

# The Impacts of Fertilizer Manufacturing on Groundwater in South Africa

By

**JOHAN PIETERSE**

*Submitted in the fulfillment of the requirements*

*for the degree of*

**MAGISTER SCIENTIAE**

*in the faculty of Science*

*Department of Geohydrology*

*University of the Free State*

*Bloemfontein*

November 2010

Supervisor: P.D. Vermeulen

## DECLARATION

I hereby declare that this dissertation submitted for the degree Masters in the Faculty of Natural and Agricultural Sciences, Department of Geohydrology, University of the Free State, Bloemfontein, South Africa, is my own work and has not been submitted to any other institution of higher education. I further declare that all sources cited or quoted are indicated and acknowledged by means of a list of references.

---

J.L. Pieterse

10 November 2010

## ACKNOWLEDGEMENTS

This project came to fruition only with the help of many individuals and institutions:

- Dr. P.D. Vermeulen for his patient guidance, expert input, and help in more than just the academic.
- Prof. G. Steyl for his assistance and expert knowledge which proved invaluable.
- Mr. F. de Lange for his assistance beyond the call of duty.
- All staff members of the Institute for Groundwater Studies at the University of the Free State who were always willing to provide assistance.
- The analytical laboratory at the Institute for Groundwater Studies who were always friendly and professional.
- Dr. F. Fourie for his expert knowledge and help with the geophysical investigation.
- Dr. P. le Roux of Soil Sciences at the University of the Free State for his help with the soil investigations on site.
- The plant manager of Sasol Nitro Potchefstroom, Kamil Cowlessor, who was willing to provide everything I needed to conduct a thorough investigation of the site.
- All other employees of Sasol Nitro Potchefstroom who were always friendly and willing to provide assistance.
- SRK Consulting for being willing to provide details of the study they conducted on the Kynoch Fertilizer Production Facility, especially Rod de Klerk and Sarah Skinner. The information obtained from this report was invaluable.

## List of Abbreviations

AC	Alternating Current
AN	Ammonium Nitrate
ANO	Ammonium Nitrate Solution
BOM	Bill of Materials
BPL	Bone Phosphate Lime
Bq/g	Becquerel per Gram
CAN	Calcium Ammonium Nitrate
CFI	CF Industries
CN	Calcium Nitrate
CSIR	Council for Scientific and Industrial Research (South Africa)
DAP	Diammonium phosphate
DC	Direct Current
DEA	South African Government Department of Environmental Affairs
DMS	Dissolved Major Salts
DNT	Dinitrotoluene
DWA(F)	The Department of Water Affairs (and Forestry) (South Africa)
EC	Electrical Conductivity
EDTA	Ethylene-Diamine-Tetra-Acetic Acid
EPA	United States Environmental Protection Agency
FAO	Food and Agriculture Organization of the United Nations
FC	Flow Characteristics
FSSA	Fertilizer Society of South Africa
HDPE	High Density Polyethylene
IAEA	International Atomic Energy Agency
IFA	International Fertilizer Industry Association
IMC	International Mineral and Chemical Corp
KFPF	The Kynoch Fertilizer Production Facility
Lat	Latitude
LD <sub>50</sub>	Lethal Dose 50%
LNAPLs	Light Non-Aqueous Phase Liquids
Lon	Longitude
Mamsl	Meters Above Mean Sea Level
MAP	Monoammonium phosphate
MDEA	Methyl Diethanolamine
MeV	Mega Electron Volt
MOP	Muriate of Potash
mSv/a	Millisievert per Annum

Naphtha	The broad term for the lightest and most volatile fraction of the liquid hydrocarbons in petroleum.
NAPLs	Non-Aqueous Phase Liquids
NPK	Fertilizer product. N refers to nitrogen, P to phosphate, and K to potassium.
NTCRA	Non Time Critical Removal Action
OMV	Oranje Mining and Transport Company
PC	Process Controller
PCBs	Polychlorinated Biphenyls
pCi/g	Picocuries per Gram
PPE	Personal Protective Clothing
PRP	Potentially Responsible Parties
PVC	Polyvinyl Chloride
RCRA	Resource Conservation and Recovery Act
RDL	Recommended Reference Dose Level
RI/FS	Remedial Investigation/Feasibility Study
RIRDC	Rural Industries Research and Development Corporation (Australia)
ROD	Record of Decision
SAB	South African Breweries
SCDHEC	South Carolina Department of Health and Environmental Control
SG	Specific Gravity
SI	Site Inspection
SNP	Sasol Nitro Potchefstroom
SOP	Sulphate of Potash
SPC	Senior Process Controller
SPCOND	Specific Conductivity
SWP	Safe Work Procedure
TDS	Total Dissolved Solids
TSP	Triple Superphosphate
TSPP	Tetrasodium Pyrophosphate
UAN	A mixture of urea and ammonium nitrate
U.S.A. (U.S.)	United States of America
USGS	United States Geological Survey
WHO	The World Health Organization
WPA	Denotation for phosphoric acid produced in the chemical reaction of rock dissolution by the dihydrate process.

## Table of contents

Chapter 1: Introduction .....	1
1.1 Objectives .....	3
1.2 Overview of methodology .....	3
1.3 Structure of the thesis .....	4
Chapter 2: The world fertilizer industry .....	6
2.1 Growth in the world fertilizer industry .....	6
2.2 Fertilizer demand and consumption around the world .....	7
2.3 The global capacity for fertilizer production .....	9
2.4 The fertilizer industry in South Africa .....	10
Chapter 3: Fertilizer production: raw materials, processes, and effluents .....	12
3.1 The nitrogen fertilizer industry .....	12
3.1.1 Ammonia production .....	12
3.1.2 Nitric acid production .....	12
3.1.2.1 Introduction .....	12
3.1.2.2 Chemistry of nitric acid production .....	12
3.1.2.3 Manufacture of dilute nitric acid .....	13
3.1.3 Ammonium nitrate and nitrochalk production .....	13
3.1.3.1 Introduction .....	13
3.1.3.2 Production of ammonium nitrate .....	14
3.1.3.3 Production of calcium ammonium nitrate (CAN) .....	15
3.1.4 Urea production .....	16
3.1.4.1 Introduction .....	16
3.1.4.2 Urea process .....	16
3.1.4.3 Description of the urea process .....	17
3.1.5 Nitrogen in the subsurface .....	19
3.1.5.1 Introduction .....	19
3.1.5.2 The nitrogen cycle and the interaction between the processes occurring in the unsaturated- and saturated zone .....	20
3.1.5.3 The remediation of nitrate in groundwater .....	22
3.1.5.4 The nitrate concentrations found on the SNP site and surrounding area .....	22
3.2 The phosphate fertilizer industry .....	23
3.2.1 Introduction .....	23
3.2.2 Phosphate rock: Raw material for fertilizers .....	24
3.2.3 Phosphate rock processing .....	26
3.2.3.1 Physical changes .....	26
3.2.3.2 Wet or dry screening .....	26
3.2.3.3 Grinding .....	26
3.2.3.4 Drying .....	26
3.2.3.5 Calcination .....	27
3.2.3.6 Defluorination .....	27
3.2.4 Sulphuric acid production .....	27
3.2.4.1 Introduction .....	27
3.2.4.2 Raw materials .....	28
3.2.4.3 Pollution sources in various process steps .....	28
3.2.5 Phosphoric acid .....	32
3.2.5.1 Introduction .....	32
3.2.5.2 Phosphoric acid by wet process .....	32
3.3 The potassium fertilizer industry .....	36
3.3.1 Introduction .....	36
3.3.2 Mining and refining methods utilized in KCl production .....	37
3.3.3 Effluents associated with the manufacturing of potassium chloride .....	38
3.3.3.1 Solid wastes .....	38
3.3.3.2 Liquid wastes .....	40
3.3.3.3 Air emissions .....	40
3.4 MAP, DAP, and NPK fertilizers .....	41
3.4.1 Introduction .....	41

3.4.2 Air pollutants .....	42
3.4.3 Water pollutants .....	42
3.5 Hot and cold blend liquid fertilizer plants .....	43
3.5.1 Introduction .....	43
3.5.2 Dust.....	43
3.5.3 Fumes .....	44
3.5.4 Liquid waste .....	44
3.5.5 Solid waste.....	44
3.6 Kynoch Fertilizer Production Facility (KFPPF) .....	44
3.7 Sasol Nitro Potchefstroom (SNP).....	46
3.7.1 Introduction .....	46
3.7.2 Raw materials.....	46
3.7.3 Production processes .....	46
3.7.3.1 Introduction.....	46
3.7.3.2 Procedure .....	46
3.7.3.3 Environmental factors .....	47
3.7.3.4 Safety and health factors .....	47
3.7.3.5 Quality factors.....	47
3.7.4 Discussion of the production process and the product produced at SNP .....	48
3.7.5 Effluents caused by operations on the SNP site .....	49
Chapter 4: Geo investigations .....	51
4.1 Geology .....	51
4.1.1 Regional geology.....	51
4.1.2 Local geology .....	51
4.1.2.1 Introduction.....	51
4.1.2.2 Soil profiling .....	55
4.1.2.3 Particle size distribution analysis.....	57
4.1.3 Aquifers in the area .....	59
4.2 Drilling (SNP).....	60
4.2.1 Drilling targets .....	60
4.2.2 Boreholes .....	62
4.3 Pumping tests and geohydrological parameter estimations (SNP) .....	62
4.4 Geophysical investigation .....	66
4.4.1 Introduction .....	66
4.4.2 Approach to the geophysical investigation.....	66
4.4.3 Geophysical investigation of SNP .....	68
4.4.3.1 Introduction.....	68
4.4.3.2 Ground geophysical investigations.....	69
4.4.3.3 Results of the ground geophysical investigations .....	70
4.5 Topography, water levels, and drainage .....	72
4.6 Climate .....	77
4.7 Recharge.....	78
Chapter 5: Chemistry .....	79
5.1 Natural groundwater quality and contamination .....	79
5.1.1 Introduction .....	79
5.1.2 The expected natural composition of groundwater in relation to rock type .....	80
5.1.3 The expected pristine groundwater quality in the Potch Industria area .....	81
5.1.4 Mechanisms of contamination .....	82
5.1.5 The subsurface transport of contaminants in the Potch Industria area.....	83
5.2 The Kynoch Fertilizer Production Facility (KFPPF).....	84
5.3 Sasol Nitro Potchefstroom (SNP).....	86
5.3.1 Soil- and water sampling targets.....	86
5.3.1.1 Soil sampling targets.....	86
5.3.1.2 Water sampling targets .....	88
5.3.2 Soil- and water sample results.....	90
5.3.2.1 Introduction.....	90
5.3.2.2 Soil chemistry .....	90
5.3.2.3 Groundwater chemistry.....	99

5.3.3 Borehole geology, electronic conductivity (EC), and soil chemical results as profiles in relation to depth .....	110
5.4 Statistical analysis of chemical data obtained from the SNP site .....	115
Chapter 6: Conceptual model of the SNP site .....	122
Chapter 7: Conclusions .....	129
7.1 Key findings .....	129
7.2 Summary of the contaminants in groundwater found in the study area .....	132
7.3 Lessons learnt, shortcomings, and limitations .....	136
Chapter 8: Recommendations .....	137
8.1 Introduction .....	137
8.2 Pollution prevention: Recommended safety measures for hot and cold blend liquid fertilizer plants .....	137
8.2.1 Effluents associated with the liquid fertilizer industry and their control measures .....	137
8.2.1.1 Introduction .....	137
8.2.1.2 Dust control .....	137
8.2.1.3 Fume control .....	138
8.2.1.4 Liquid control .....	139
8.2.1.5 Solid waste .....	140
8.2.1.6 Noise .....	140
8.2.2 Containment systems for liquid fertilizer plants .....	140
8.2.2.1 Introduction .....	140
8.2.2.2 Loading and unloading systems .....	141
8.2.2.3 Reaction and mixing systems .....	141
8.2.2.4 Raw material and product storage .....	142
8.2.2.5 Washing and parking areas .....	142
8.2.2.6 Operational areas .....	143
8.3 Current safety procedures in place at SNP .....	143
8.4 Current waste disposal guidelines in place at SNP .....	144
8.4.1 Introduction .....	144
8.4.2 Procedures .....	145
8.4.2.1 Waste types and disposal area/site .....	145
8.4.2.2 Waste handling .....	145
8.4.2.3 Additional information .....	148
8.4.2.4 Environmental factors .....	148
8.4.2.5 Safety and health factors .....	148
8.4.2.6 Quality factors .....	148
8.5 Safety measures recommendations for SNP and the liquid fertilizer industry in general .....	148
8.5.1 Introduction .....	148
8.5.2 Comments .....	148
8.5.3 Suggestions .....	149
8.6 Remediation recommendations for the SNP site .....	150
8.7 Other recommendations .....	151
Chapter 9: References .....	152
Appendix A: Fertilizer manufacturing .....	159
A.1. Ammonia production .....	159
A.1.1 Introduction .....	159
A.1.2 Raw materials and methods used in ammonia production .....	159
A.1.2 Discussion of process steps and their effluents .....	163
A.1.2.1 Natural gas desulphurization .....	163
A.1.2.2 Steam reforming .....	164
A.1.2.3 CO shift conversion and CO <sub>2</sub> removal: Process condensate treatment .....	164
A.1.2.4 Methanation, compression, and NH <sub>3</sub> synthesis: Purge gas treatment .....	165
A.2 Radioactive components .....	166
Appendix B: Remediation .....	169
B.1 Introduction .....	169
B.2 Remediation methods .....	171
B.2.1 Introduction .....	171
B.2.2 Pump and Treat .....	173



B.2.3 Hydraulic Containment.....	173
B.2.4 Air sparging/soil vapour extraction .....	174
B.2.5 In-situ redox manipulation .....	175
B.2.6 Permeable reactive barriers .....	175
B.2.7 Phytoremediation .....	176
B.2.8 Natural attenuation.....	177
B.2.9 Intrinsic and enhanced bioremediation .....	177
Appendix C: Case Studies.....	178
C.1 CF Industries.....	178
C.2 Central Chemical.....	179
C.3 International Mineral and Chemical Corp (IMC) .....	181
Appendix D: Borehole logs and profiles .....	183

## List of figures

Figure 1: Aerial photograph of SNP and surroundings. The location of Potchefstroom is indicated on the inserted map of South Africa. Delineations; red: SNP, yellow: KFPF, orange: gypsum tailings dam, green: Oranje Mining and Transport Company, blue: Poortjies dam. ....	2
Figure 2: Fertilizer use per capita (Hodge, 1994). ....	6
Figure 3: Projected medium-term evolution of regional fertilizer demand (in Mt Nutrients). Blue indicates the average use for the period 2006/7 to 2008/9, and the red the projected variation for 2013/14 (IFA, 2009) .....	7
Figure 4: Fertilizer consumption in South Africa from 1955 to 2008 (FSSA, 2008a). ....	11
Figure 5: Production of calcium ammonium nitrate using ammonium nitrate wet lime originating from the Odda process (Nitzschmann, 1994). ....	15
Figure 6: Urea process (Hidetoshi, 1994). ....	17
Figure 7: Schematic representation of the integrated "three-zone" approach showing the interacting processes that govern the occurrences of nitrate in groundwater (Almasri, 2006). ....	20
Figure 8: Map of the groundwater nitrate distribution in Southern Africa (Tredoux <i>et al.</i> , 2009). ....	22
Figure 9: Manufacture of sulphuric acid, with main stages for processing gas from sulphur burning, pyrite roasting, and non-ferrous metallurgy (Ciobanu, 1994). ....	29
Figure 10: Cross section of perimeter dam and rim ditch (Ando, 1994). ....	34
Figure 11: Generalized stratigraphy under the waste management area of potassium chloride production in Saskatchewan (Reid and Klein, 1994). ....	39
Figure 12: Map of the main storage facilities and operation points on the KFPF site. KFPF is delineated in yellow. ....	45
Figure 13: Simplified map of the location of storage facilities and various operations on the SNP site. ....	48
Figure 14: Geological map of the Potchefstroom area. ....	52
Figure 15: Aerial map of the SNP site indicating the locations of the boreholes. ....	53
Figure 16: Borehole log of BH002-D. Coordinates; lat (S°): 26.71542, lon (E°): 27.06651. ....	53
Figure 17: Borehole log of BH005-D. Coordinates; lat (S°): 26.71582, lon (E°): 27.06757. ....	54
Figure 18: Three dimensional contour map of the lava formation under the SNP site (Elevation in mamsl). ....	54
Figure 19: Aerial map of the SNP site indicating the locations of soils samples, auger points, and profile pits. ....	55
Figure 20: Photograph of profile pit (AC1) (approximately 1.2m deep) showing a weathered quartzitic layer over a more compacted zone (The Department of Soil Sciences, University of the Free State). ....	56
Figure 21: Example of drilled borehole (BH003-D) and information plate. ....	61
Figure 22: Map showing the approximate transmissivity values of different zones of the SNP site (values shown are in m <sup>2</sup> /d). ....	64
Figure 23: Two Dimensional Resistivity Traverses at the SNP Site. ....	67
Figure 24: Photo of traverse 1. ....	67
Figure 25: Photo of traverse 1. ....	68
Figure 26: Two-dimensional resistivity profile along Traverse 1 (1m unit electrode spacing). ....	69
Figure 27: Two-dimensional resistivity profile along Traverse 2 (2m unit electrode spacing). ....	69
Figure 28: The boreholes used for water elevation contours. KFPF is delineated in yellow and SNP in red. ....	72
Figure 29: Contour and vector map of the surface elevation of the Potchefstroom area. The location of SNP is indicated in red (elevation values in mamsl and coordinates in lat/lon). ....	73
Figure 30: Three dimensional contour map of the surface elevation of the Potchefstroom area. The location of SNP is indicated in red (coordinates in lat/lon and elevation values in mamsl). ....	74
Figure 31: Contour and flow vector map of the water level elevation of the Potch Industria area. The location of SNP is indicated in red (coordinates in lat/lon and elevation values in mamsl). ....	75
Figure 32: Three dimensional contour map of the water level elevation of the Potch Industria area. The location of SNP is indicated in red (coordinates in lat/lon and elevation values in mamsl) .....	76
Figure 33: The Potchefstroom monthly average precipitation and evaporation (A-pan equivalent) rates (Aucamp, 2000). ....	77
Figure 34: The Potchefstroom monthly average minimum and maximum temperatures (Aucamp, 2000). ....	78

