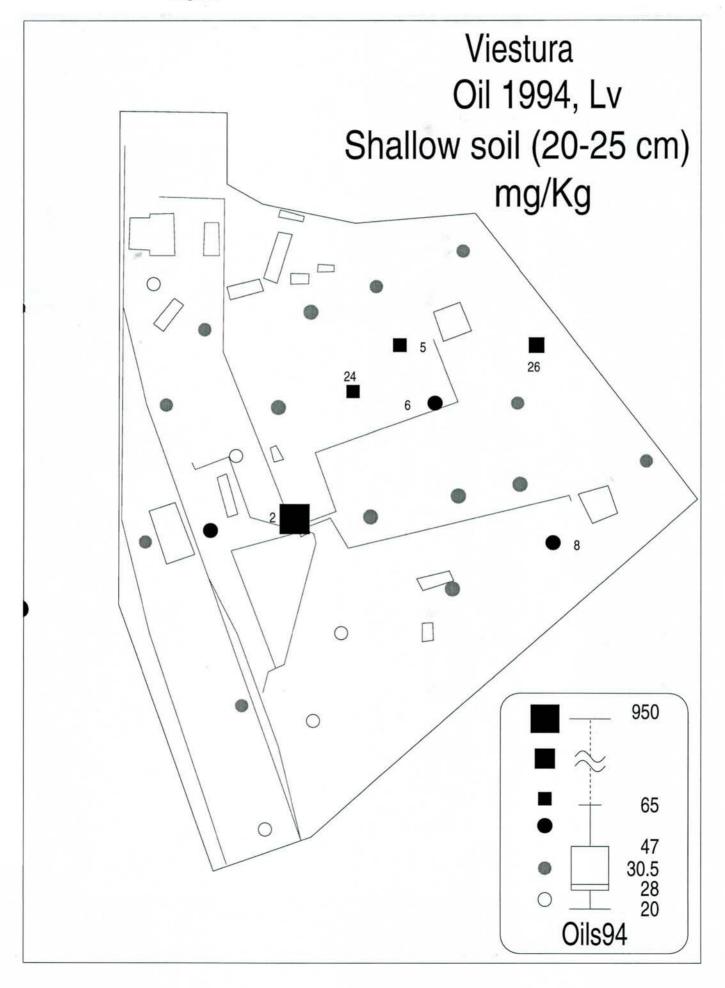


Figure 15. Oil concentrations in shallow soils as measured in 1994. Latvian data. Classes based on discrete intervals.