Figure 35: The groundwater mean recharge values for the North West Province (Geography Department, Potchefstroom University (North West University), Date unknown). .....	78
Figure 36: Processes affecting contaminant transport. The thickness of the corresponding line indicates typically the relative importance of the process in the soil and above, at, and below the water table (Romijn, 2002). .....	82
Figure 37: Map indicating the predominant groundwater contaminants and their general location on the KFPF site. KFPF is delineated in yellow and the emergency dam in red (Skinner, 2007).....	85
Figure 38: Proposed soil sampling targets and position of boreholes. ....	86
Figure 39: Photo indicating the chemical damage to the pavement and building on the northern side on the SNP plant.....	88
Figure 40: Location of boreholes ROSS6 and SAB1, and boreholes on the SNP site (delineated in red). ....	89
Figure 41: The general location of contaminants found in soil samples. ....	90
Figure 42: Photos of storage tank area in the centre of the site. ....	92
Figure 43: Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Shallow" depth (0 - 1.2m). Red: not allowable concentrations, Yellow: allowable concentrations (short term), Green: allowable concentrations (lifetime consumption), Blue: no standards (according to SANS241:2006) (mg/l).....	93
Figure 44: Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Middle" depth (9 - 14m). Red: not allowable concentrations, Yellow: allowable concentrations (short term), Green: allowable concentrations (lifetime consumption), Blue: no standards (according to SANS241:2006) (mg/l).....	95
Figure 45: Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Deep" depth (ca. 18 - 24m). Red: not allowable concentrations, Yellow: allowable concentrations (short term), Green: allowable concentrations (lifetime consumption), Blue: no standards (according to SANS241:2006) (mg/l).....	97
Figure 46: The general location of predominant contaminants found in the groundwater samples.	99
Figure 47: Chromium concentration over time during pump test (BH004-D). ....	101
Figure 48: Chromium concentration over time during pump test (BH005-D). ....	101
Figure 49: Chromium concentration over time during pump test (BH006-D). ....	101
Figure 50: Distribution, classification, and proportionality of contaminants of concern found in water samples at "Shallow" depth (ca. 2m below water levels). Red: not allowable concentrations, Yellow: allowable concentrations (short term), Green: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l). ....	102
Figure 51: Distribution, classification, and proportionality of contaminants of concern found in water samples at "Middle" depth (ca. 10 - 13m below water levels). Red: not allowable concentrations, Yellow: allowable concentrations (short term), Green: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l). ....	104
Figure 52: Distribution, classification, and proportionality of contaminants of concern found in water samples at "Deep" depth (ca. 15 - 19m below water levels). Red: not allowable concentrations, Yellow: allowable concentrations (short term), Green: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l). ....	106
Figure 53: STIFF diagrams of "shallow" water samples (water samples taken ca. 2m below water levels). ....	108
Figure 54: STIFF diagrams of "medium" depth water samples (water samples taken ca. 10 - 13m below water levels). ....	109
Figure 55: STIFF diagrams of "deep" water samples (water samples taken ca. 15 - 19m below water levels). ....	109
Figure 56: Borehole geology, EC, and chemical parameters (for soil samples) represented as profiles in relation to depth (BH001-D).....	112
Figure 57: Borehole geology, EC, and chemical parameters (for soil samples) represented as profiles in relation to depth (BH003-D).....	113
Figure 58: EC profiles of boreholes and the position of boreholes on map (EC measured in mS/m). ....	114
Figure 59: Chromium concentration over time for pumping test done on BH004-D with fitted trend line. ....	120
Figure 60: Chromium concentration over time for pumping test done on BH006-D with fitted trend line. ....	120

Figure 61: Map indicating the line used to calculate the chromium concentration as a function of distance from the source. ....	121
Figure 62: Chromium concentration as a function of distance and fitted trend line (from source to ROSS6).....	121
Figure 63: Three dimensional conceptual model of the SNP site (Google Sketchup: see file on included CD for three dimensional animation). ....	123
Figure 64: Conceptual model: cross sections 1, 2, and 3 indicated on the SNP site. ....	124
Figure 65: Conceptual model: cross sections of the SNP site's subsurface (T measured in m <sup>2</sup> /d). ....	125
Figure 66: Flow diagram of steam reforming of natural gas and naphtha (HT: High Temperature, LT: Low Teperature (Turtureanu, 1994).....	160
Figure 67: Flow diagram of heavy oil gasification (Turtureanu, 1994). ....	161
Figure 68: Flow diagram of the pulverized coal gasification process (Turtureanu, 1994). ....	162
Figure 69: Parameter variation during pH neutralization (Popovici, 1994).....	170
Figure 70: The pump and treat method (EPA, cited by Stewart 2008).....	173
Figure 71: An example of air sparging (North Carolina Division of Pollution Prevention and Environmental Assistance, cited by Stewart, 2008) .....	174
Figure 72: An example of in-situ redox manipulation (Field Hydrology and Chemistry Group of the Pacific Northwest National Laboratory of the US Department of Energy, cited by Stewart, 2008)	175
Figure 73: Examples of permeable reactive barriers (Right: Dewind one pass trenching. Left: from EPA Research Highlights, cited by Stewart, 2008) .....	176
Figure 74: Phytoremediation (EPA, cited by Stewart, 2008) .....	176
Figure 75: Borehole logs of the eight boreholes on the SNP site. ....	186
Figure 76: Borehole geology, EC profile (groundwater), and chemical results profiles (for soil samples) of all eight boreholes. ....	194

## List of tables

Table 1: Regional and sub-regional fertilizer consumption and estimated annual growth for 2007/8 to 2011/12 (FAO, 2008).....	8
Table 2: The specifications for nitrate in potable water in South Africa (Tredoux <i>et al.</i> , 2009).....	19
Table 3: Heavy metals content in phosphate rock compared to typical content expected in soil (Sierra, 1994).....	25
Table 4: Possible polluting agents in sulphuric acid processing (Ciobanu, 1994).....	30
Table 5: Examples of phosphogypsum composition (%) (Ando, 1994).....	33
Table 6: Estimated cadmium content of rocks in current use in industrial plants (Man, 1994).....	35
Table 7: Primary potassium deposits utilized in the manufacturing of potassium fertilizers (Klein <i>et al.</i> , 1994).....	37
Table 8: The general composition of tails from Saskatchewan mines (Reid and Klein, 1994).....	38
Table 9: Analysis of the constituents of the solid and liquid waste produced by the potash mine in Saskatchewan (Reid and Klein, 1994).....	39
Table 10: Particulates in air emissions from dryers (Klein <i>et al.</i> , 1994).....	41
Table 11: Description of profile pit AB10 at SNP (The Department of Soil Sciences, University of the Free State).....	56
Table 12: Particle size distribution results using the Bouyoucos (Rapid) method (%).....	58
Table 13: Coordinates of proposed drilling positions.....	61
Table 14: Basic borehole dimensions.....	62
Table 15: Borehole construction, depth, diameter, casing-, gravel pack-, and sanitary seal data... 63	63
Table 16: Summary of the yield and transmissivity of the pump-tested boreholes. "N/A" indicates values that were excluded due to too large variation from the T-value estimation using the recovery data.....	65
Table 17: Constituents normally occurring in groundwater (Romijn, 2002).....	79
Table 18: Examples of various compositions of groundwater in relation to rock type (mg/l) (Romijn, 2002).....	80
Table 19: Descriptive statistical analysis of the chemical results (major contaminants of concern only) of the soil and groundwater samples.....	117
Table 20: The correlation coefficient of 40 auger samples.....	118
Table 21: Correlation coefficient of 118 borehole soil samples (obtained during drilling).....	118
Table 22: Correlation coefficient of 71 water samples.....	119
Table 23: Summary of the contaminants in groundwater caused by fertilizer manufacturing.....	133
Table 24: Sasol Nitro Safe Work Procedure (SWP) (SWP-P-P-07, 2007).....	144
Table 25: Waste types and disposal area/site (10-6, 2009).....	145
Table 26: Raw materials used in ammonia production and their description (Turtureanu, 1994).....	159
Table 27: Examples of Uranium and P <sub>2</sub> O <sub>5</sub> content found in phosphates of different regions (%) (Bunus, 1994).....	166
Table 28: Uranium content in technical phosphoric acid (Bunus, 1994).....	167
Table 29: Radioactivity of natural phosphates and gypsum (Bunus, 1994).....	168
Table 30: The activity concentrations of phosphate rock mined at Phalaborwa, South Africa (IAEA, 2005).....	168

## Chapter 1: Introduction

The fertilizer industry has experienced exceptional growth in the last few decades. This is due to advantages in agricultural production and productivity which have led to economic development and the raising of living standards, and the increasing pressure population growth has put on global food demand. As a result of the industry's rapid growth, and the increasing global awareness concerning environmental issues, fertilizer production facilities have come under growing pressure to comply with ever more stringent environmental regulations (Hodge, 1994).

There are numerous contaminants associated with the fertilizer industry. These may be released into the environment through dusts, fumes, air emissions, liquid pollutants, or solid wastes. Some of these contaminants potentially pose serious health and environmental risks. Although the fertilizer industry is heavily regulated in most parts of the world, its impact on the environment is nevertheless significant.

Groundwater is one of the aspects of the environment heavily effected by the fertilizer industry, and the aim of this study is to provide more clarity on the extent of the pollution caused by the fertilizer industry on the quality of groundwater.

The site investigated is located in the industrial area of Potchefstroom, South Africa (Potch Industria), and includes Sasol Nitro Potchefstroom (SNP), the Kynoch Fertilizer Production Facility (KFPPF), and the surrounding area (see Figure 1). SNP is a hot and cold blend liquid fertilizer plant, and KFPPF manufactured fertilizers on a full scale from 1967 until mid 2006. An in-depth investigation was conducted on the SNP site by the researcher, and data from the KFPPF site were provided by SRK Consulting who carried out a study there in 2007.

There are three main ingredients in fertilizers, viz. nitrogen (N), phosphate (P), and potassium (K). Other ingredients are sometimes added, e.g. zinc, which helps in plant growth, and clays, which is used to stabilize suspensions and prevent the settling of insoluble components. Most operations in fertilizer production, however, are concerned with the mining and manufacturing of the raw materials needed to produce the three main ingredients. These operations are also responsible for the bulk of the contaminants released into the environment.

The predominant contaminants associated with the fertilizer industry, also found in the investigated area, are; nitrate ( $\text{NO}_3$ ), ammonium ( $\text{NH}_4$ ), phosphate ( $\text{PO}_4$ ), sulphate ( $\text{SO}_4$ ), fluoride compounds (F), chloride (Cl), cadmium (Cd), and zinc (Zn). Various other heavy metals and radionuclides, especially Radium ( $^{226}\text{Ra}$ ), posing potential health and environmental risks may be released into the environment during the manufacturing of phosphoric acid from phosphate rock. The types and quantities depend on the content of the phosphate rock.



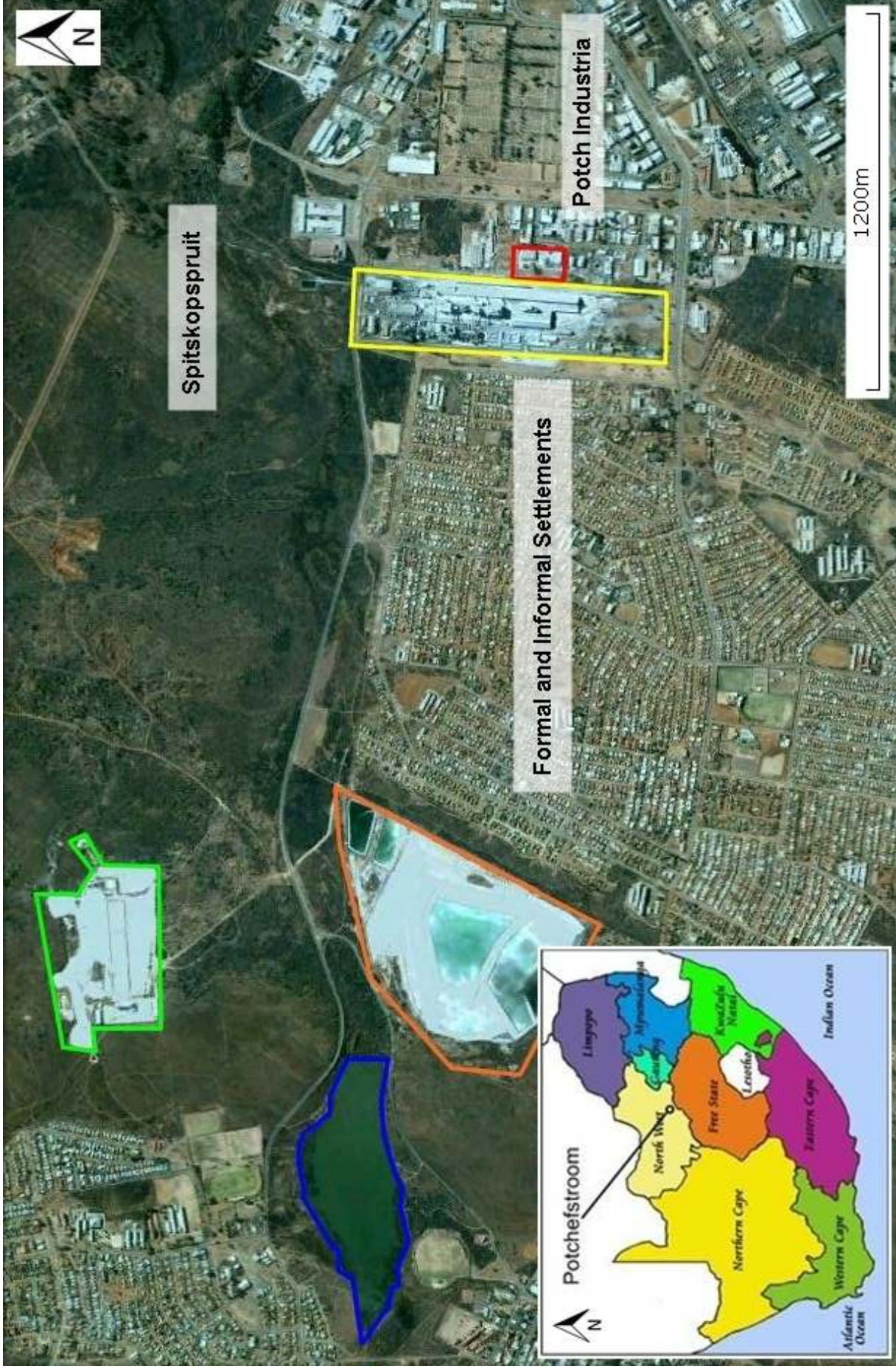


Figure 1: Aerial photograph of SNP and surroundings. The location of Potchefstroom is indicated on the inserted map of South Africa. Delineations; **red**: SNP, **yellow**: KFPF, **orange**: gypsum tailings dam, **green**: Oranje Mining and Transport Company, **blue**: Poorrijes dam.

## 1.1 Objectives

The objective of the study is to determine the environmental risks (immediate and long-term) associated with the operations at SNP (fertilizer mixing and loading) and KFPF (full scale fertilizer production).

The following deliverables are required:

- Quantifying the extent, location, and characteristics (physical, chemical, and toxicological) of potential contaminants (e.g. nitrate and sulphate),
- A conceptual understanding of the groundwater/geology of the area,
- Identify the movement of the plume, if any, and,
- Identify significant short- and long-term risks to the environment and human health.

A partial list of risks relevant to this study:

- Groundwater impacts,
- Impact on the quality of the groundwater used by users in Potch Industria, and,
- Impact on surface water (Spitskopspruit and confluence into the Wasgoedsspruit and then the Mooi River).

## 1.2 Overview of methodology

The steps to meet these objectives are as follows:

- Acquiring as much data from the study done by SRK Consulting on KFPF as possible,
- Gathering background information about the geological and geohydrological characteristics of the area,
- Geophysical study (Resistivity) to determine any anomalies in the subsurface significant to groundwater flow dynamics,
- Determining drilling, soil-, and water sampling targets,
- Drilling boreholes for monitoring purposes (groundwater samples and water levels),
- Conducting pumping tests to determine aquifer characteristics,
- Doing an EC profile of each borehole to determine the positions of possible zones of transport,
- Gathering water samples to determine contaminants of concern,



- Taking soil samples at various points and depths to determine which and in what concentrations contaminants of concern occur,
- Analysis and interpretation of all data,
- Construction of a geohydrological conceptual model,
- Considering various remediation options,
- Drawing conclusions, and,
- Recommending safe practices for the prevention of environmental contamination and industrial incidents.

### 1.3 Structure of the thesis

This thesis consists of nine chapters and four appendixes, viz.

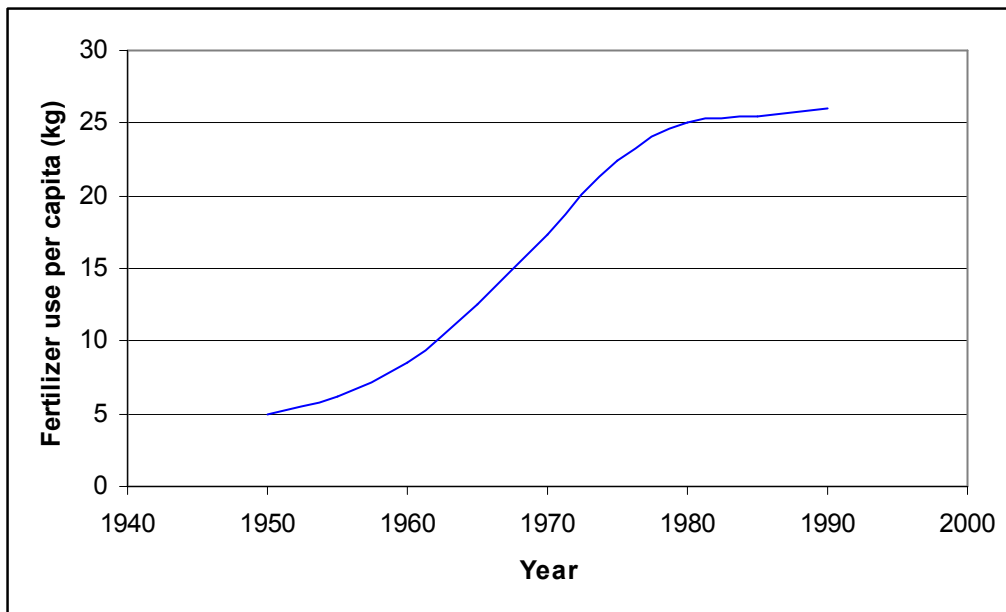
- Chapter 1 is an introduction to the investigated area, the fertilizer industry, and the aims of the study.
- Chapter 2 is a discussion on the growth trends, demand, consumption, and capacity for production in the fertilizer industry around the world and more specifically in South Africa.
- Chapter 3 is a general discussion of the main manufacturing processes and the resulting effluents of the various components making up fertilizers. Also discussed are the operating processes occurring on both the Kynoch Fertilizer Production Facility (KFPPF) and the Sasol Nitro Potchefstroom (SNP) plant, and their respective expected effluents.
- Chapter 4 is a discussion of the various “geo investigations” done in the study area. These include discussions on;
  - The regional and local geology,
  - The aquifers in the area,
  - The drilling performed, pumping tests conducted, and the geohydrological estimations obtained from these,
  - The geophysical investigation (Resistivity) conducted,
  - The topography, water levels, and drainage, and,
  - The climate and recharge of the region.
- Chapter 5 is a discussion on the various results obtained from the chemical analysis of the numerous soil and groundwater samples taken from the site. Included is an introduction discussing natural groundwater quality, mechanisms of contamination, and a statistical analysis.

- Chapter 6 is a conceptual model of the SNP site. The aim of the geohydrological conceptual model is to provide a basic visual representation and written description of the complex system.
- Chapter 7 is a discussion of the conclusions that can be drawn from the study. It includes a summary of the contaminants resulting from fertilizer manufacturing and a discussion of the limitations and shortcomings of the study.
- Chapter 8 is a discussion of the general recommended safe practices in the fertilizer industry, the guidelines set by Sasol Nitro, and suggestions for the improvement of current practices on SNP and the liquid fertilizer industry in general. It also includes the recommended remediation options for SNP.
- Chapter 9 lists the relevant references used as sources for the study.
- Appendix A discusses the various ammonia and radioactive components released into the environment as a result of the fertilizer manufacturing industry in South Africa. The manufacturing processes of ammonia were not included in the body of the dissertation due to it not being manufactured on either the SNP or KFPF sites, and because the discussion is quite lengthy. Radionuclides were not tested for in the study area, but may pose potential health and environmental risks, and it was hence deemed necessary to include a discussion on it in the appendix.
- Appendix B discusses the procedural approach of remediation and various different methods.
- Appendix C is a discussion on three case studies of investigations done on fertilizer manufacturing facilities around the world.
- Appendix D contains all the borehole logs and profiles.

## Chapter 2: The world fertilizer industry

### 2.1 Growth in the world fertilizer industry

The use of fertilizers increases agricultural production and productivity significantly which has been tremendously advantageous for economic development and the raising of living standards. Due to these benefits, the demand for fertilizers over the past few decades has grown drastically. With this growth in demand and associated growth in industry came an increasing awareness from the public, legislators, and environmentalists on fertilizer production and its risks. Figure 2 illustrates the increase in use of fertilizer per capita from 1950 to 1990.



**Figure 2: Fertilizer use per capita (Hodge, 1994).**

The fertilizer industry over the past few decades has had to continually comply with the growing number of legislation regarding production activities as a result of increasing environmental concerns. There exists a disparity between nations regarding the development, enforcement, and nature of environmental regulations, although attempts have been and are being made to extend regulations to all nations. The success of universalizing regulations will have a great influence on addressing environmental issues, and on the growth and geographical location of future fertilizer production facilities.