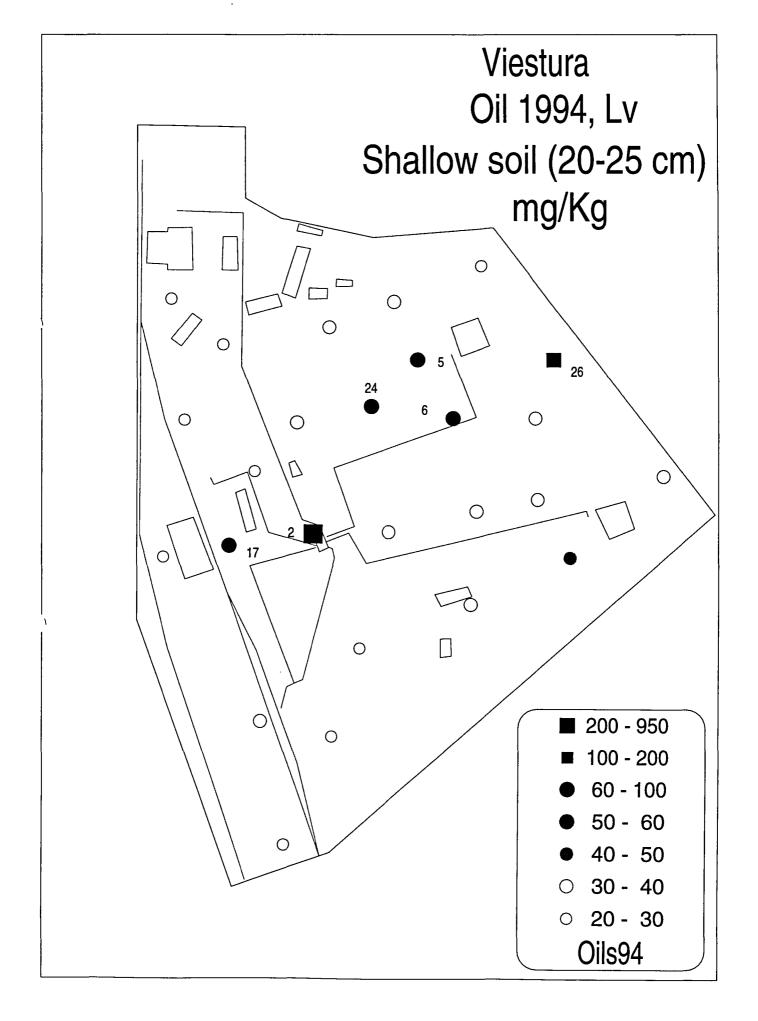


Figure 16. Oil concentrations in deep subsoils as measured in 1994. Latvian data. Classes based on boxplot.

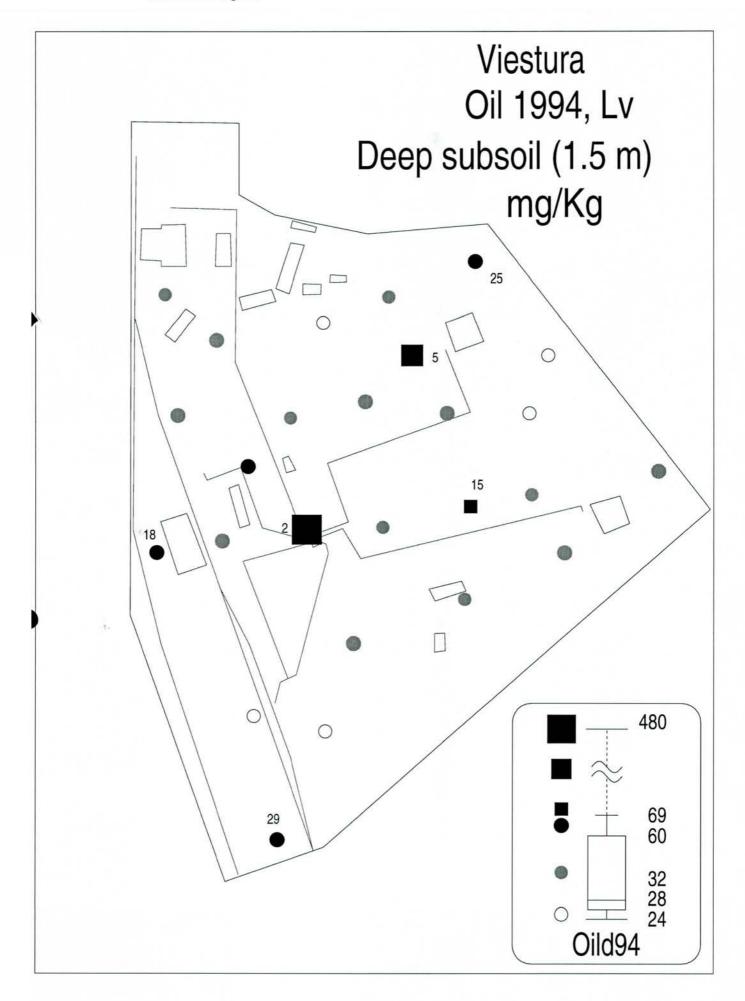


Figure 17. Oil concentrations in deep subsoils as measured in 1994. Latvian data. Classes based on discrete intervals.

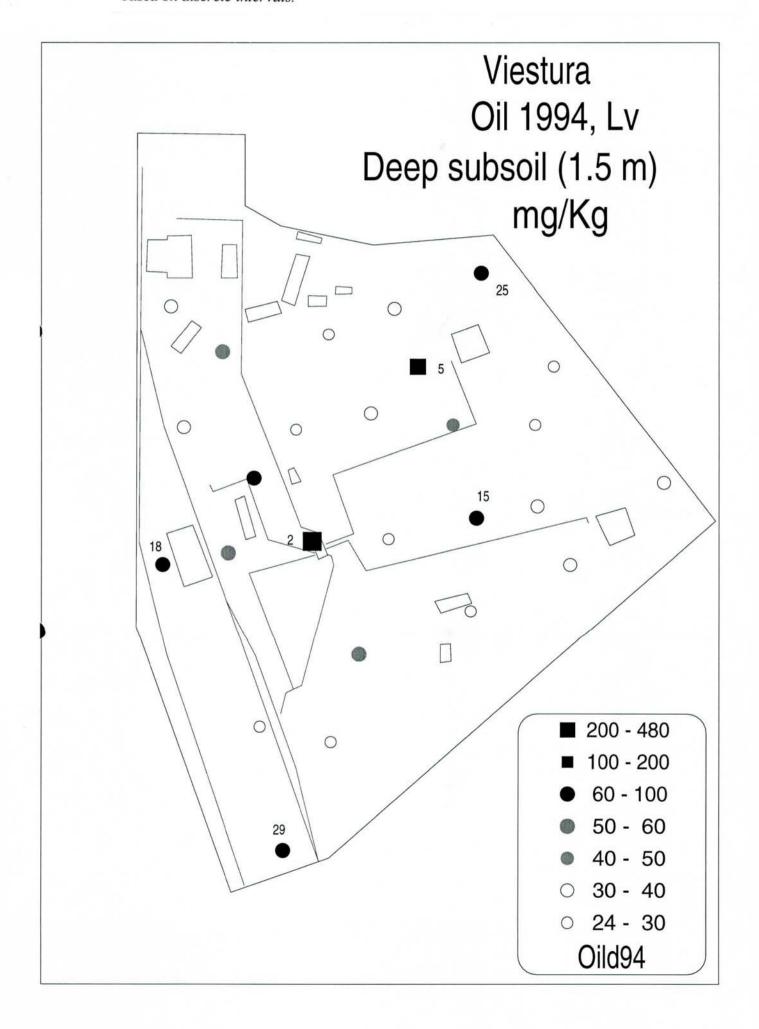


Figure 18. Oil concentrations in shallow soils as based on Latvian data from sampling in 1994 through to1997. Classes based on boxplot.