Fertilizer use in developed countries is approaching the level where there is optimum economic return, which means that growth in the industry has become less rapid. Developing countries are still lagging behind, but their rate of increase in production is much higher than developed countries and this trend is expected to continue for the next few decades.

The increasing awareness of environmental issues and the associated increase in regulations to minimize the environmental impact of the fertilizer industry will expectedly continually have to be suffered by the industry in future, not just in developed countries, but also continually more so in developing countries (Hodge, 1994).

## 2.2 Fertilizer demand and consumption around the world

According to the U.S. Census Bureau (2010), the world population of 6.8 billion as in 2010 is expected to increase to 9.2 billion by 2050. The rate of growth in developed countries is expected to be much lower than in developing countries. As the world population increases, the demand for food, and correspondingly, the demand for fertilizers, will increase.

Based on estimations made by Hodge (1994), the future total world fertilizer use will grow from 130 million tons in 1985 and 165 million tons in 2000 to 227 million tons in 2020. According to figures from the International Fertilizer Industry Association (IFA) (2008a), the total world consumption of fertilizers is expected to grow from 173.5 million tons in 2008 to 193.1 million tons in 2012, and according to the Food and Agriculture Organization of the United Nations (FAO) (2008), fertilizer demand will increase from 197 million tons in 2008 to 216 million tons in 2011/12. Figure 3 indicates the projected medium-term evolution of the regional fertilizer demand, as estimated by the IFA (2009).

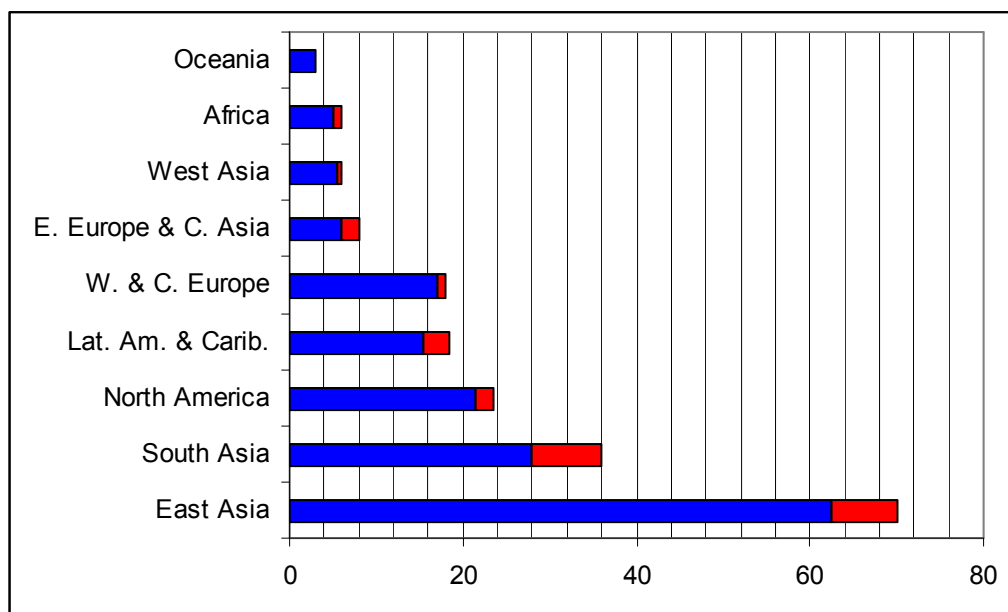


Figure 3: Projected medium-term evolution of regional fertilizer demand (in Mt Nutrients). Blue indicates the average use for the period 2006/7 to 2008/9, and the red the projected variation for 2013/14 (IFA, 2009)

Due to the worst recession since the Second World War, aggregate nutrient demand went down by 5.1% in 2008/9 from the previous year, i.e. from 168.1 to 159.6 million tons. The demand for nitrogen however has not been affected as much as the other nutrients, simply because farmers cannot afford to cut down on nitrogen fertilizer application without affecting crop production yield

too much. N, P, and K fertilizer demand is down 1.6, 7, and 14% respectively. Regions not affected by a drop in consumption are South and Central Asia, Eastern Europe, and Africa. The worst affected regions are West and Central Europe, and North and Latin America (IFA, 2009).

The gradual recovery of the world economy and prevailing strong agricultural market fundamentals are expected to bring about the slow recovery of fertilizer demand, viz. 3.6% in 2009/10. The demand for N, P, and K is expected to rise by 2.6, 6.1, and 4.1% respectively. A strong recovery is expected from North America with more modest recoveries from East Asia, and Central and Western Europe. Consumption in South Asia is expected to continue to increase but at a lower rate than in 2008/9, and consumption in South America is expected to further drop (IFA, 2009).

In the medium term, world fertilizer demand is also expected to gradually recover from its decline. In 2013/14 fertilizer demand is expected to increase 2.3% annually. Because of its decline in 2008/9, the demand for P and K fertilizers is expected to rise more rapidly (IFA, 2009).

**Table 1: Regional and sub-regional fertilizer consumption and estimated annual growth for 2007/8 to 2011/12 (FAO, 2008).**

<i>Regions and sub-regions</i>	<i>N</i>		<i>P</i>		<i>K</i>	
	<i>Share of world consumption (%)</i>	<i>Annual growth (%)</i>	<i>Share of world consumption (%)</i>	<i>Annual growth (%)</i>	<i>Share of world consumption (%)</i>	<i>Annual growth (%)</i>
<i>World</i>		1.4		2		2.4
<i>Africa</i>	3.4	2.9	2.5	1.0	1.6	2.0
<i>North America</i>	13.5	0.3	12	0.5	17.1	0.7
<i>Latin America</i>	6.3	2.4	13	2.8	17.5	2.9
<i>West Asia</i>	3.5	1.7	3.3	1.0	1.4	2.4
<i>South Asia</i>	19.6	2.2	20.5	3.5	10.9	4.2
<i>East Asia</i>	38.3	1.3	36.1	1.9	35.2	3.3
<i>C. Europe</i>	2.7	1.8	1.5	1.2	2.4	1.0
<i>W. Europe</i>	8.4	-0.3	5.6	-0.7	9.5	0.0
<i>E. Europe &amp; C. Asia</i>	3.0	2.4	2.0	4.5	3.1	1.6
<i>Oceania</i>	1.4	4.9	3.5	1.7	1.3	2.1

According to the IFA (2008a), the world fertilizer market entered a demand-pull cycle in early 2007. This was due to the overall increase in consumption and shortage of available supply. The production of fertilizers in 2007 reached record levels due to the industry trying to cope with the rising demand. The price of fertilizers also reached record levels. This can also be attributed to the availability of raw materials becoming scarcer. Table 1 indicates the regional and sub-regional fertilizer consumption and estimated growth prospects for 2007/8 to 2011/12 (FAO, 2008).

## 2.3 The global capacity for fertilizer production

The world's scientists have continually expressed their concerns that the production of food will not keep up with the demands made by the growth in population. However, in the 3 decades leading up to 1994, the world's food production nearly tripled. Fertilizer input and improved plant varieties are the main reasons given for this growth spurt (Hodge, 1994).

According to the FAO (2008), the total production of fertilizers is expected to grow from 206.5 million tons in 2007/08 to 241 million tons in 2011/12. The FAO (2008) also estimates that world fertilizer supply (nitrogen, phosphate and potash nutrient) will increase by ca. 3% every year between 2007/08 and 2011/12, more than adequate to cover the demand for growth of 1.9% annually.

The costs of production, raw materials, energy, market conditions, increasing environmental compliance, and other factors are influencing the geographical location of new fertilizer production facilities, the continued operation of existing facilities, and the decommissioning of old fertilizer facilities. The fertilizer industry has been especially challenged by the increasingly austere rules and regulations concerning fertilizer production pollution control and environmental compliance. Due to the aforementioned factors, and the sharper increase for demand for fertilizers in the developing world due to the rapid population growth there, the growth rate of fertilizer production has been influenced in such a manner that the growth rate in developing countries are now much higher than in developed countries. Economic considerations though will overall have the biggest influence on determining where new fertilizer production facilities will be located (Hodge, 1994).

Fertilizer production in Western Europe declined during the late 80's and early 90's. Western Europe lost 2 million tons of nitrogen production capacity between 1985 and 1990 and 0.7 million tons in the preceding 5 years. The production and consumption of fertilizers in North America have stayed relatively constant during the period of the late 80's and early 90's. The export of phosphate rock, phosphate fertilizers, and potash fertilizers from North America constitute a significant portion of the world's trade in these products and it is expected to continue with this trend for the next 10 years because of the low costs of manufacturing of these products in North America (Hodge, 1994).

According to the FAO (2008), Africa will remain a major phosphate exporter and increase nitrogen exports while importing all of its potash. There are ten countries in Africa who are primarily responsible for the fertilizer consumption in Africa, with Egypt, South Africa, and Morocco the main consumers. North America is expected to remain a net importer of nitrogen and a primary supplier of potash, while having an increasing phosphate shortage. Asia is predicted to produce a rapidly increasing excess of nitrogen and to have to continue to import phosphate and potash.

Fertilizer prices have increased drastically since the beginning of 2008. The major factors contributing to this increase are; a surge in agri-commodity demand, resulting in a surge in fertilizer demand, the rise in energy costs, the rise in ocean freight costs, higher steel and equipment prices, a shortage of specialized labour, a historical lack of investment in the fertilizer industry, and the recent devaluation of certain currencies (IFA, 2008b).

Since 2004 there has been a more positive outlook for the fertilizer industry which has led to investments, although at different levels for the three major nutrients. However, rapid changes in the market since 2006 have not given the fertilizer industry time to respond to the growing demand. Developing greenfield operations can take between three and ten years depending on the products and processes (IFA, 2008a).

## **2.4 The fertilizer industry in South Africa**

The use of organic fertilizer in South Africa started as early as Jan van Riebeeck, when he instructed Corporal Marcus Robbeljert to clean the stables twice a week in order to provide manure for the gardens. Apart from manure, guano was also used from very early on, and the first shipment arrived in 1666. It is estimated that the first time chemical fertilizers were used in South Africa was in 1890, when a small amount of “corn and hay” fertilizer was imported for a certain Van Heerden from Malmesbury. The first local fertilizer factory dates back to 1903 when SAFCO began producing phosphate from bones in Durban. Since then, various production companies have been established, viz. Kynoch (1919), SASOL, ISKOR, and FOSKOR (all three established in the early 1950's), among other.

South Africa has a very well developed fertilizer industry that is currently operating far below its true capacity. South Africa has much to offer in terms of helping to establish regulatory systems in the Sub-Saharan African region, and there exists a great challenge in helping to built up the soil fertility in the whole region. This is crucial in order to ensure food supply to a population expected to grow from ca. 800 million in 2010 to ca. 1800 million by 2050.

South Africa recorded its highest ever sales of fertilizer in 1981, when 3 290 243 physical tons were sold. This is equivalent to 872 113 tons of plant food. Sales have declined since then and settled to ca. 2 million tons per annum. The total percentage of plant food has however increased from 11.7% in 1955 to 31.6% in 2007. Sales in 2005 fell to their lowest in 35 years, due to an overproduction of maize the previous year.

Sasol supplies almost all of the ammonia, FOSKOR the majority of phosphates, and all South Africa's potassium requirements are imported.

Gauteng, Mpumalanga, Limpopo, and the North West provinces account for ca. 40% of the total fertilizer consumption in South Africa, while the Free State, Western Cape, and Kwazulu Natal account for ca. 20% each. Figure 4 indicates the fertilizer consumption in South Africa from 1950 to 2008, referring to nitrogen (N), phosphate (P), potassium (K), and the total consumption.

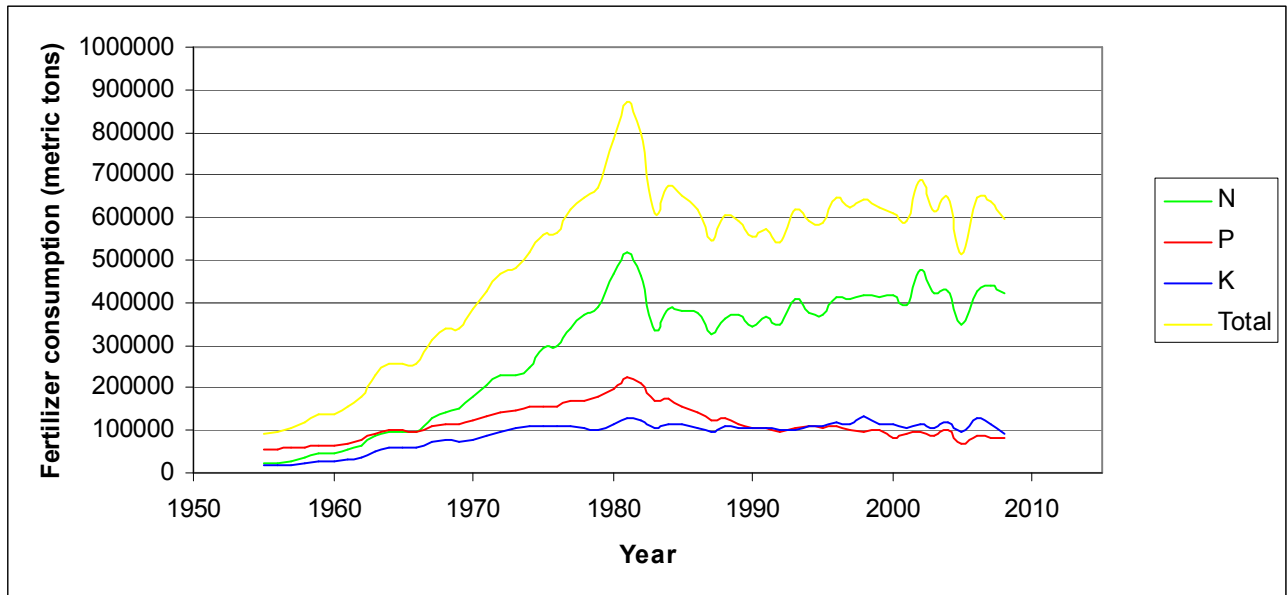


Figure 4: Fertilizer consumption in South Africa from 1955 to 2008 (FSSA, 2008a).

The South African fertilizer industry is currently fully exposed to world market forces, and operates in a completely deregulated environment with no import tariffs or government sponsored measures, as was the case in previous years (FSSA, 2008b).



## Chapter 3: Fertilizer production: raw materials, processes, and effluents

### 3.1 The nitrogen fertilizer industry

#### 3.1.1 Ammonia production

Ammonia was not produced on either the SNP or KFPF sites. For this reason, and also because its manufacturing processes are complicated and lengthy, the reader is requested to refer to Appendix A for an in-depth discussion of the various manufacturing processes and their respective effluents.

#### 3.1.2 Nitric acid production

##### 3.1.2.1 Introduction

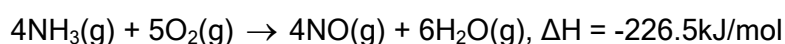
Nitric acid is an important intermediate product for the production of chemical fertilizers, and hence is produced in large amounts. It is manufactured in concentrations ranging between 55 and 65%, and is known as “diluted acid”. The primary effluent gases resulting from the manufacturing of nitric acid are nitrogen oxides (NO<sub>x</sub>) and oxygen (2 to 4vol%), and nitrogen and water vapours in lesser amounts. Nitrogen oxides are toxic to plants and animals, and in addition, corrosive as a result of their conversion into acids when coming into contact with precipitation. Worldwide pollution regulations set the limit for nitrogen oxides (NO<sub>x</sub>) released into the atmosphere at a concentration of 200ppm.

NO<sub>x</sub> is a mixture of nitrogen monoxide (NO) and nitrogen dioxide (NO<sub>2</sub>) in an undefined ratio. NO is colourless and NO<sub>2</sub> brownish red. Regulations mandate a colourless gas, and in order to cope with this requirement, NO<sub>2</sub> in the tail gas should be below 150ppm (vol.) (Cristescu, 1994).

##### 3.1.2.2 Chemistry of nitric acid production

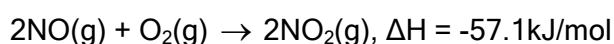
The raw materials used for nitric acid production are ammonia, oxygen (from air), and water. There are two stages in the chemical process:

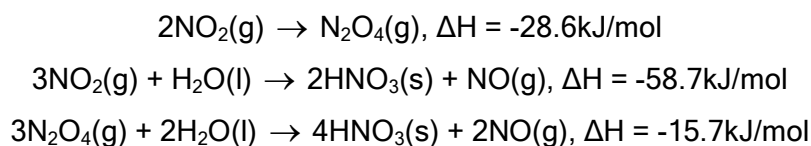
*Stage 1:* The oxidation of ammonia in the presence of a PtRh catalyst:



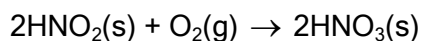
There are simultaneous undesired secondary reactions of ammonia oxidation, viz. the release of N<sub>2</sub> and N<sub>2</sub>O, and decomposition as N<sub>2</sub> and O<sub>2</sub> of a small part of the oxide formed. Practically, the NO/NH<sub>3</sub> conversion efficiency ranges between 94 and 98%.

*Stage 2:* The oxidation of nitrogen monoxide to nitrogen dioxide, followed by water absorption:





In addition to the oxidation in a gaseous medium of nitrogen monoxide, oxidation is also possible in a liquid medium, with the help of dissolved oxygen:



Oxidation in a liquid medium is very important for pollution control (Cristescu, 1994).

### 3.1.2.3 Manufacture of dilute nitric acid

The differences among the industrial processes in the manufacturing of dilute nitric acid are based on the various pressures at which the two stages mentioned above take place. There are two basic groups of processes:

1. *Mono-pressure processes*: ammonia oxidation and nitrogen oxide absorption take place at the same pressure (10 - 12atm).
2. *Dual-pressure processes*: ammonia oxidation takes place between 3 and 5atm and nitrogen oxide absorption between 10 and 12atm.

No detailed economic calculations show a clear advantage for either process.

The older nitric acid plants, when there were no regulations for NO<sub>x</sub> emissions, were built to operate at lower pressures. These plants are supposed to be equipped with special purification systems in order to comply with most current pollution control regulations (Cristescu, 1994).

### 3.1.3 Ammonium nitrate and nitrochalk production

#### 3.1.3.1 Introduction

Calcium ammonium nitrate (CAN, nitrochalk) is widely used as a source of nitrogen and is a standard solid fertilizer. Also often used is granulated ammonium nitrate (usually containing 33.5wt% N). The main starting materials used in the manufacturing of CAN are ammonium nitrate (AN) and calcium carbonate (CaCO<sub>3</sub>, lime). AN can be directly synthesized from nitric acid and ammonia, but can also be produced in the course of the nitrophosphate process. Limestone and dolomite are predominantly used as sources of lime.

CAN and AN are typically supplied as granular fertilizers. Granulation can be achieved by using various types of equipment, viz. prilling towers, pug mills, and drum granulators. Pan granulation processes have also been developed and used commercially. Safety standards, product quality, and problems involving materials of construction and pollution control, caused by high melt

temperatures and huge quantities of air required in prilling towers, have led to them being gradually phased out.

The BASF CAN process using ammonium nitrate wet  $\text{CaCO}_3$  is discussed, which is considered to be a process achieving high environmental standards (Nitzschmann, 1994).

### **3.1.3.2 Production of ammonium nitrate**

The reaction products of the neutralization of  $\text{NH}_3$  with  $\text{HNO}_3$  are an ammonium nitrate solution and steam/process vapours. The neutralization is usually performed in a single- or two-stage neutralizer, at ambient or elevated pressure. There are many different types of neutralizers in use.

The heat of neutralization may be used for the concentration of the ammonium nitrate solution, the production of export steam, the evaporation of liquid ammonia, and the preheating of ammonia and/or nitric acid, depending on the type and design of the neutralizer, the concentration of nitric acid, and the actual operating conditions. The process vapours and/or steam can also be used for evaporation of the ammonium nitrate solution to the desired final concentration.