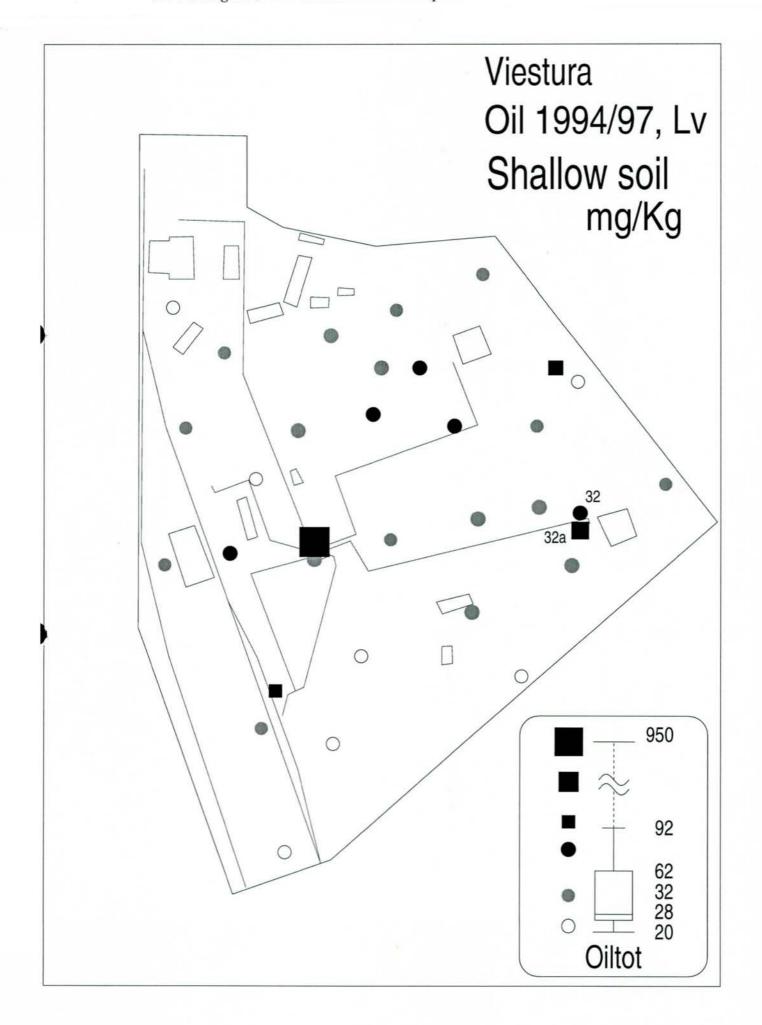


Figure 19a. Dissolved oil concentrations in groundwater, based on Latvian analyses from 1996. Classes based on boxplot (excluding cemetry wells).

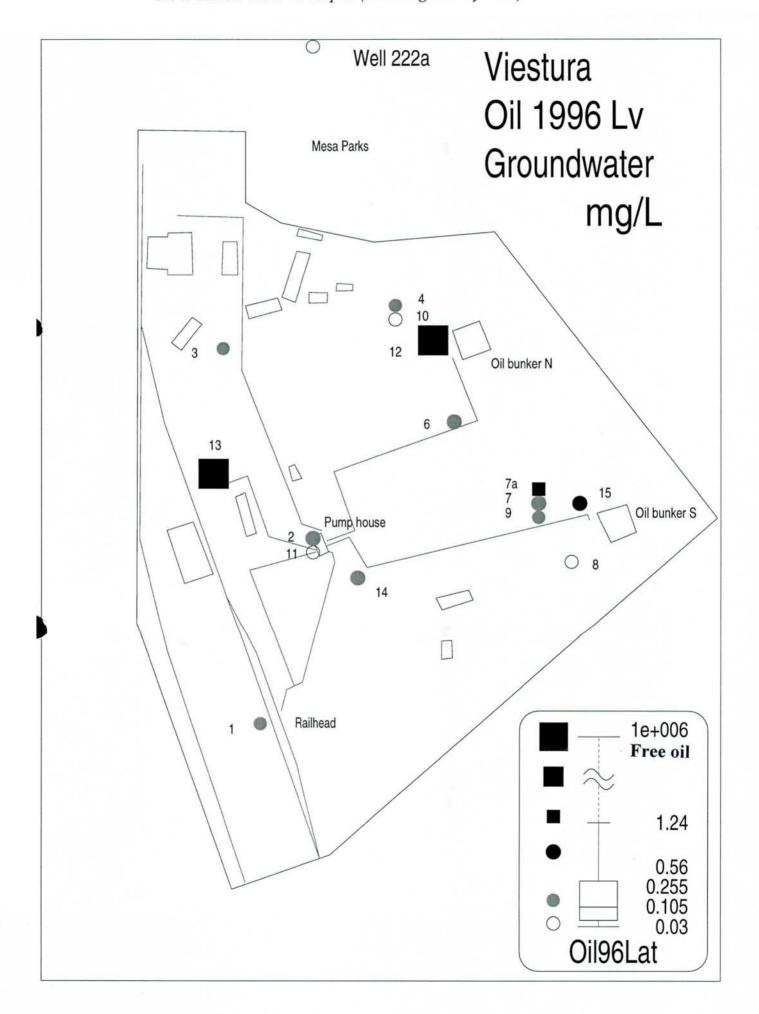


Figure 19b. Dissolved oil concentrations in groundwater, based on Latvian analyses from 1996. Classes based on boxplot (including cemetry wells).

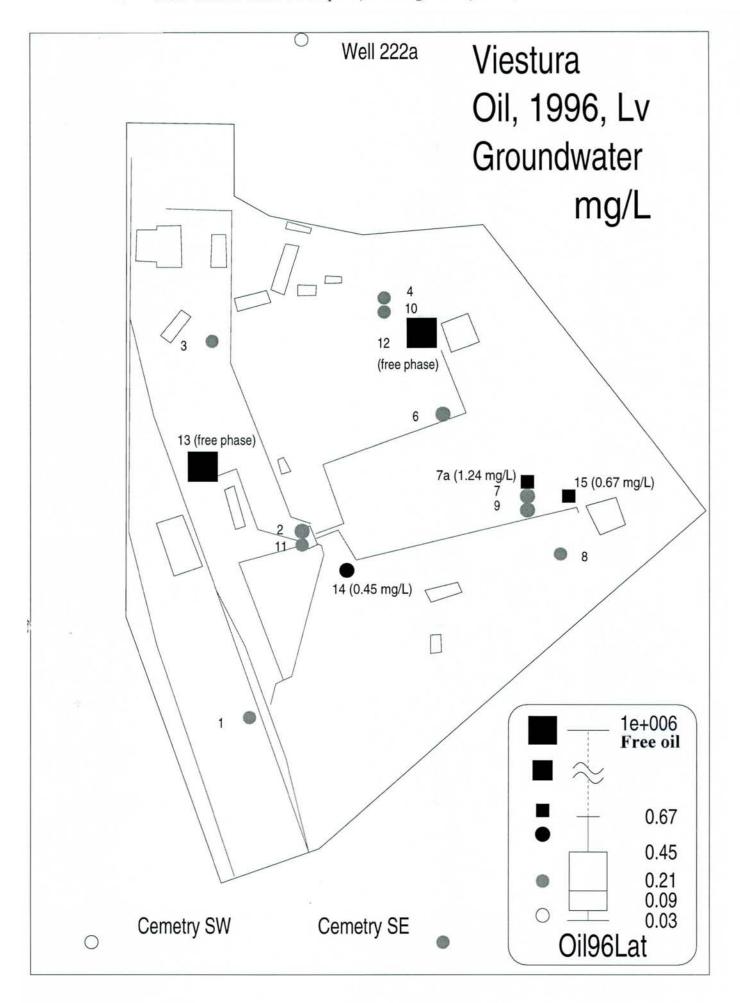


Figure 20a Correlations between (a) iron and conductivity / total anion content. Note use of both log. and linear scales.

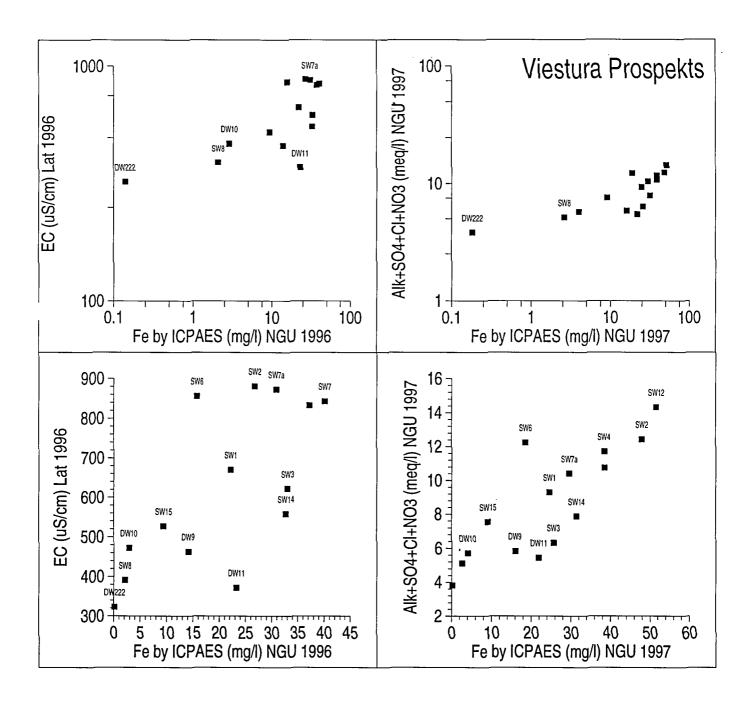


Figure 20b Correlations between (b) oil and iron / conductivity for 1996. Note use of both log. and linear scales.