Small amounts of ammonium nitrate and ammonia or nitric acid is found in the process vapours from neutralization and evaporation. These contaminants are removed with proper process design, but emissions of ammonium nitrate mists are hard to remove, due to their submicron size. When the process vapours are condensed, the remaining waste air will contain only small amounts of inerts, such as methane, hydrogen, and nitrogen. These inerts originate from the ammonia gas and contain only small amounts of  $\text{NH}_3$ . They could be used, for example, in the preheating of air, which is necessary in the drying of granulated fertilizers.

Prilling involves the solidification of droplets that fall down a tower, which forms the granular product. The droplets are usually formed using a rotating perforated bucket, and are cooled by a countercurrent stream of ambient air. The ammonium nitrate melt fed to the prilling tower should have a water content of less than 1%. This is also the case for prilling CAN or NP(K) fertilizers. The waste air from prilling or granulation contains ammonia and ammonium nitrate.

The rotating drum granulation method has advantages over the prilling tower method, viz. lower slurry temperatures and therefore reduced safety risks, reduced requirements for the materials of construction, and the absence of the necessary preheat additives (e.g., calcium carbonate for CAN or potassium salts for NPK). Due to these advantages, and the superior product quality obtained, the rotating drum granulation process has taken the place of prilling as the preferred solidification technique.

Of particular health and environmental concern to the prilling technique is the removal of submicron ammonium nitrate particles from the waste air. These particles are not removed with conventional techniques and are quite visible as a persistent blue haze. Fiber mist eliminators could be installed to remove them. Other systems for controlling emissions from prilling towers have also been developed (Nitzschmann, 1994).

### 3.1.3.3 Production of calcium ammonium nitrate (CAN)

Ammonium nitrate (94wt%) is either produced from  $\text{NH}_3$  and  $\text{HNO}_3$  in an AN synthesis section, or obtained by evaporation. In the case of evaporation, dilute AN (60wt%) results from the CN conversion reaction, which is part of the Odde process for manufacturing nitrophosphates. The Odde process involves applying nitric acid to phosphate rock to produce a mixture of phosphoric acid and calcium nitrate. A falling film evaporator is used to concentrate AN-94wt% to ca. 97 -

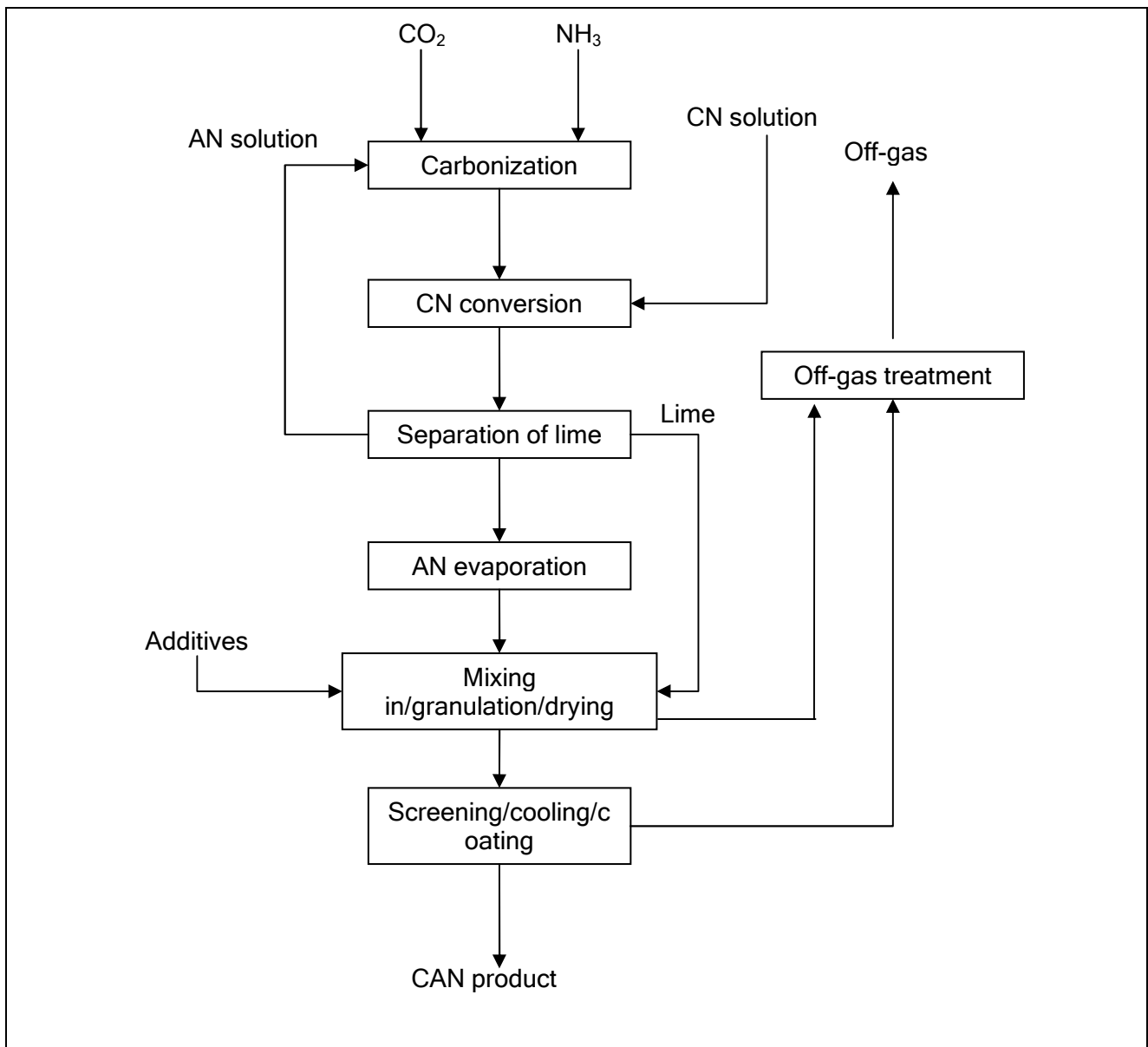


Figure 5: Production of calcium ammonium nitrate using ammonium nitrate wet lime originating from the Odde process (Nitzschmann, 1994).

98.5wt%. The concentrated AN is then used for AN/lime mixing. Figure 5 is a flow diagram of the production steps of calcium ammonium nitrate using ammonium nitrate wet lime originating from the Odda process.

The ammonium nitrate wet lime produced in the Odda process is neither washed with water nor dried. The calcium carbonate produced in CN conversion is merely filtered on a belt filter and treated with neutral ammonium nitrate. The resultant ammonium nitrate wet CaCO<sub>3</sub> contains up to 25wt% of AN solution. This wet lime is used in the AN/lime mixing section without further treatment. The product quality can be enhanced by adding inorganic additives.

The conditioned melt is then sprayed directly into a granulation drum. From here it undergoes the following steps: drying, screening, crushing of oversized material, recycling of over- and undersized material, cooling, and lastly, conditioning of the withdrawn on-size CAN product (Nitzschmann, 1994).

### 3.1.4 Urea production

#### 3.1.4.1 Introduction

The urea processes are based on how the unreacted materials are separated from urea synthesis solution and recovered, and are classified as follows;

1. *Once-through process*: Unreacted raw materials (CO<sub>2</sub> and NH<sub>3</sub>) are discharged to other plants in order to recover the NH<sub>3</sub>.
2. *Partial recycle process*: Unreacted raw materials (CO<sub>2</sub> and NH<sub>3</sub>) are partially separated in the first-stage decomposer and recovered in the first-stage absorber. The remainder is discharged to other plants for NH<sub>3</sub> recovery.
3. *Total recycle process*: Multi-stage decomposers are used to completely separate unconverted raw materials (CO<sub>2</sub> and NH<sub>3</sub>), which is then recovered in the multi-stage absorbers. It is then recycled back to the reactor for full recovery of CO<sub>2</sub> and NH<sub>3</sub> (Hidetoshi, 1994).

#### 3.1.4.2 Urea process

A typical flow diagram of the urea process is shown in Figure 6.

This is the chemical equation for the urea synthesized in the reactor;



NH<sub>3</sub> is supplied in the liquid- and CO<sub>2</sub> in the gaseous phase. Both these feedstocks contain unavoidable amounts of inert gases (e.g. H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>) (Hidetoshi, 1994).

### 3.1.4.3 Description of the urea process

#### 3.1.4.3.1 Introduction

The total-recycle stripping process based on the ACES process is discussed as a typical example of the process flow. Each section in the process is discussed.

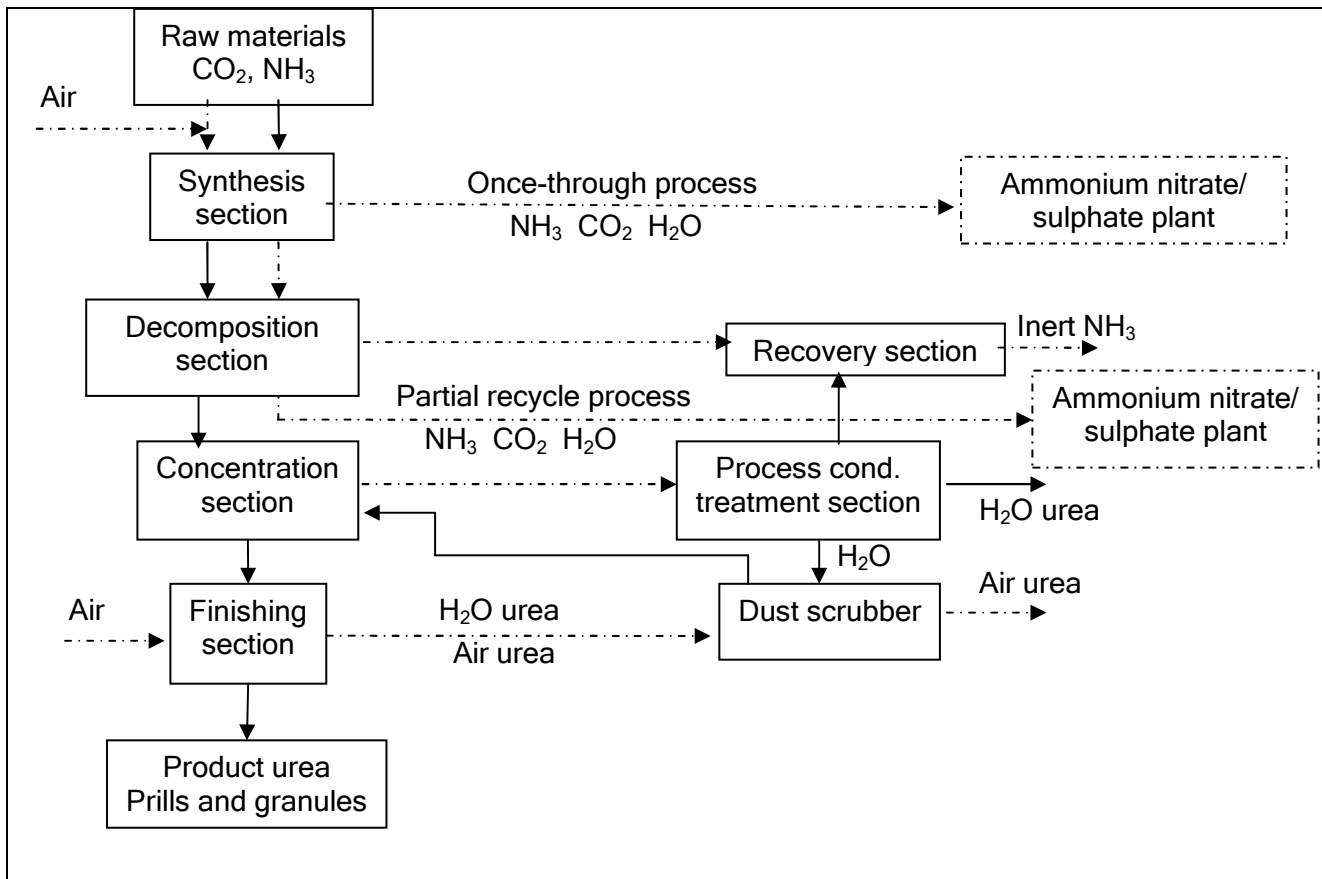


Figure 6: Urea process (Hidetoshi, 1994).

#### 3.1.4.3.2 Synthesis section

Urea is synthesized from NH<sub>3</sub> and CO<sub>2</sub> in a reactor operated at 175kg/cm<sup>2</sup>G, 190°C, and a NH<sub>3</sub>/CO<sub>2</sub> molar ratio of 4.0 to perform 68% of a one-pass CO<sub>2</sub> conversion rate. NH<sub>3</sub> is fed directly to the reactor, and compressed gaseous CO<sub>2</sub> fed to the bottom of a stripper as a stripping medium.

Passivation of the construction materials of the equipment is achieved by feeding air and CO<sub>2</sub> to the stripper. The urea synthesis solution, consisting of a mixture of excess NH<sub>3</sub>, ammonium carbamate, and water, is directed to the top of the stripper. Here the excess NH<sub>3</sub> is separated from the urea synthesis solution, after which it falls down to a falling film heater. Here, unconverted ammonium carbamate and excess NH<sub>3</sub> are decomposed and separated by CO<sub>2</sub> stripping and external steam heating.

Gas from the top of the stripper is introduced to the carbamate condenser, where the gaseous mixture is condensed and absorbed into the carbamate solution. The non-condensed gaseous mixture and carbamate solution are recycled back to the reactor.

The inerts in this section, i.e.  $N_2$ ,  $H_2$ ,  $CH_4$ , and  $O_2$ , which are contaminated by  $NH_3$ , and  $CO_2$ , poses a potential pollution problem. They are purged to the scrubber from the top of the reactor for the recovery of  $NH_3$  and  $CO_2$ , together with the inerts. The urea leaving from the stripper is further purified by the succeeding decomposition section (Hidetoshi, 1994).

#### **3.1.4.3.3 Decomposition section**

$NH_3$ ,  $CO_2$ , and water in the urea synthesis solution are further decomposed by stepwise decomposers, and absorbed by the respective absorbers. The urea solution is now concentrated to 99.7wt% for urea prill production, or 98.5wt% for urea granule production in the concentration section (Hidetoshi, 1994).

#### **3.1.4.3.4 Concentration section**

The urea solution from the decomposition section is fed to the vacuum concentrator for its preliminary concentration. It is then concentrated to the required level through the vacuum evaporator (Hidetoshi, 1994).

#### **3.1.4.3.5 Finishing section**

The urea solution from the concentration section is solidified for the production of either prills or granules. The urea dust in the effluent air from the prilling and granulating processes are scrubbed by sprayed aqueous urea solution through the packet bed dust scrubber, in order to reduce the urea dust emission (Hidetoshi, 1994).

#### **3.1.4.3.6 Recovery section**

The gaseous mixtures in the decomposition section are absorbed and recovered in respective absorbers. This is done using the process condensate as an absorbent. It is then recycled back to the synthesis section (Hidetoshi, 1994).

#### **3.1.4.3.7 Process condensate treatment section**

Water vapour evaporated in the concentration section is condensed in surface condensers under vacuum, together with urea mists, gaseous  $NH_3$ , and  $CO_2$ . Together they form the process condensate, which is then sent to the process condensate stripper and the urea hydrolyzer for treatment. The treated condensate can then be used for various purposes, e.g. boiler feed water, or makeup water to the cooling water (Hidetoshi, 1994).

### 3.1.5 Nitrogen in the subsurface

#### 3.1.5.1 Introduction

It was deemed necessary to include a special section on nitrate in groundwater, due its mobility in the subsurface, it being the predominant contaminant found in the groundwater resulting from operations on the SNP site (and the fertilizer industry in general), and the serious health risks it poses to infants and livestock.

Nitrate pollution is a serious problem in many parts of the world. The main anthropogenic source in highly developed countries is agricultural nitrate, largely derived from excessive fertilizer and manure application. Due to the expected growth of the fertilizer industry in developing countries, this problem is set to get worse. In rural areas where groundwater is extensively used for human and livestock consumption, special regulations are necessary.

Nitrate as such is not considered highly toxic when ingested by adults. The oral LD<sub>50</sub> for sodium nitrate is 4300mg/kg (LD<sub>50</sub> is the “Lethal Dose” 50%, i.e. the dose necessary to kill half the members of a tested population after a specific test duration). Nitrite, formed by reduction of nitrate, is however considered highly toxic, and the oral LD<sub>50</sub> of sodium nitrite is 120mg/kg. Sodium nitrite is a salt used in meat processing.

Nitrogen reduction occurs in the digestive systems of infants and livestock, which makes them particularly at risk to high nitrate levels. Nitrite binds with hemoglobin in the blood to cause methaemoglobinaemia (“blue baby syndrome”) in infants, which can be fatal. Methaemoglobinaemia can be treated with methylene blue (intravenously), or ascorbic acid.

**Table 2: The specifications for nitrate in potable water in South Africa (Tredoux *et al.*, 2009).**

Nitrate-N specifications (mg/l) (DWA)		
Potability class	Idea	<6
	Acceptable	6 - 10
	Marginal	10 - 20
	Poor	20 - 40
	Unacceptable	>40
Livestock	Acceptable	<110

Nitrate poisoning has been identified as responsible for livestock losses in many countries. In 2001, South Africa lost more than 60 heads of cattle due to nitrate poisoning. Table 2 indicates the specification for nitrate in potable water in South Africa. These are standards given by the Department of Water Affairs (DWA) and correspond to the World Health Organization (WHO) guidelines.



### 3.1.5.2 The nitrogen cycle and the interaction between the processes occurring in the unsaturated- and saturated zone

“Nitrogen is one of the main biogeochemical elements and along with carbon, oxygen, [sulphur] and phosphorus, these elements in their biogeochemical cycles constitute the main life-supporting system for our planet. The most important reactions involving nitrogen are of a biochemical nature and are either driven by microorganisms or enzymes. For this reason the impact of nitrates on groundwater needs to be viewed in terms of the nitrogen biogeochemical cycle [Figure 7 (only includes section applicable to this study)]. Whereas nitrogen compounds in most environments play a beneficial role, the presence of such compounds in water is generally detrimental.” (Tredoux *et al.*, 2009).

“Nitrogen inputs, whether due to natural fixation of nitrogen, fertilizer application, or pollution, all contribute to the pool of soil organic nitrogen. A series of (bacterially mediated) transformations are needed to convert the organic nitrogen to nitrate, which could potentially be leached to the groundwater. Anthropogenic inputs increase the soil nitrogen pool to such an extent that leaching of nitrate is enhanced. This is also true for fertilizer application to land, as well as the tilling of the soil which enhances the nitrification of soil organic nitrogen. Depending on the conditions in the unsaturated zone and in the aquifer, denitrification, i.e. reduction of the nitrate to nitrogen, is also possible. This is an important natural process which assists in maintaining the balance with respect to the nitrate in the groundwater.” (Tredoux *et al.*, 2009).