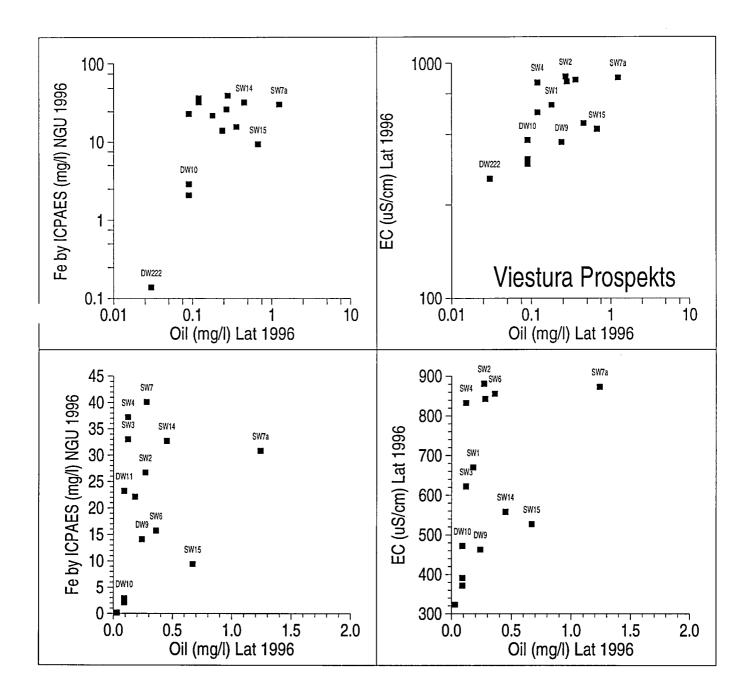


Figure 20c Correlations between (c) oil and iron / total anion content for 1997. Note use of both log. and linear scales.

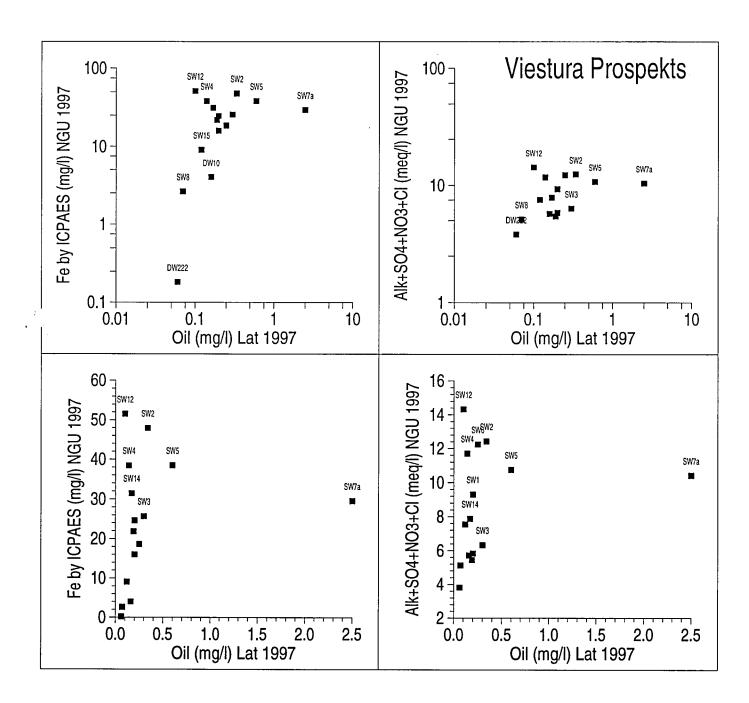
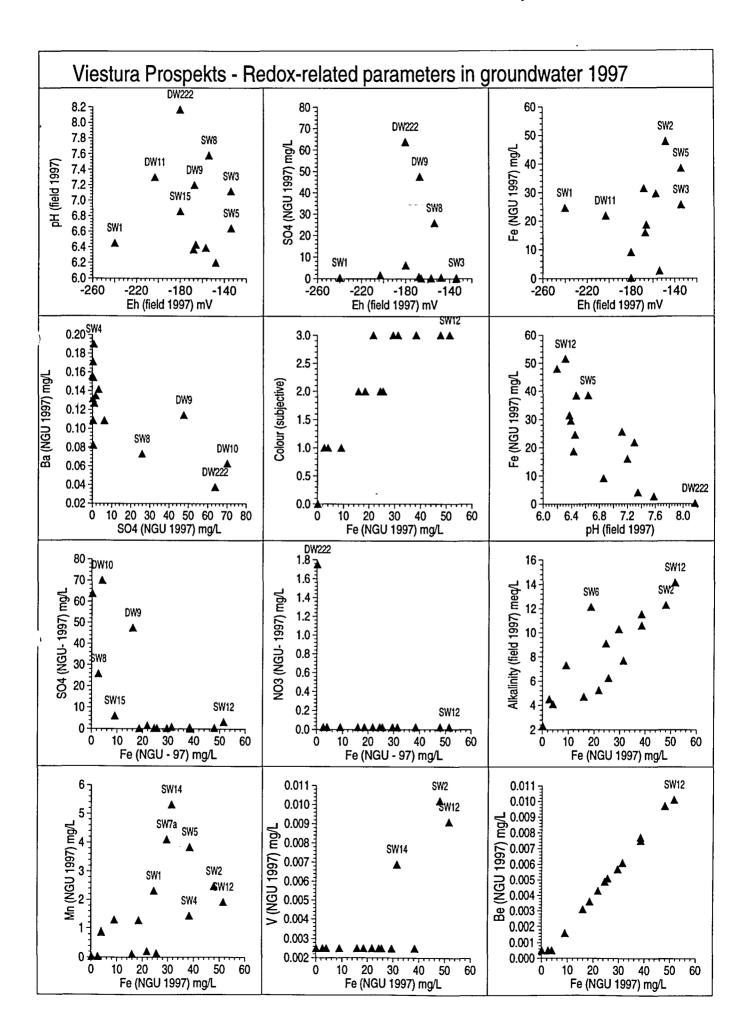


Figure 21. Redox-related parameters in groundwater, 1997. Note interference between Fe and Be.



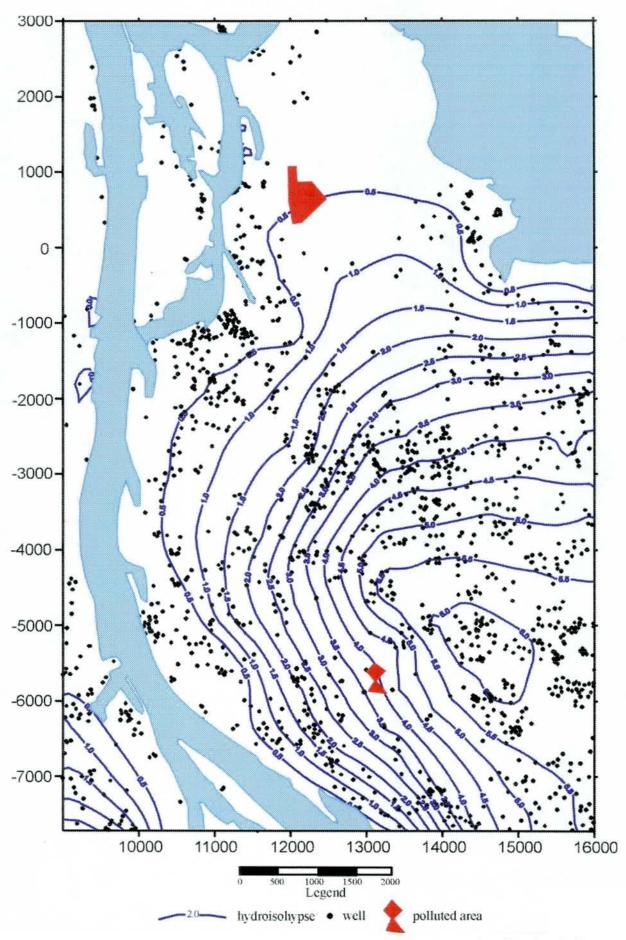


Figure 22. Modelled area of Riga, showing distribution of groundwater head in the shallow Quaternary aquifer (m a.s.l.).