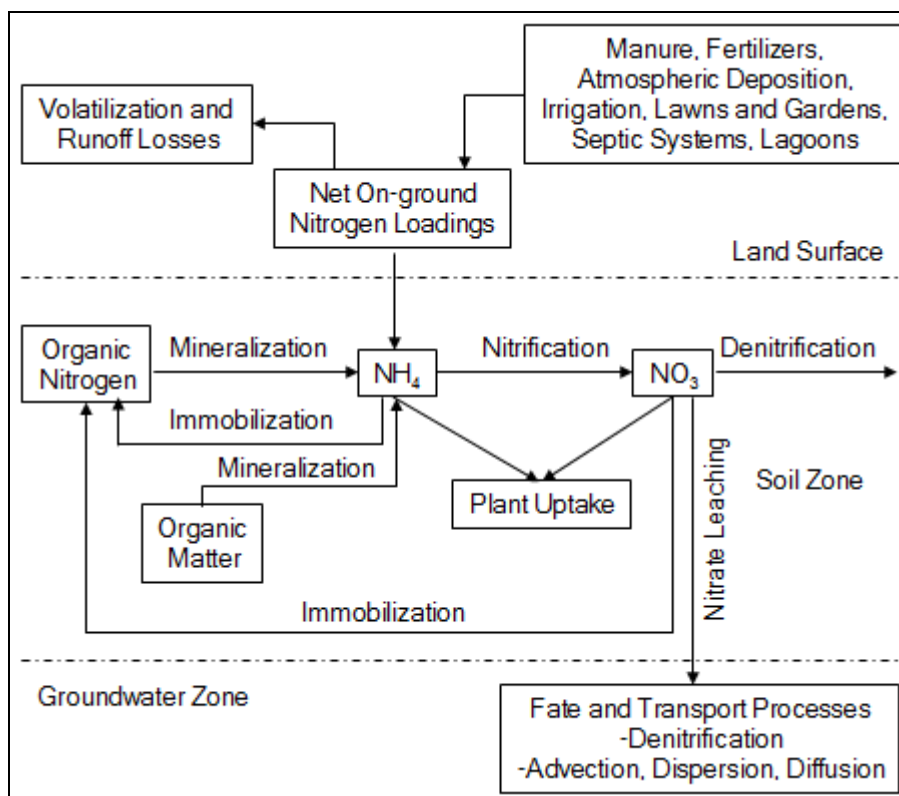
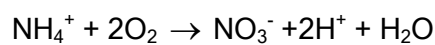


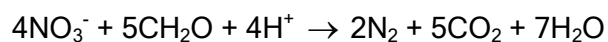
Figure 7: Schematic representation of the integrated "three-zone" approach showing the interacting processes that govern the occurrences of nitrate in groundwater (Almasri, 2006).

The nitrification process occurs in two stages, viz. ammonia is first oxidized to nitrite (NO<sub>2</sub>) by autotrophic ammonia-oxidizing bacteria (*Nitrosomonas*) and then to nitrate by autotrophic nitrite-oxidizing bacteria. Nitrite is quickly reduced or oxidized due to it being a generally unstable form of nitrogen. Nitrate then leaches into the saturated zone and is extremely soluble in water. It is not easily adsorbed by soil, which means that it migrates freely with the groundwater. In the saturated zone, nitrate can undergo denitrification into atmospheric nitrogen by heterotrophic bacteria (*Paracoccus* and *Pseudomonas*). The ammonium anion is immobilized as a result of adsorption to soil (Joekar-Niasar, 2009).

The chemical equation for the nitrification of ammonia (aerobic conditions: unsaturated zone) (Joekar-Niasar, 2009);



The chemical equation for the denitrification of nitrate (anaerobic conditions: mainly in the saturated zone, but partially in the unsaturated zone) (Joekar-Niasar, 2009);



“Nitrate leaching from the unsaturated zone is a complex interaction of many factors such as land use practices, on-ground nitrogen loading, groundwater recharge, soil nitrogen dynamics, soil characteristics, and the depth to the water table” (Almasri, 2006). See Figure 7 for a schematic representation of the interacting processes that govern the occurrences of nitrate in groundwater. The spatial distribution of nitrate concentration in groundwater is a function of; on-ground nitrogen loading from various sources present on the surface, the soil dynamics, and groundwater conditions (Almasri, 2006).

A study done by Stanton *et al.* on “The occurrence of agricultural chemicals in northeast Nebraska glacial till, 2002 - 04”, suggests that nitrate found accompanied by chloride in the unsaturated zone may imply that it is occurring naturally as a result of evapotranspiration (or at least partially so).

Figure 8 illustrates the distribution of groundwater nitrate (NO<sub>3</sub> as N) in Southern Africa. 50 000 groundwater sources were used to create the map. It is worth noting that there are areas with elevated nitrate levels in seemingly scarcely populated regions. This is common in semi-arid regions where significant loss of nitrogen from the soil zone may occur, causing the enrichment of groundwater with high levels of nitrate (Tredoux *et al.*, 2009).

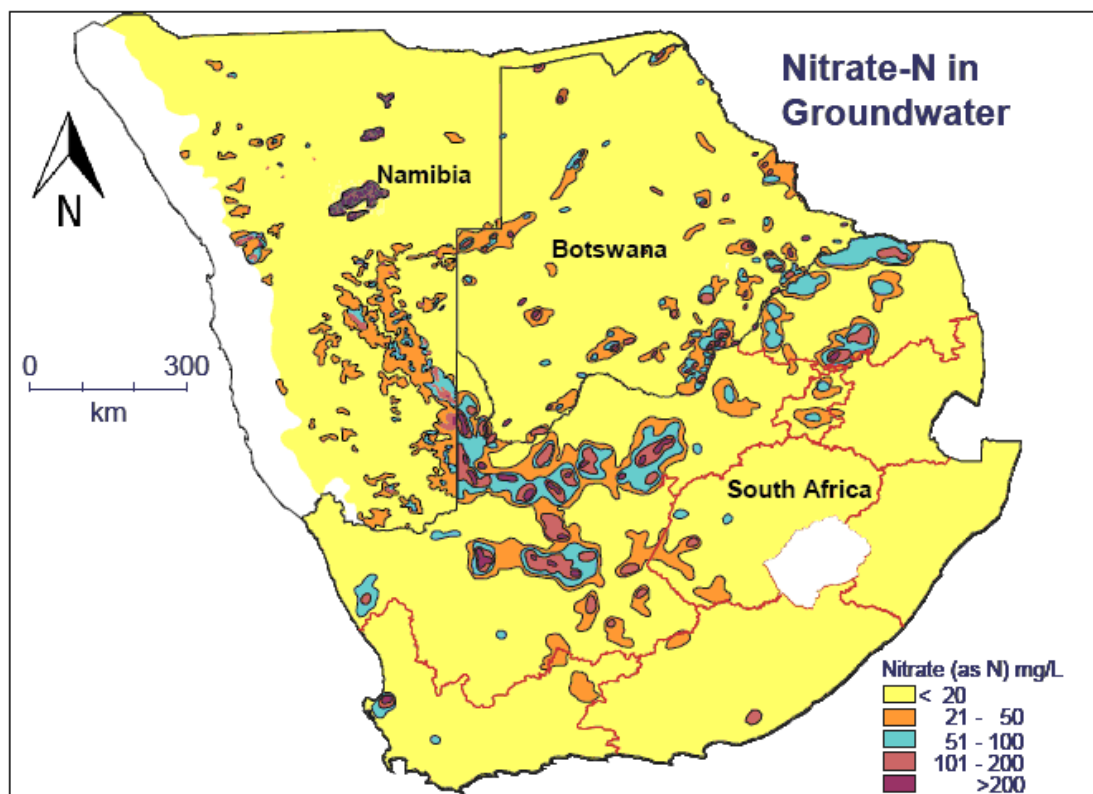


Figure 8: Map of the groundwater nitrate distribution in Southern Africa (Tredoux *et al.*, 2009).

### 3.1.5.3 The remediation of nitrate in groundwater

The removal of nitrate from groundwater is not easy. Nitrate may be non-selectively removed by ion-exchange or desalination, e.g. by reverse osmosis. Biological denitrification, a nitrate specific method, is widely used abroad in treatment plants, but requires expert technical knowledge. This method, also by in situ treatment methods, may be considered for town supply, but finding another water source is the preferable solution in rural areas (Tredoux *et al.*, 2009). Research is currently being done by the Council for Scientific and Industrial Research (CSIR) in Stellenbosch regarding the effectiveness of sawdust being used as feed for bacteria responsible for the denitrification of nitrate.

### 3.1.5.4 The nitrate concentrations found on the SNP site and surrounding area

(See Chapter 5 for a detailed analysis of the chemical results of the soil and groundwater samples taken from the SNP site and surrounding area).

The nitrate ( $\text{NO}_3$  as N) concentrations found on the SNP site ranges between 0.0004 - 1.9736kg/ton for soil samples, and between 144.2 - 938mg/l for groundwater samples. Groundwater samples taken from the KFPF site consistently show concentrations >100mg/l. Concentrations >900mg/l have also been found.

The highest concentration of nitrate found in a borehole other than those used by SNP and KFPF, was at Mighty Products Company at 6 Ross Street, whose borehole is located ca. 100m north of

the SNP site, and ca. 100m west of the KFPF site (see Figure 40 for the location of borehole ROSS6). A concentration of 532.84mg/l was found in the sample taken from their borehole by the researcher on the 12<sup>th</sup> of May 2010. Nitrate concentrations show a general decreasing trend with distance from the SNP and KFPF sites (to the north, east, and south; the gypsum tailings dam located ca. 2km west of the KFPF site has a detrimental impact on groundwater quality in the area between it and the KFPF site).

Nitrite (NO<sub>2</sub>) concentrations found on the SNP site ranges between 0 (trace) - 0.0514kg/ton for soils samples, and between 0 (trace) - 5.06mg/l for groundwater samples. Only trace amounts were found in Mighty Products Company's borehole. No information is available about the concentrations of nitrite found on the KFPF site. The lesser concentrations of NO<sub>2</sub> found are due to NO<sub>2</sub> being a relatively instable form of nitrogen, and hence undergo oxidation or reduction fairly quickly.

## **3.2 The phosphate fertilizer industry**

### **3.2.1 Introduction**

Phosphorus is a vital component in the existence of all living organisms. Phosphate rock belongs to the apatite class of minerals, and is also called apatite and phosphorite. Apatite refers to macrocrystalline fluorapatite of igneous origin, and phosphate rock to microcrystalline calcium fluorophosphate of sedimentary origin in trade markets.

In the industry, phosphate rock is defined as the beneficiated product of phosphate ore. Phosphate rock consists of calcium phosphate mineral apatite, with quartz, fluoride, calcite, dolomite, clay, and iron-aluminium oxide as gang constituents. These different chemical formulas are all commonly referred to as phosphate rock: Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F (fluorapatite), Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl (chlorapatite), and Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH) (hydroxyapatite). The predominant quantity of phosphate rock used in the world is of sedimentary origin, with the exception of kola apatite mined in northern Europe, which is of igneous origin.

The most common contaminants in the phosphate industry posing a potential threat to the environment are fluorine, uranium oxide, radon, cadmium, and thorium. Phosphate rock is however extremely insoluble and can be classified as "neutral" and not "water degradable" when considering its transport, storage, and processing (physical changes). It first needs to be treated with mineral acids like, sulphuric-, nitric-, and phosphoric acid, to make it suitable for the production of chemical fertilizers. An excess of acid decomposes the phosphate rock, which allows for the contaminants to be released or separated.

The phosphate content or grade is usually expressed as a percentage of  $P_2O_5$ . It may also be expressed as a percentage of bone phosphate lime (BPL), which was used when bones were still the major source of phosphate in fertilizer manufacturing. (BPL content =  $2.185 \times$  percent  $P_2O_5$ ).

There are an abundance of laws regulating surface mining and processing in the phosphate industry with the aim of minimizing the impact on the environment. There are however some issues with the industry not being able to fully comply with these regulations, due to costs and technological development (Sierra, 1994).

In South Africa, there are strict regulations controlling the mining and processing of phosphate rock. Foskor, the main supplier of phosphates in South Africa, retained their ISO 14001 (environmental management), ISO 9001 (quality management), OHSAS 18001 (occupational health and safety management), and SANS 16001 (HIV/AIDS management) certifications, which are all requirements for mining and processing phosphate rock in South Africa. In addition to these regulation standards, Foskor must also comply with the SANS 451:2008 standard for spirometry as of 2010 (Foskor, 2010).

### 3.2.2 Phosphate rock: Raw material for fertilizers

Phosphate rock is a vital raw material in the manufacturing of several chemical fertilizers, viz.;

1. *Normal superphosphate*: Finely ground phosphate rock is treated with sulphuric acid in order to convert insoluble tri-calcium phosphate to mono-calcium phosphate. Normally contains 18 - 21%  $P_2O_5$ .
2. *Wet-process phosphoric acid*: Phosphate rock is acidulated with sulphuric acid to transform all the calcium in the rock from calcium phosphate to calcium sulphate.
3. *Triple superphosphate (TSP)*: Phosphate rock acidulated with phosphoric acid to produce a granular fertilizer (44 - 47% available  $P_2O_5$ ).
4. *Ammoniated superphosphate*: The resultant products when aqueous or anhydrous ammonia is used for the neutralization of the free acid in superphosphates. Ammoniacal solutions of nitrates and urea are also used. Ammoniated superphosphates, which were used exclusively as a "base" for NPK fertilizers, have been displaced by more highly concentrated phosphates.
5. *Ammonium phosphates*: Ammonium phosphates are the resultant product when anhydrous ammonia is used to neutralize orthophosphoric acid. Impurities in the phosphoric acid limit the amount of plant food, and classifies it into grades, the most popular ones being;
  - 5.1. *Monoammonium phosphate (MAP)*: 10% N, 50%  $P_2O_5$ ; 11% N, 48%  $P_2O_5$ .
  - 5.2. *Diammonium phosphate (DAP)*: 18% N, 46%  $P_2O_5$ .

(For a complete study of the production of granular triple superphosphate (TSP) and single superphosphate (SSP), and their environmental impact, see Chapter 22 in: Hodge, C. A. and

Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press).

In all the above mentioned phosphate products, acidic fluoride compounds evolve from the reaction vessels. Emissions need to be treated. The most notorious and abundant by-product of phosphate fertilizer manufacturing is gypsum (calcium sulphate), which is separated by filtration during the production of wet-process phosphoric acid. Gypsum is regarded as a strong pollutant due to its acidic characteristics, but more particularly because it is the carrier of a large percentage of the radon contained in the phosphate rock.

A big environmental and health concern is the specific elements (heavy metals) present in phosphate rock, which is also found in small amounts in phosphate fertilizers. An estimated 70 - 80% of the trace elements present in phosphate rock become part of the phosphate fertilizer. Table 3 indicates the heavy metals and the respective average amounts found in phosphate rock, compared with the respective amounts expected to be found in soil (Sierra, 1994).

As indicated in Table 3, the input of heavy metals through fertilization is small in comparison with that naturally present in soil, with the exception of cadmium. Cadmium is highly toxic to human beings, and the main external sources of cadmium are from metallurgic smelting dust and inorganic phosphate fertilizers. Due to its health and environmental risks, cadmium is a highly undesired element in fertilizers. Concentrations in the soil build up over time with the continuous application of phosphate fertilizers on agricultural land (Sierra, 1994).

**Table 3: Heavy metals content in phosphate rock compared to typical content expected in soil (Sierra, 1994).**

<i>Element</i>	<i>Average content (mg/kg)</i>	
	<i>Rock</i>	<i>Soil</i>
<i>Arsenic</i>	7	6
<i>Cadmium</i>	25	0.35
<i>Chromium</i>	150	70
<i>Cobalt</i>	2	8
<i>Copper</i>	30	30
<i>Lead</i>	6	35
<i>Manganese</i>	30	1000
<i>Mercury</i>	0	0.06
<i>Molybdenum</i>	5	1.2
<i>Nickel</i>	35	50
<i>Zinc</i>	100	90

In South Africa, the main source of phosphate rock is from the Phalaborwa Igneous Complex. The typical cadmium concentrations found in these rocks are 4mg/kg rock and 23mg/kg phosphorus. This is below European import standards, which is a concentration of cadmium <60mg/kg phosphorus (RIRDC, 1999).

### **3.2.3 Phosphate rock processing**

#### **3.2.3.1 Physical changes**

A very small quantity of the phosphate rock is used for direct application in agricultural or industrial products. Rubber trees cultivated in acidic soils in Australia and Indonesia, for example, do well with the direct application of finely ground phosphate rock. However, almost all of the chemical processes that use phosphate rock as a raw material require it to be subjected to one or more of the physical changes described below (Sierra, 1994).

#### **3.2.3.2 Wet or dry screening**

Phosphate rock is regularly classified and valued according to its particle size before it is subjected to chemical treatment. Wet or dry screens are used as a preparation step to enhance the chemical reaction and increase the amount of  $P_2O_5$  recovered. The ideal particle size for phosphate rock is considered to be smaller than 35mesh and larger than 325mesh. A high content of intermediate sized particles causes dust problems when loading, unloading, and handling the product. A high content of coarse particles results in a lower reactivity index, and hence a lower yield of  $P_2O_5$  (Sierra, 1994).

#### **3.2.3.3 Grinding**

The phosphate rock delivered from mines hardly ever has the desired particle size. The main purpose of rock grinding is to increase the surface area of the rock exposed in the chemical reaction, in order to increase reactivity and conversion. There are five variables determining the degree to which phosphate rock needs to be subdivided:

1. Rock origin; feed size.
2. Recovery required.
3. How the rock will be processed.
4. Retention time and designed circulation.
5. Level of agitation in reactors.

In present industry practices, wet grinding is preferred over dry grinding, due to energy saving and pollution control advantages.

Mills are the main section of the grinding circuit. A few examples of mills used in the phosphate industry are; rod-, ball-, and spring-loaded roller mills. The type of mill used depends on the configuration of the grinding circuit, the nature and size of the feedstock, and the control required to satisfy particle sizing (Sierra, 1994).

#### **3.2.3.4 Drying**

Phosphate rock dryers reduce the moisture content of wet stored rock to users or according to shipping specifications. Rotary dryers are preferred when a high tonnage rate is required and fluid-

bed reactors when higher energy efficiency is desired. Bunker C fuel oil or natural gas provides the heat required to dry the rock (Sierra, 1994).

### **3.2.3.5 Calcination**

When phosphate rock is calcinated, it is heated to below its melting point in order to bring about a state of thermal decomposition, and for destructive distillation of organic compounds. It is used also to improve beneficiation of the ore. Calcination systems are similar to those used for drying (Sierra, 1994).

### **3.2.3.6 Defluorination**

In order to increase the amount of available  $P_2O_5$  in phosphate rock, it is put through a process of defluorination by fusion at elevated temperatures. Fluorine is removed through volatilization (as HF).

Depending on the rock origin, certain reagents may be added to facilitate the removal of fluorine without fusion, or it can also be done by actually melting the rock. For effective defluorination to occur, water vapour normally has to be present. The process requires a temperature of at least  $1320^{\circ}C$ .

Quick cooling is essential in order to obtain high solubility, and to prevent the  $P_2O_5$  from reverting to an insoluble form. The final product is categorized on the basis of the total amount of  $P_2O_5$  present, and is essentially fluorine free. The fused tricalcium phosphate is a good source of phosphorous and calcium for supplementing livestock and poultry feed, and the recovery of gaseous HF could be commercially attractive due to its concentration (Sierra, 1994).

## **3.2.4 Sulphuric acid production**

### **3.2.4.1 Introduction**

Acid rain has become an increasing environmental problem, and is caused primarily by significant quantities of  $SO_x$  and  $NO_x$  released into the atmosphere from various point sources. The predominant source of  $SO_x$  is considered to be from sulphur containing solid and liquid fossil fuels used in great quantities in thermo-power stations. The second most predominant source is  $SO_x$  released into the atmosphere by the chemical industry, and in particular, the sulphuric acid industry.  $SO_x$  does not only cause atmospheric pollution, but rivers and soils can be contaminated as well.

Huge amounts of  $SO_2$  and  $H_2SO_4$  are released into the atmosphere. In 1994, an estimated 2.13 million tons/year of  $SO_2$  and 320 000 tons/year of  $H_2SO_4$  were released into the atmosphere, arising from unabsorbed  $SO_3$  when expressed as  $H_2SO_4$  totaling ca. 3.6 million tons/year (Ciobanu, 1994).



### **3.2.4.2 Raw materials**

The predominant raw materials used in the manufacturing of sulphuric acid are sulphur, pyrites, and SO<sub>2</sub>-containing gases from non-ferrous metallurgy. The principles involved in the materials flow and technological phases corresponding to the raw materials are indicated in Figure 9 (Ciobanu, 1994).

### **3.2.4.3 Pollution sources in various process steps**

The most adverse pollution effects in the sulphuric acid industry are created when pyrites are used as a raw material. Using gases from non-ferrous metallurgy as a raw material generates the next most noxious effects, and the sulphur-based process is the least harmful of the three. Table 4 lists the polluting agents that may appear in various stages of the three types of sulphuric acid processing.

There are numerous health and environmental risks in sulphuric acid processing. Effluents released cause various environmental problems, plants operate at very high temperatures (900 - 1050°C), and sulphuric acid is handled at various strengths, which can be extremely corrosive. For these reasons, special care should be taken during plant design, construction, and operation to minimize environmental pollution.

There are ever more stringent environmental regulations controlling the discharge of sulphur containing flue gases into the atmosphere. The amount of sulphur released into the atmosphere is reduced by flue gas desulphurization, as discussed in A.1.2.1 (Ciobanu, 1994).

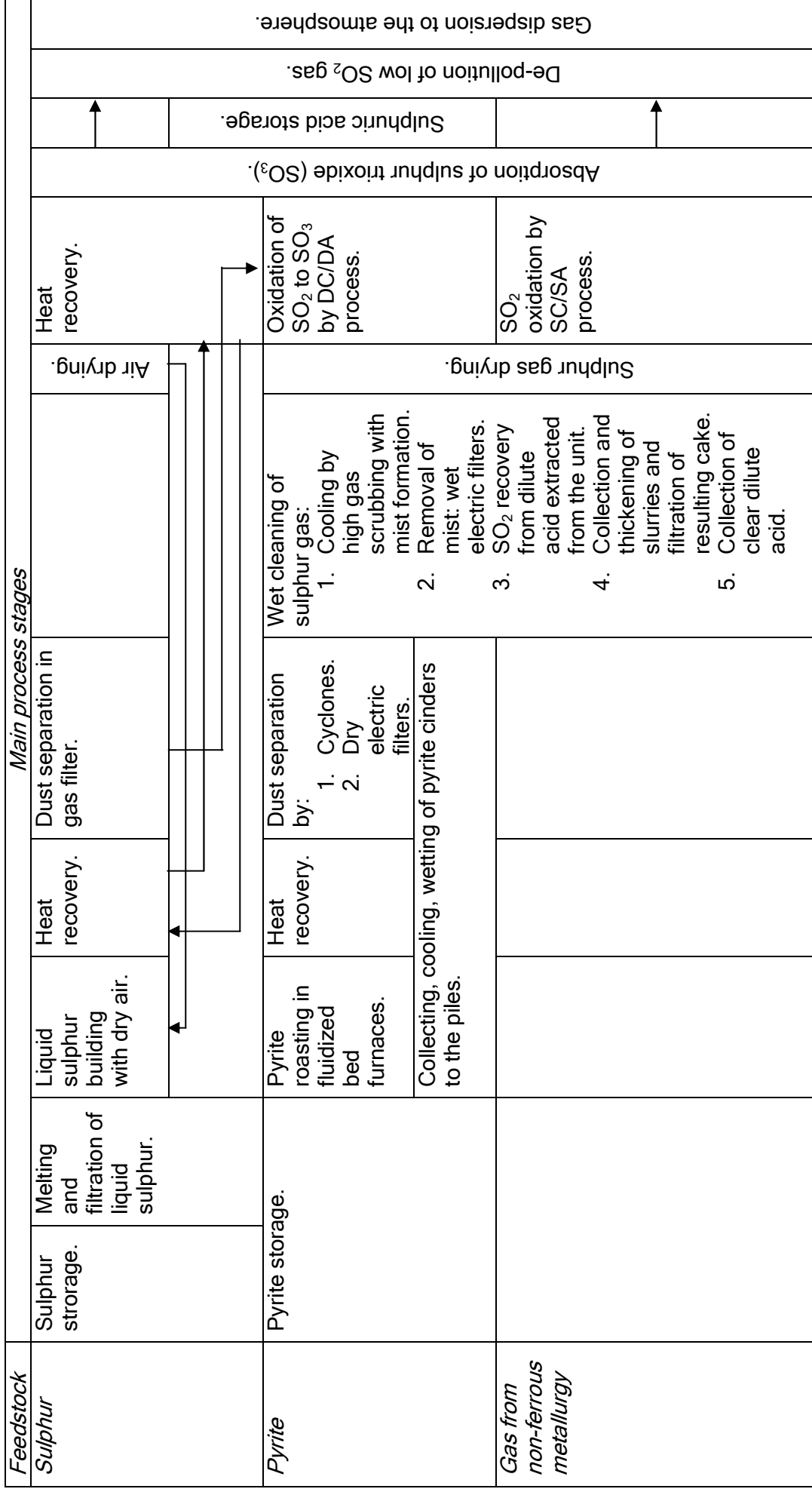


Figure 9: Manufacture of sulphuric acid, with main stages for processing gas from sulphur burning, pyrite roasting, and non-ferrous metallurgy (Ciobanu, 1994).

**Table 4: Possible polluting agents in sulphuric acid processing (Ciobanu, 1994).**

Technological stage	Raw material		
	Elemental sulphur	Pyrite	Gases from non-ferrous metallurgy
1. Raw material storage	Sulphur dust (powder) SO <sub>2</sub> -containing gases originating from self-ignition.	Pyrite dust	
2. Raw material preparation sulphur melting	Sulphur aerosol with water vapour from sulphur melting. Gases with SO <sub>2</sub> originating from sulphur self-ignition.		
3. SO <sub>2</sub> -carrying gases from burning of raw materials	SO <sub>2</sub> -containing gases.	Pyrite dust from the feeding point SO <sub>2</sub> -containing gases and cinder dust especially at start-up of burning.	
4. Waste heat recovery from SO <sub>2</sub> gases	SO <sub>2</sub> -containing gases.	SO <sub>2</sub> -containing gases Pyrite cinder dust.	
5. Dry purification of SO <sub>2</sub> -containing gases		Cinder dust during mechanical handling.	
6. Collection, cooling, wetting, and handling of pyrite cinder during transport to stockpile		Pyrite cinder dust, SO <sub>2</sub> -containing gases from the cinder cooling drum.	
7. Wet purification of SO <sub>2</sub> -containing gases		Acid sludge with H <sub>2</sub> SO <sub>4</sub> , SO <sub>2</sub> -saturated, containing As, Se, Te, Fe, and other compounds.	Acid sludge with H <sub>2</sub> SO <sub>4</sub> , SO <sub>2</sub> -saturated, containing Pb, Zn, Cu, Fe, Cd, As, Se, Te, etc.
8. Drying of SO <sub>2</sub> -containing gases; air drying in case A	Possible leakage of concentrated sulphuric acid because of reduction in system tightness or technical defects.	Possible leakage of concentrated H <sub>2</sub> SO <sub>4</sub> mist forming at 175250mg/cm <sup>3</sup> saturation of the drying acid with SO <sub>2</sub> .	
9. Conversion of SO <sub>2</sub> to SO <sub>3</sub>	SC/SA (single conversion/single absorption) process. SO <sub>2</sub> to SO <sub>3</sub> conversion: 98.982%. Untransformed SO <sub>2</sub> : about 13.3kg SO <sub>2</sub> /ton H <sub>2</sub> SO <sub>4</sub> . When vanadium catalyst with cesium promoter is used, the transforming degree of SO <sub>2</sub> to SO <sub>3</sub> could reach 99%; when not transformed, SO <sub>2</sub> decreases to 6.6kg SO <sub>2</sub> /ton H <sub>2</sub> SO <sub>4</sub> . DC/DA (double conversion/double absorption) process. SO <sub>2</sub> to SO <sub>3</sub> conversion: 99.5997%. Untransformed SO <sub>2</sub> : about 2.6kg SO <sub>2</sub> /ton H <sub>2</sub> SO <sub>4</sub> .		

**Table 4 (continued): Possible polluting agents in sulphuric acid processing (Ciobanu, 1994).**

Technological stage	Raw material	
	Elemental sulphur	Pyrite
10. SO <sub>3</sub> absorption	Gases from non-ferrous metallurgy	
	SC/SA process.	
	Final absorption recovery: 99.9%.	
	Possible forming of mist in the tower due to the absorption process disturbing about 5001750mg/N.m <sup>3</sup> gas.	
	Non-absorbed gas to be released in the atmosphere, equivalent to 2kg H <sub>2</sub> SO <sub>4</sub> /ton H <sub>2</sub> SO <sub>4</sub> .	
	DC/DA process.	
11. Sulphuric acid storage	Final absorption recovery: 99.9%.	
	Forming of mist in the intermediary tower due to the absorption process disturbing about 5001750mg/N.m <sup>3</sup> gas.	
	Non-absorbed SO <sub>3</sub> to be sent to the atmosphere, equivalent to 2kg H <sub>2</sub> SO <sub>4</sub> /ton H <sub>2</sub> SO <sub>4</sub> .	
	Leaking of concentrated H <sub>2</sub> SO <sub>4</sub> during loading and unloading, or due to mechanical defects in the equipment.	
	Forming H <sub>2</sub> accumulated under the tank cover, due to the corrosion process.	
	Release of SO <sub>2</sub> dissolved in the drying acid in cases B and C.	
12. Reduction of SO <sub>2</sub> + SO <sub>3</sub> content of final gases	Pollution reduction for the DC/DA process 2 + 2 with H <sub>2</sub> O <sub>2</sub> or H <sub>2</sub> SO <sub>5</sub> .	
	To be considered for plants operating using the SC/SA process, where the final gases could be important and where plant changeover to the DC/DA process would be difficult, especially in cases B and C.	
13. Dispersion of final gases containing SO <sub>2</sub> and SO <sub>3</sub>	By applying one of the known methods to catch SO <sub>2</sub> - and SO <sub>3</sub> -containing gases, one can expect to reduce the pollutants in the atmosphere by 90.97%.	
	Final gases with SO <sub>2</sub> and SO <sub>3</sub> traces have to be dispersed in the atmosphere at a height above ground that will ensure lower concentrations than those of federal local standards.	
	Determination of the dispersing stack: height is a specific calculation based on the quantities of SO <sub>2</sub> and SO <sub>3</sub> released, possibly added to similar emanations in the area, climatic conditions, etc.	

(A comprehensive study of the various stages of the three types of sulphuric acid processing corresponding to the raw materials, and the polluting agents that may appear at the respective stages (listed above in Figure 9 and Table 4), was done by Teodor Ciobanu, and can be found in Chapter 14 of Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press. The processes are extremely complex and extensive, and fall outside the scope of this study.

### 3.2.5 Phosphoric acid

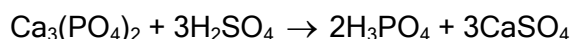
#### 3.2.5.1 Introduction

Phosphoric acid is produced from phosphatic ores mined in various parts of the world. The two main geological origins of phosphatic ores are;

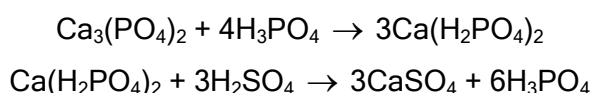
1. *Igneous*. As found in Kola, South Africa, Brazil, etc.
2. *Sedimentary*. As found in Morocco, Algeria, Jordan, U.S.A., etc.

The phosphate minerals in both groups are of the apatite group. The most commonly encountered variants are Fluorapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH})_2$ ) and Francolite ( $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F},\text{OH})_{2+x}$ ).

Phosphoric acid is produced when sulphuric acid is added to phosphate rock. The basic chemistry is extremely simple: The tricalcium phosphate in the phosphate rock is converted by the reaction with sulphuric acid into phosphoric acid and the insoluble salt, calcium sulphate;



The reaction is self-limiting, due to the insoluble calcium sulphate forming on the surface on the phosphate rock. This problem is limited by initially keeping the rock in contact with recirculated phosphoric acid to convert it as far as possible to the soluble monocalcium phosphate, and then by precipitating calcium sulphate with sulphuric acid:



The calcium sulphate exists in various different crystal forms, depending predominantly on temperature, the  $\text{P}_2\text{O}_5$  concentration, and free sulphate content.

There are various process routes available for the production of phosphoric acid. The Dehydrate-, Hemihydrate- (HH) and Recrystallisation process routes are some of the most commonly used (EFMA, 2000).

#### 3.2.5.2 Phosphoric acid by wet process

Discussed in this section are the various effluents causing environmental pollution related to “phosphoric acid by wet process”.

### 3.2.5.2.1 Fluorine-containing gases

Fluorine containing gases are unwanted effluents of the phosphate fertilizer industry, and pose potentially serious health and environmental risks. Phosphate ore typically include fluoride minerals, which is emitted as gaseous HF and SiF<sub>4</sub> throughout the fertilizer manufacturing process.

According to the regulations of the Clean Air Act of 1991 in the United States, no more than 10g of fluorine per ton of equivalent P<sub>2</sub>O<sub>5</sub> feed to the plant may be discharged into the atmosphere. For this reason, certain areas of a phosphate fertilizer plant need to be vented to fluorine scrubbers. These areas include any combination of reactors, filters, evaporators, and hot wells (Parish, 1994).

### 3.2.5.2.2 Phosphogypsum

For every ton of P<sub>2</sub>O<sub>5</sub> produced, 5 tons of by-product phosphogypsum also results. Phosphogypsum produced by the conventional dihydrate process has little use, but better quality phosphogypsum useful for wallboard and cement has been produced by improved processes in Japan and other countries limited by space available for waste disposal. Phosphogypsum can be useful as a fertilizer for soils deficient in Ca and S, and acid soils rich in Al and Al<sup>3+</sup> (it converts harmful Al<sup>3+</sup> to AlSO<sub>4</sub><sup>+</sup>). Some countries also use a portion of phosphogypsum to produce sulphuric acid and cement by calcination with clay. Gypsum is slightly soluble in water, and when applied as a fertilizer, usually penetrate 10 - 30cm into the soil, depending on the amount of gypsum and water applied. Table 5 indicates examples of phosphogypsum composition resulting from various processes.

**Table 5: Examples of phosphogypsum composition (%) (Ando, 1994).**

<i>Process</i>			<i>P<sub>2</sub>O<sub>5</sub></i>		<i>F</i>	<i>SiO<sub>2</sub></i>	<i>R<sub>2</sub>O<sub>3</sub></i>
	<i>CaO</i>	<i>SO<sub>3</sub></i>	<i>Total</i>	<i>Water soluble</i>			
<i>Dihydrate</i>	30.75	44.71	0.81	0.17	0.88	2.23	1.33
	31.43	44.60	0.29	0.09	0.24	0.98	0.59
<i>Hemihydrate dihydrate</i>	32.22	44.11	0.31	0.09	0.84	0.63	0.23
	32.50	45.53	0.20	0.02	0.77	0.33	0.15
	31.93	44.03	0.32	0.12	0.34	1.43	0.63
<i>Hemihydrate</i>	30.50	44.32	0.40	0.10	0.42	1.12	1.14

The information presented in this section is of the methods practiced at the New Wales plant of IMCAgrico Company in Mulberry, Florida.

Gypsum is commonly discharged from filters as a wet cake and immediately slurried with pond water (water from the process water cooling pond). This slurry is then fed to a gypsum storage area. Generally, in a new plant the slurry can be discharged by gravity directly to the gypsum storage area. As the storage area fills up, a surge tank and pumping system is required to lift the slurry to the top of the gypsum stack.

When the slurry reaches the top of the gypsum stack, it is distributed around the stack perimeter for deposition into the settling areas. This is done using pipelines and/or rim ditches. Rim ditches are established by building a berm between the settling area and perimeter dam. Figure 10 illustrates a cross section of a typical perimeter dam and rim ditch.

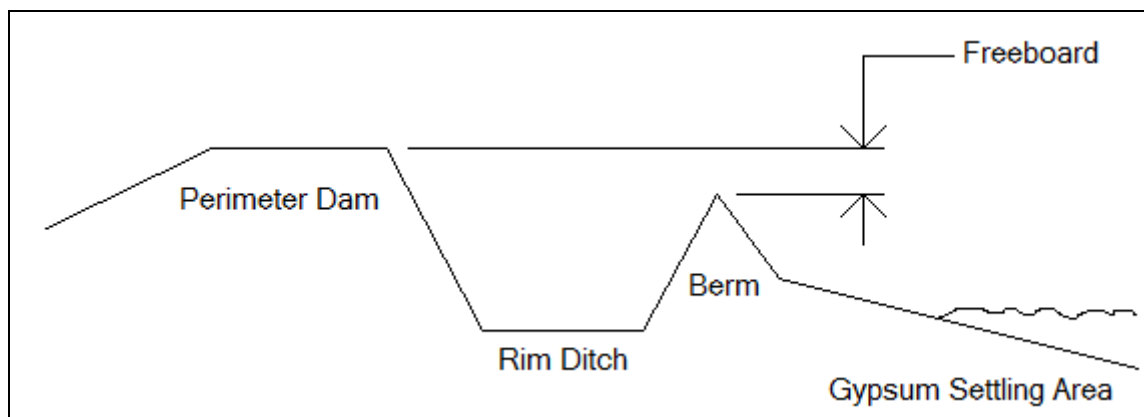


Figure 10: Cross section of perimeter dam and rim ditch (Ando, 1994).

Most of the slurry water percolates through the gypsum stack to collection ditches at the base of the stack and/or to the process water cooling pond. Many gypsum stacks have spillway systems with pipes in order to decant and transport water from the settling areas to the cooling pond. Pond water should be managed properly (Ando, 1994).

### 3.2.5.2.3 Radioactive components

The types and amounts of radionuclides released into the environment and found in fertilizer end products depend on the content of the phosphate rock. The reader is requested to refer to Appendix A for an in-depth discussion on the radioactive components of concern in the fertilizer industry. It was not deemed necessary to include the discussion at this point as it is very technical, and no tests for the presence of radionuclides were conducted in the study area. Table 30 indicates the concentrations of radionuclides found in the phosphate rock mined at Phalaborwa.

### 3.2.5.2.4 Heavy metals

Food carries most of the heavy metals taken up by the body. These heavy metals accumulate in tissues and take a long time to be expelled by the body. Although fertilizers contribute to the heavy metals pollution of soil, the contribution is smaller than that of other industries, such as; the non ferrous industry, fossil fuel burning, industries using heavy metals or their salts, and waste disposal.

The overwhelming majority of toxic metals are found in phosphate rock, and thus implicitly in fertilizers. Most of these metals are necessary for life, but concentrations in excess of permissible levels leads to bio-toxic phenomena. The most predominant of the heavy metals present in phosphate rock are; Cd, Ni, Pb, Zn, Cu, V, Mn, Mo, and Hg.

Cadmium plays no part in the known vital biochemical functions of plants or animals, and, as it builds up, is one of the most toxic elements to the living body. Cadmium is hence a cumulative toxic substance. It has a half-time amounting to 40 days and ca. 20 years in the liver and kidneys. Its toxicity lies in its affinity for the reactive enzyme groups, which contain nitrogen and sulphur. Excessive levels of cadmium in the body leads predominantly to neuro-pathological symptoms and kidney insufficiency. The misbalance of vital minerals such as phosphorus and calcium has also been found which can lead to Itai-Itai disease. Due to these risks, the WHO (World Health Organization) in 1972 recommended a maximum daily intake of 70µg.

The origin of the ore determines in what form cadmium may be present in phosphate rock:

1. Contained in the crystalline lattice of apatite as a substitute for the Ca<sup>2+</sup> ion,
2. In the organic component of the phosphate ore, or,
3. Bound to calcite, accompanying the phosphate ore.

The amount of cadmium and other heavy metals present in fertilizers depends on the nature of the phosphate rock, the manufacturing process, and the concentration of phosphorus in the end product. Table 6 indicates the estimated cadmium content of rocks in current use in industrial plants.

**Table 6: Estimated cadmium content of rocks in current use in industrial plants (Man, 1994).**

<i>Country of origin</i>	<i>Cadmium content (ppm)</i>
<i>CIS, Kola</i>	1
<i>U.S., Florida</i>	615
<i>U.S., Idaho</i>	40340
<i>U.S., North Carolina</i>	36
<i>Morocco</i>	875
<i>Israel</i>	1530
<i>Tunisia</i>	2535
<i>Togo</i>	4280
<i>Senegal</i>	6690
<i>Mauru</i>	90

In the wet phosphoric acid process, heavy metals contained in the phosphate rock are redistributed between phosphoric acid and waste phosphogypsum. Various techniques exist to remove cadmium from phosphates, such as; calcination (developed by DorrOliver), and solubilization with acid solutions. Acid purification processes, such as; cadmium removal by precipitation, cadmium removal by flotation, ion-exchange-, and liquid-liquid extraction processes, are also widely used (Man, 1994).