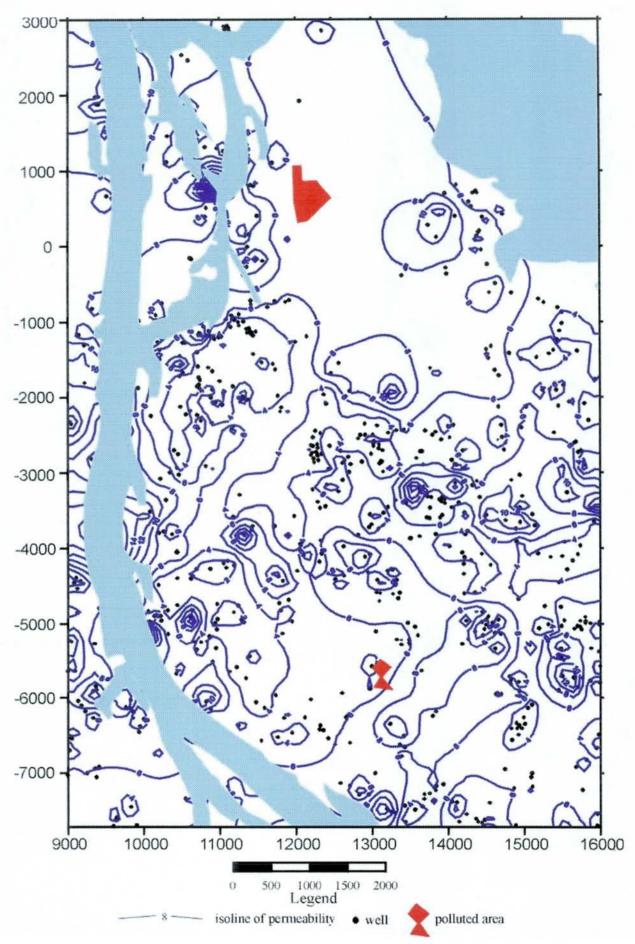


Figure 23. Modelled area of Riga, showing distribution of hydraulic conductivity in the shallow Quaternary aquifer. Units m/day

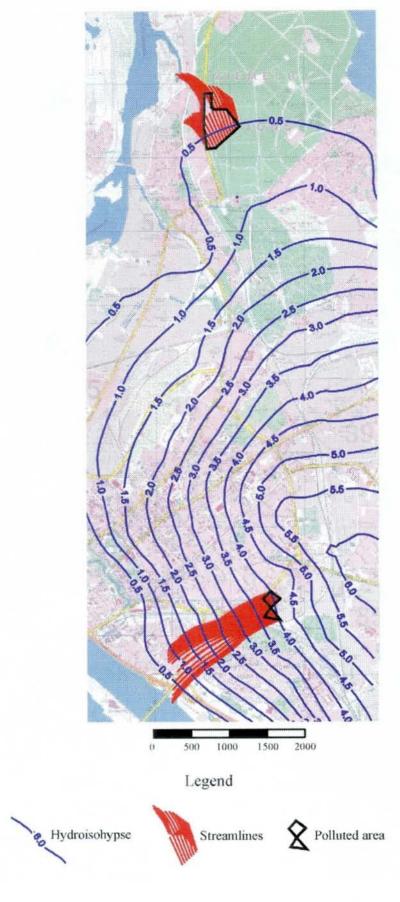


Figure 24. Modelled area of Riga, showing calculated directions of contaminant transport from the Viestura Prospekts and Valmieras iela sites.



Figure 25. Modelled migration of contamination from the Viestura Prospekts and Valmieras iela sites after elapsed time intervals of 5, 10, 20, 30 and 40 years.