As mentioned in section 3.2.2, the main source of phosphate rock in South Africa is from the Phalaborwa Igneous Complex. The typical cadmium concentrations found in these rocks are 4mg/kg rock and 23mg/kg phosphorus. This is below European import standards, which is a concentration of cadmium <60mg/kg phosphorus (RIRDC, 1999).



### 3.3 The potassium fertilizer industry

#### 3.3.1 Introduction

Potassium (K) is one of the three vital nutrients essential to plant life, and is necessary for photosynthesis and protein formation. It also activates and controls the reaction rates of enzymes, and increases the tolerance of plants to diseases. In combination with a variety of compounds (due to its high reactivity and affinity for other elements), potassium is the seventh most common element on earth. It has commercial value however, only when found in large and relatively concentrated deposits of potassium salts. These deposits are large bodies of marine evaporites and bodies of salty water such as certain landlocked seas, lakes, and natural brines. Sodium chloride is a major component in all these deposits. Potassium salts are also known as potash salts, and the word *potash* traditionally refers to potassium oxide ( $K_2O$ ) content, although no oxide is present.

“The production of potassium salts in 1991 came from 50 mines located in 15 countries and was about 46.5 million metric tons or about 26 million metric tons of  $K_2O$ . About 90% of this production was potassium chloride (60 to 62%  $K_2O$ ) or muriate of potash (MOP), and about 4% was potassium sulphate (50 to 53%  $K_2O$ ) or sulphate of potash (SOP). About 96% of the overall production was used in agriculture as potash fertilizer” (Klein *et al*, 1994).

Muriate of potash is manufactured from sylvite (KCl). Sylvite is the preferred potassium-based agro-mineral, because it has the highest potassium content (ca. 63%), it occurs abundantly in nature and the process to extract sylvite from hosting ores is relatively simple. Sylvite is found in sylvinite-, carnallite-, and kainite ores, and in hartsalts. Sylvite can also be formed synthetically from naturally occurring surface and subsurface brines that contain dissolved potassium and chlorides.

When fertilizers having low chloride content are needed to meet crop and soil requirements, potassium sulphate is the most common substitute for potassium chloride. Potassium sulphate is predominantly manufactured from langbeinite ( $K_2SO_4 \cdot 2MgSO_4$ ), synthetic schoenite, and potassium chloride and sulphuric acid.

Table 7 indicates the primary potassium deposits utilized in the manufacturing of potassium fertilizers found in different parts of the world.

The main environmental concern in the manufacturing of potassium chloride from sylvinite ores is the salinization of surface and subsurface water, and of the land. In this section, a discussion on the major effluents produced during the manufacturing of potassium chloride is included. The potassium chloride industry in Saskatchewan, Canada is taken as a case study. The reasons for

this are that it is considered to be one of the largest industries of its sort in the world, it encompasses the major methods of mining, beneficiation, and other processing methods used globally, its mines and refineries are located in agricultural areas and some close to urban areas, and operations are subject to severe and fluctuating climatic conditions. Reference is also made to methods in the potash industry used in other regions in the world (Klein *et al*, 1994).

**Table 7: Primary potassium deposits utilized in the manufacturing of potassium fertilizers (Klein *et al*, 1994).**

<i>Deposit type</i>	<i>Minerals</i>	<i>K<sub>2</sub>O%</i>	<i>Deposit location</i>
Sylvinites	KCl + NaCl + Clay	1040	Canada, Russia, Ukraine, U.S., U.K., France, Germany, Brazil, Argentina
Carnallite	KCl + MgCl <sub>2</sub> .6H <sub>2</sub> O + NaCl + Clay	1016	Spain, Congo, Ethiopia, Israel, Thailand
Hartsalts	KCl + MgSO <sub>4</sub> .H <sub>2</sub> O + NaCl + Clay	1020	Germany
Kainite	4KCl + 4MgSO <sub>4</sub> .11H <sub>2</sub> O + NaCl	1318	Italy
Langbeinite	K <sub>2</sub> SO <sub>4</sub> + 2MgSO <sub>4</sub> + NaCl	712	U.S.
Dead Sea	Brine		Israel, Jordan
Great Salt Lake	Brine		U.S.

### 3.3.2 Mining and refining methods utilized in KCl production

The Saskatchewan potash mines are situated in the south-central and south-eastern region of the province in the middle of fertile agricultural land. The underlying sylvinitic-type ores are considered among the world's largest and richest in potassium. These deposits contain ca. 30 - 40% KCl, 50 - 60% NaCl, and 1 - 8% insolubles, predominantly in the form of clay, silt, sand, and dolomite. The majority of the ores are mined using conventional methods (ores ca. 1000m deep), but a portion is also solution mined (ores significantly deeper than 1000m).

The conventional mining method used involves three basic stages in a typical surface refinery;

1. *The beneficiation stage:* Includes ore crushing and grinding, ore de-sliming, separation of the potassium chloride particles from a mixture of KCl and NaCl (mainly by froth flotation), and tailings preparation for disposal.
2. *The product preparation stage:* Includes KCl concentrate de-brining, float drying in either natural gas-fired rotary or fluid-bed dryers, screening, compaction/granulation, product conditioning, and product storage.
3. *The dissolution/crystallization stage:* Includes solids dissolution, a 24 effect vacuum-cooling crystallization circuit, and product de-brining. When a separate refined product is manufactured, this stage also incorporates product drying and storage and in some refineries compaction/granulation, screening, and product conditioning. A heat sink is required for crystallization, which is provided with recycled brine or water/brine from a cooling tower.

Solution mining involves injecting unsaturated brines directly into the ore bodies to dissolve the KCl it contains. The impregnated brine is then transported to the surface and fed to the refinery for further processing. The two basic processing stages involved in the surface refinery are;

1. Precipitation of sodium chloride from solution using a quadruple-effect evaporation circuit, separation and de-brining of sodium chloride precipitate from the evaporator's discharge, and the preparation of tails for their disposal.
2. The potassium chloride production stage, which includes a multiple-effect vacuum cooling crystallization circuit, product separation and de-brining, drying, screening, compaction/granulation, product conditioning, and storage.

Large and relatively shallow ponds and brine from epeiric water bodies or flooded mines may be used on a seasonal basis to manufacture potassium chloride. The precipitate is fed to the surface refinery for processing into a marketable product (Klein *et al*, 1994).

### 3.3.3 Effluents associated with the manufacturing of potassium chloride

There are solid- and liquid effluents, as well as air emissions in a typical conventional processing operation. The principle concern with these effluents is the contamination of the environment with salt. Various waste management methods for fertilizer pollution control have been developed by the potash industry in Saskatchewan in order to minimize the risk of such contamination. In this section follows a discussion on the effluents released (Reid and Klein, 1994).

#### 3.3.3.1 Solid wastes

The composition of solid effluents varies with the composition of ores being mined. Table 8 indicates the general composition of tails (solid effluent) from the Saskatchewan mines, and Table 9 the constituents of the solid and liquid waste produced by the potash mine in Saskatchewan.

**Table 8: The general composition of tails from Saskatchewan mines (Reid and Klein, 1994).**

	<i>Tails produced from:</i>	
	<i>South-eastern mines (%)</i>	<i>Northern mines (%)</i>
NaCl	95.98	90.95
KCl	23	13
MgCl	23	0.5
Water insolubles	1.52	515
<i>Composition of insolubles:</i>		
Quartz	1.52	515
K-Spar	7.510	12.516
Dolomite	55.65	28.532
Anhydrite	0.16	0.3
Illite	61.25	17.521
Chlorite	2.5	4.555
Septechlorite	5.565	16.5185

Table 9: Analysis of the constituents of the solid and liquid waste produced by the potash mine in Saskatchewan (Reid and Klein, 1994).

<i>Composition of tails slurry</i>	
Density	1.44
pH	6.40
Temperature	22°C
Solids	32%
<i>Composition of solids in slurry (%)</i>	
Na	35.5
K	1.3
Cl	53.8
Mg	0.8
Ca	0.7
SO <sub>4</sub>	0.8
Water insolubles	7.1
Al <sub>2</sub> O <sub>3</sub>	0.7
Fe <sub>2</sub> O <sub>3</sub>	0.3
SiO <sub>2</sub>	2.3
<i>Composition of liquid portion of tails slurry (%)</i>	
KCl	7.7
NaCl	17.7
CaCl <sub>2</sub>	0.5
MgCl <sub>2</sub>	1.1
Specific gravity	1.226

Figure 11 illustrates the generalized stratigraphy under the waste management area of potassium chloride production in Saskatchewan. The waste management area is diked and contains a salt pile and brine pond. It is normally located in a low-lying region, which may have been a slough or marsh, on a 1 - 4m thick deposit of silt, sand, and gravel. This deposit is permeable and contains a surficial aquifer, and bedrock shales form the bottom of the deep aquifer. The main environmental problem of potash production operations at Saskatchewan is to prevent brine from escaping into the surficial and sometimes inter-till aquifer.

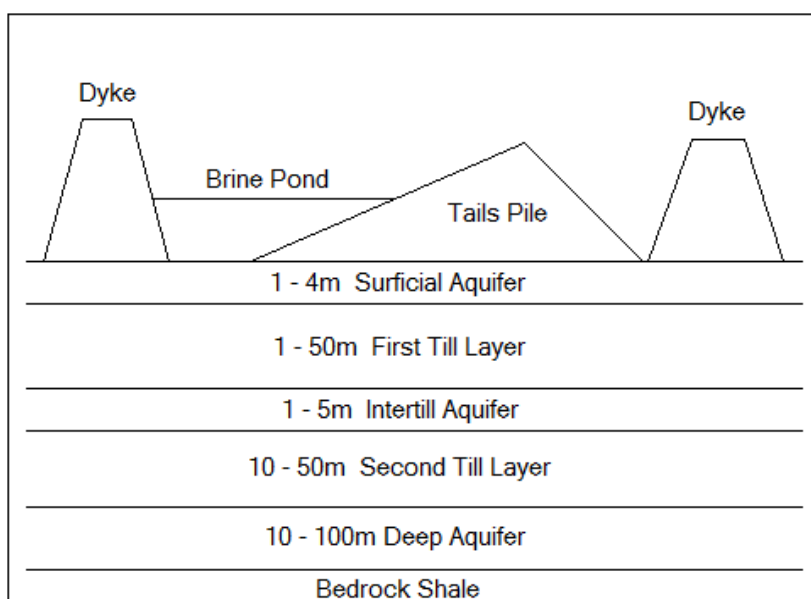


Figure 11: Generalized stratigraphy under the waste management area of potassium chloride production in Saskatchewan (Reid and Klein, 1994).

### 3.3.3.2 Liquid wastes

The main source of liquid waste is from fresh water used in the beneficiation and refining process, and from precipitation falling on the mine site on or close to the waste management area. Liquid waste is held in the brine pond before being reclaimed for; tails slurry, makeup brine in the refining process, heat sinks in vacuum cooling crystallizers, or for disposal.

For every metric ton of potash ( $K_2O$ ) produced, ca.  $1m^3$  of fresh water is used, and ca. 80% of this water enters the brine pond as part of the brine in tails slurry. The brine in the pond is typically saturated with NaCl.

In order to prevent brine from escaping from the perimeter, liquid waste is also collected via collection ditches, drains, and wells. Most of this liquid waste is however natural groundwater.

Regulation and practicality determines the method and site of disposal for brine. In Saskatchewan, excess brine is injected into deep wells due to regulations preventing brine from being disposed of into any surface water body, or any aquifer (or aquifer connected to an aquifer) with useable water (Klein *et al*, 1994).

### 3.3.3.3 Air emissions

Potassium chloride is relatively soft with a hardness index value of 2 on the Mohs scale. It is brittle when subjected to impact, grinding, shear, and abrasion, and consequently tend to produce dust when handled. Potassium chloride product is not regulated under legislation in Canada and the U.S., because it is not considered “hazardous”, “dangerous”, or “toxic”. There is however regulation on national, state, provincial, and even municipal level regarding the types and levels of dust that may be discharged into the atmosphere.

The primary sources of air emissions from a typical conventional potassium chloride production plant are product dryers (most environmentally significant), refinery air exhaust, mine ventilation exhaust, and fugitive dust. The principle concern in air emissions from these processes is the chemical composition of the particles emitted.

Air emissions from dryers in Saskatchewan contain ca. 90 - 95% KCl and 3 - 10% NaCl. The emissions are acidic and may contain up to 5% organics in some cases. Other elements, including toxic metals, occurring in dryer dust are present only in very small or trace amounts. Table 10 indicates the typical concentrations of particulates emitted from dryers in Saskatchewan (Klein *et al*, 1994).

Table 10: Particulates in air emissions from dryers (Klein *et al*, 1994).

Element	Concentration (ppm)	
	Fertilizer-grade dryer	Chemical-grade dryer
<i>K</i>	469 000	520 000
<i>Cl</i>	469 000	410 000
<i>Na</i>	50 000	3 000
<i>Br</i>	260	150
<i>Fe</i>	340	<20
<i>Ca</i>	230	<20
<i>S</i>	<20	<20
<i>Rb</i>	50	50
<i>Si</i>	900	<100
<i>O</i>	20	<10
<i>P (ortho)</i>	<30	<30
<i>Mn</i>	10	<10
<i>Pb</i>	<50	<50
<i>Hg (ppb)</i>	1.17	1.33
<i>Mg</i>	530	<40
<i>Ni</i>	10	10
<i>Al</i>	310	<50
<i>As</i>	14	130
<i>Co</i>	<10	<10
<i>Ci</i>	<5	<5
<i>SiO<sub>2</sub></i>	<1 000	<1 000
<i>Ba</i>	50	<50
<i>F</i>	500	400
<i>V</i>	53	46
<i>Cd</i>	<0.5	<0.5
<i>Ag</i>	<2	<2
<i>H<sub>2</sub>O</i>	120	700

### 3.4 MAP, DAP, and NPK fertilizers

#### 3.4.1 Introduction

MAP (monoammonium phosphate) and DAP (diammonium phosphate) are manufactured from ammoniated slurry of wet process phosphoric acid by granulation, drying, and cooling. By adding a potassium salt during the granulation process, NPK products are obtained. This production process is called slurry granulation. A variety of grades of NPK products are also manufactured by a process called power blending granulation. This process involves the blending and granulation of powdery MAP, DAP, or superphosphates with nitrogen compounds such as urea and ammonium sulphate, and potassium chloride or sulphate.

Dusts, ammonia, fluorine, SO<sub>x</sub>, and NO<sub>x</sub>, are the main air pollutants, and fluorine, suspending solids, nitrogen, and phosphorous are the major water pollutants due to the production of these fertilizers. Various methods exist to reduce the levels of these pollutants discharged into the environment to comply with environmental regulations (Ando, 1994).

### 3.4.2 Air pollutants

A bag filter or wet scrubber is used to remove dusts. It often happens that a small amount of ammonium chloride fumes is contained in the dryer waste gas, and these fumes are also frequently visible even when the particulate content meets regulation. Some local governments will often ask the fertilizer factory to reduce these fumes, and a mist cottrell (wet electrostatic precipitator) is used to do this. Ammonium chloride is formed by the reaction of potassium chloride with ammonia salts in the granulator and dryer.

The waste gas leaving an ammoniator granulator or neutralizer of phosphoric acid contains ammonia, which is normally recovered by scrubbing with phosphoric or sulphuric acid and then returned to the granulator.

Gases from the granulator and dryer also contain fluorine compounds ( $\text{SiF}_4$  and HF). These are usually not controlled due to their low concentrations. They undergo only limited removal by scrubbing with phosphoric or sulphuric acid for ammonia recovery, and if necessary, fluorine is removed by water scrubbing. The resultant scrubber liquid contains fluorine in two forms, viz. HF and  $\text{H}_2\text{SiF}_6$ .

A quantity of  $\text{SO}_x$  and  $\text{NO}_x$  is contained in the waste gas from the dryer, which is derived from the fuel to produce the hot air. The concentrations of these gases are monitored to comply with regulations enforced by local governments (Ando, 1994).

### 3.4.3 Water pollutants

The main sources of wastewater at MAP, DAP, and NPK plants are water scrubbers and waste gases. Waste gases containing ammonia are usually subjected to scrubbing for ammonia recovery, and the scrubber liquid is fed to the neutralizer or granulator without being discharged. Waste gases at powder blending granulation plants are normally subjected to dust removal by a bag filter, yielding no wastewater. Some plants however have water scrubbers yielding wastewaters requiring treatment. Effluent standards for pollutants have been developed by governments for wastewaters discharged into surface water bodies.

To precipitate fluorine and phosphate in wastewaters, slaked lime is generally used. Fluorine is present in the forms fluoride ( $\text{F}^-$ ) and fluorosilicate ( $\text{SiF}_6^{2-}$ ), and  $\text{CaF}_2$  is precipitated from both these ions with the addition of lime.  $\text{CaF}_2$  is slightly soluble in water to give a lower than the effluent standard of fluorine. The  $\text{CaF}_2$  precipitates contain larger amounts of fluorine. The crystal size of the precipitates is normally very small, and can only be removed when coagulated to form much larger particles.

Gelatinous aluminium hydroxide is precipitated by the addition of lime to acidic wastewaters containing dissolved aluminium. The gelatinous aluminium hydroxide aids with the coagulation of fine  $\text{CaF}_2$  particles. Gelatinous silica, formed when the lime reacts with  $\text{SiF}_6^{2-}$  ions to precipitate  $\text{CaF}_2$ , also aids with coagulation to some extent.

The fluorine in treated water often exceeds effluent standards due to the effects of various impurities. Fluorine is difficult to remove when the wastewater is neutral or alkaline, because the lime is not properly dissolved. In a case like this, calcium chloride can be used to remove fluorine. Otherwise, the water can be acidified by hydrochloric acid prior to the addition of lime.

Some fertilizer plants add boron to mixed fertilizers as a micronutrient. It is difficult for fluorine to precipitate with the addition of lime in wastewater containing boron, due to the formation of  $\text{BF}_4^-$  ions which is very stable. Boron containing wastewater should not be mixed with fluorine containing wastewater, due to fluorapatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  precipitating with the addition of lime. Fluorapatite is much less soluble than  $\text{CaF}_2$ . The apatite normally consists of very small crystals which tend to coagulate to form gelatinous material (Ando, 1994).

(For a full discussion on the treatment of water rich in fluorine, see Chapter 29 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press).

### **3.5 Hot and cold blend liquid fertilizer plants**

#### **3.5.1 Introduction**

The processing of fluid fertilizers is not normally associated with major pollution problems. The numerous operations involved, however, can give rise to significant levels of contamination that require control measures. The highest risk of a pollution incident is perhaps during the mixing of raw materials. High temperatures resulting from the heat of neutralization of, for example, ammonia and phosphoric acid, may cause boiling and the development of high vapour pressure. This may lead to surges with possible overflows and the emission of fumes and gases at toxic levels (Palgrave, 1994).

#### **3.5.2 Dust**

There is a wide variety of solid raw materials used. These may vary from granular products, such as MAP, through a variety of crystalline materials, such as potassium chloride, to some very finely divided clays, such as attapulgite or bentonite. The dust potential depends on the methods of handling (Palgrave, 1994).



### **3.5.3 Fumes**

The predominant emissions likely to occur are ammonia, water vapour, and certain fluorine compounds, which almost exclusively arise during the neutralization stage.

Ammonia gases are most frequently released during deliveries made into storage, where vapour unavoidably escapes through connections between the vehicle and storage facilities. With the transfer of aqueous ammonia into a tank, a corresponding volume of air containing ammonia fumes is displaced. These fumes should be vented through a scrubber.

The emission of water vapour itself is not regarded as a significant pollutant. It may be in admixture with ammonia and fluorine compounds when originating in the processing operations, but sufficient methods to deal with them are likely to remove water vapour as well. Water vapour emerging from secondary cooling towers could pose problems for neighbours. The careful siting of such a facility could solve the problem.

Fumes containing hydrofluoric acid, silicon tetrafluoride, fluorosilicic acid, or possibly some ammonium derivatives may also be produced during the neutralization of wet-process phosphoric acid (Palgrave, 1994).

### **3.5.4 Liquid waste**

Liquids are released through vessel overflow and the occasional leakage from valves, flanges, pump and impeller seals, etc. A series of gullies, leading from areas where leakage is likely to occur, into a specially constructed lagoon at a convenient low area of the site is often constructed. The lagoon accumulates rainwater to be utilized as feed water for further fluid fertilizer manufacture, and containing spillages that are automatically recycled (Palgrave, 1994).

### **3.5.5 Solid waste**

The fluid fertilizer industry produces very little solid waste. Insoluble components may become a problem in plants where only clear liquids or solutions are produced, but these insolubles usually contain nutrients allowing them to be incorporated in either solid or suspension grades. The wastes originating from cleaning operations and long term storage may be significant. These may include, for example, gypsum from tanks that have been on wet-process phosphoric acid duty or corrosion products from long term storage (Palgrave, 1994).

## **3.6 Kynoch Fertilizer Production Facility (KFPF)**

KFPF, located to the west of SNP, was a full scale fertilizer production facility from 1967 up to mid 2006. The decommissioning of the site commenced in October 2006. KFPF is many times bigger than SNP, and a wide range of fertilizers were manufactured. The four main raw materials used were ammonia, phosphate rock, potassium chloride, and sulphur. A gypsum tailings dam is located

ca. 2km west of KFPF, and slurry from the factory to the dam was pumped at an estimated 185 000ton/annum. The ownership of the gypsum tailings dam was transferred to Oranje Mining and Transport Company (OMV) in August 2007. A study on the KFPF site was conducted by SRK Consulting in 2007 (Skinner, 2007).

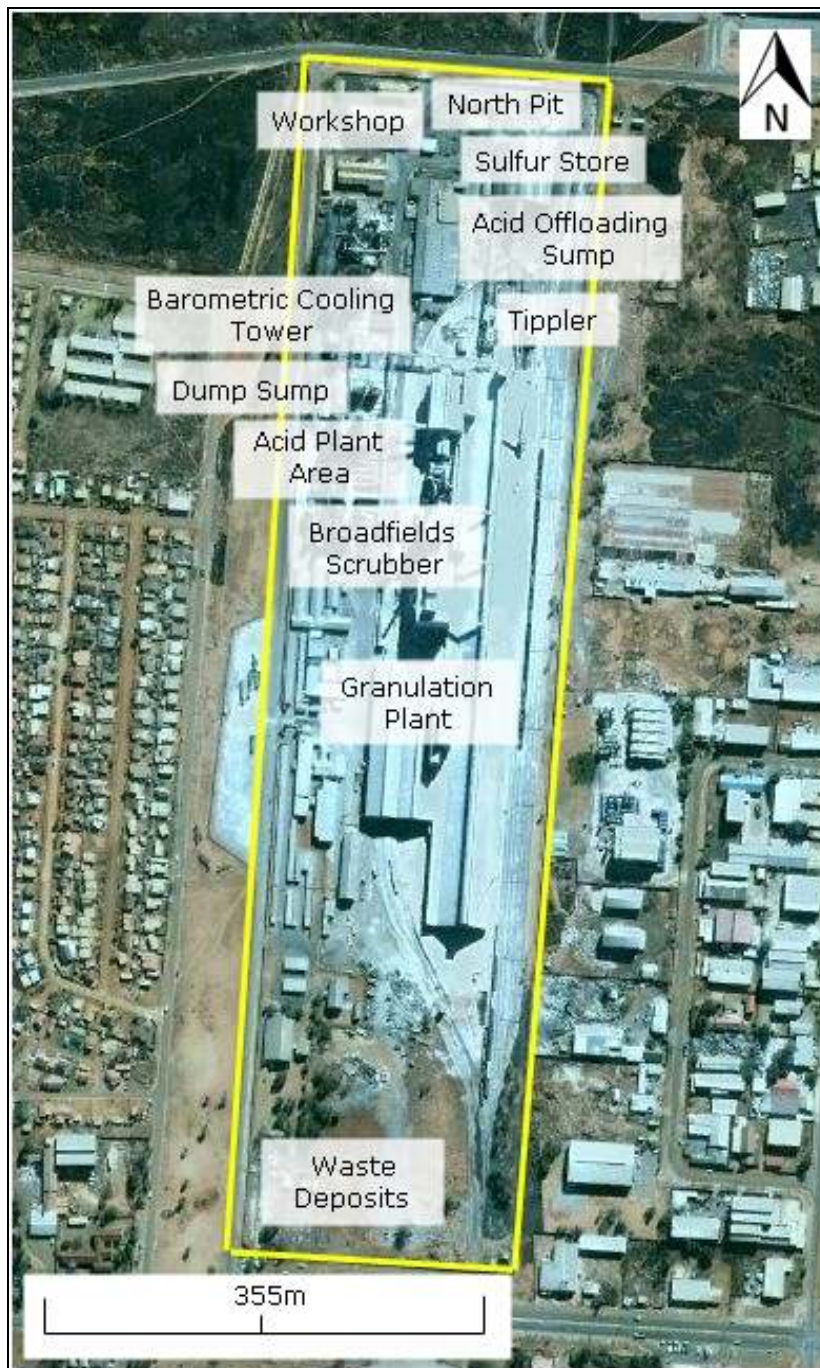


Figure 12: Map of the main storage facilities and operation points on the KFPF site. KFPF is delineated in yellow.

Most of the processes discussed in Chapter 3 (except for ammonia production) were used in the manufacturing of fertilizers by KFPF, and for this reason, the author does not find it necessary to discuss the processes and their resulting effluents as it would be deemed repetition. Sufficient data comprehensively describing the operations on KFPF were also not available. The reader is asked

to refer to Chapter 3 for the details of these processes in the manufacturing of fertilizers. Figure 12 is included to indicate the location of the significant storage facilities and operation points on the KFPF site. KFPF is delineated in yellow.

Due to the size and scale of the operations on the KFPF site, and the general direction of the flow of groundwater, it is expected that noticeable quantities of contaminants found in the subsurface of the SNP site be from KFPF. The decommissioning and rehabilitation of the site that started in October 2006 is expected to have reduced concentrations of contaminants considerably.

The most predominant contaminants found on the KFPF site, were; nitrate ( $\text{NO}_3$ ), ammonium ( $\text{NH}_4$ ), sulphate ( $\text{SO}_4$ ), phosphate ( $\text{PO}_4$ ), Fluoride (F), Chloride (Cl), Zinc (Zn), Iron (Fe), and Chromium (Cr).

### **3.7 Sasol Nitro Potchefstroom (SNP)**

#### **3.7.1 Introduction**

SNP is a hot and cold blend liquid fertilizer plant. Figure 13 is a simplified map of the location of the storage facilities and various operation points on the SNP site. SNP mainly sells liquid NPK products.

#### **3.7.2 Raw materials**

SNP does not manufacture or mine for raw materials used in its mixed or straight fertilizer products, viz. all raw materials are either brought in from other Sasol plants, or third parties. The raw materials used and sold by SNP, are; anhydrous ammonia ( $\text{NH}_3$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), ammonium nitrate 21% ( $\text{NH}_4\text{NO}_3$ ), potassium chloride (KCl), urea ( $(\text{NH}_2)_2\text{CO}$ ), zinc sulphate ( $\text{ZnSO}_4$ ), ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ), and clay. The clay is used in suspension products and is made together with Agrigel (Attapulgit) ( $(\text{Mg,Al})_2\text{Si}_4\text{O}_{10}(\text{OH})\cdot 4(\text{H}_2\text{O})$ ) and Tetrasodium Pyrophosphate (TSPP) ( $\text{Na}_4\text{P}_2\text{O}_7$ ).

#### **3.7.3 Production processes**

##### **3.7.3.1 Introduction**

The following is taken from the official Sasol Nitro “The Production of Suspension Liquid Fertilizer” (Reference nr: 6-4) document, and was created (on the 9<sup>th</sup> of May 2006) to ensure that “all suspension products are manufactured according to [the] specified bill of materials and documented operating procedures”.

##### **3.7.3.2 Procedure**

- The plant receives an order to manufacture a specific product for delivery to a client.

- The bill of materials (BOM) for this product is printed from SAP to give a batch card with the masses of raw materials to be weighed by the SPC or PC.
- The batch card is altered to indicate the correct following order and quantify the masses accordingly by the SPC or PC, and signed.
- The production procedure is to be followed stepwise by the operator:
  1. The weight of water to be used is transferred to the reactor.
  2. If any ammonium nitrate solution (ANO) is to be used, this is transferred into the reaction vessel.
  3. The weight of phosphoric acid ( $H_3PO_4$ ) is then transferred into the reactor.
  4. The mass of the solution is recorded for future adjustments.
  5. Using ammonia ( $NH_3$ ), adjust the pH of the solution to between 5.8 and 6.0.
  6. To compensate for loss of water evaporation, due to the highly exothermic nature of the reaction, water is transferred into the vessel to the recorded mass in 4.
  7. KCl, urea, and zinc sulphate are transferred into the reactor.
  8. Clay is transferred into the reactor vessel according the batch card.
  9. EDTA (Dequest) is added at the rate of 100ml to 1 ton of produced product to prevent crystallization.
  10. The process is allowed to react sufficiently until all raw materials have completely dissolved. By holding a sieve under the recycling stream and catching any un-dissolved particles, monitor this.
  11. Density readings of products are taken and must be in the region of 1.18 - 1.3kg/cm<sup>3</sup> at ambient temperature according to the concentration of product range.
  12. The operator records the final pH and density reading onto the batch card.
  13. The operator signs the batch card prior to releasing the produced product for storage or dispatch.

### **3.7.3.3 Environmental factors**

- Product spillages due to reaction processes must be contained in the production area and not allowed to run off into drains.

### **3.7.3.4 Safety and health factors**

- Prescribed PPE (personal protective equipment) must be worn at all times during production.

### **3.7.3.5 Quality factors**

- It is imperative that production process be followed according to procedure to comply with recorded specifications.

### 3.7.4 Discussion of the production process and the product produced at SNP

The storage of raw materials, mixing of different ratios of NPK product, and the transfer of product to and from vehicles are the main operations on the SNP site.

The NPK products are sold in specific ratios of N-, P-, and K content. NPK (5:3:2) 22% is a typical description of a product. This would indicate that the ratio of N:P:K is 5:3:2, and that the total volume of fertilizer (N, P, and K) makes up 22% of the total volume of product. The rest of the product (78%) is made up of water. There are standard ratios and content of NPK products for sale, but clients can also make specific requests.  $ZnSO_4$  is sometimes added as a source of Zn, which is important for plant growth.

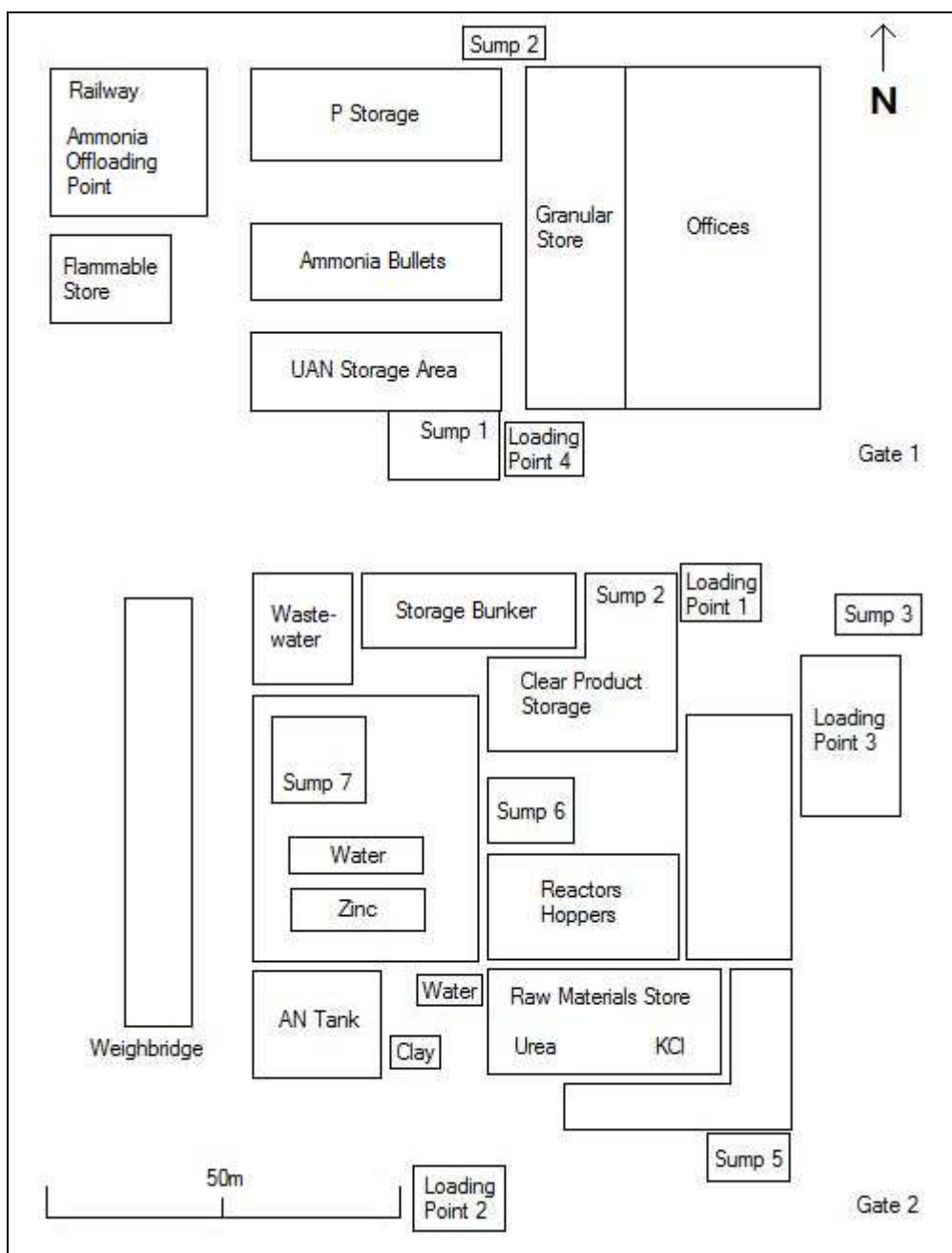


Figure 13: Simplified map of the location of storage facilities and various operations on the SNP site.

The raw materials used at SNP for “N”, “P”, and “K” respectively, are; anhydrous ammonia, ammonium nitrate, and urea for “N”, phosphoric acid for “P”, and potassium chloride (or muriate of potash (MOP) 60 to 62% K<sub>2</sub>O) for “K”. Anhydrous ammonia, ammonium nitrate, potassium chloride, and ammonium sulphate can also be sold as straight products (diluted) to be used for the direct application onto soils.

Ammonium sulphate is largely used for alkaline soils. When introduced into the soil, the sulphate ion is released and forms sulphuric acid which lowers the pH. The vital nitrogen is also simultaneously released.

Attapulgite is a colloidal clay mineral. It has numerous colloidal and non-colloidal applications in a wide variety of industries. In the liquid suspension fertilizer industry attapulgite is used to stabilize suspensions and prevent the settling of insoluble components. It is exceptionally suitable for this application due to its highly stable colloidal properties in high concentrations of salts.

TSP is a mildly alkaline sequestering agent with marked emulsification and dispersion properties. In the food industry it is used as a constituent of phosphate mixes and emulsifying-salt blends, in the immersion treatment of seafood, and as a general buffer, sequestrant, and stabilizing agent. In industry, it is generally used when a higher quality product is required, e.g. alkaline and synthetic detergents, textiles, water treatment, and mineral processing. SNP use TSP to keep the clay in suspension.

### **3.7.5 Effluents caused by operations on the SNP site**

As mentioned previously, the processing of fluid fertilizers is not normally associated with major pollution problems. The numerous operations involved, however, can give rise to significant levels of contamination that require control measures. The highest risk of a pollution incident is perhaps during the mixing of raw materials.

A wide variety of solid raw materials are used. These vary from granular products, such as anhydrous ammonia, through a variety of crystalline materials, such as potassium chloride, to some very finely divided clays, such as attapulgite. These pose the potential for dust pollution.

Concerning fumes, the predominant emissions likely to occur are ammonia, water vapour, and certain fluorine compounds, which almost exclusively arise during the neutralization stage. Fumes containing hydrofluoric acid, silicon tetrafluoride, fluorosilicic acid, or possibly some ammonium derivatives may also be produced during the neutralization of wet-process phosphoric acid.

As evident from results obtained from various soil and water samples, liquid effluents are released on the SNP site, most likely through vessel overflow and the occasional leakage from valves,

flanges, pump and impeller seals, etc.  $\text{PO}_4$  and  $\text{SO}_4$  is a particular problem in this regard causing significant damage to buildings, especially on the northern side of the site where  $\text{H}_3\text{PO}_4$  (phosphoric acid) is stored.  $\text{PO}_4$  displaces the calcium and magnesium in the cement which results in it becoming brittle. In addition to this, it absorbs water which causes it to expand and cause further structural damage. Although there are numerous sumps in operation in the SNP site, not all leakage and spillage are able to be captured and contained by them.

The principle environmental concern with potassium chloride is the contamination of the environment with salt.

Zinc sulphate is harmful when swallowed, may cause severe eye damage, skin and throat irritation, and gastrointestinal disturbances. It is severely toxic to aquatic organisms, and may cause long-term damage to the environment.

Ammonium sulphate causes irritation to the skin, eyes, and respiratory tract.

TSP is not classified as a hazardous substance.

Contaminants found in significant concentrations in groundwater samples, were; nitrate, ammonium, sulphate, chloride, calcium, magnesium, and chromium. The major contaminants found in soil samples, were; nitrate, ammonium, phosphate, sulphate, cadmium, calcium, potassium, zinc, fluoride, manganese, nickel, and chromium. The source of chromium is an old tannery that was located on the southern side of the SNP site. Operations on the tannery have ceased approximately two decades ago and the site is now used to manufacture wooden pallets.

## Chapter 4: Geo investigations

### 4.1 Geology

#### 4.1.1 Regional geology

Generally, the SNP and surrounding area are underlain by sedimentary and igneous rocks belonging to the Pretoria subgroup of the Transvaal sequence, and Vaalian Intrusive Rock a few kilometers to the east of the SNP site (see Figure 14).

The gypsum tailings dam, ca. 2km west of the SNP site, is underlain by the Timeball Hill formation, which consists of mainly dark chert-poor dolomite (Malmani). The SNP and KFPF sites are situated on the Hekpoort formation, which consists predominantly of andesite, agglomerate, and tuff. Between the tailings dam and the SNP and KFPF sites is a thin band of rock of the Boshhoek formation, which consists primarily of quartzite and conglomerate.

Just east of the SNP site is a narrow band of rock of the Strubenkop formation, which consists of mainly ferruginous shale and quartzite, and just east of this band is a narrow band of rock of the Daspoort formation, which consists predominantly of quartzite and shale and is ferruginous in places. A few kilometers east of the SNP site lies a narrow band of Vaalian Intrusive Rock which consists mainly of diabase. This Vaalian intrusive rock increases considerably in size further north.

The nature of the quartzitic rock layer underlying the SNP site and overlying the Hekpoort formation suggests that the Boshhoek and/or Strubenkop formations may overlie the Hekpoort formation to some extent in the SNP area. Looking at the high concentrations of iron at deeper levels under the SNP site, it is likely to be the Strubenkop formation, due to it having a higher iron content.

*The 1:250,000 geological map (Figure 14) is the intellectual property of the Council for Geosciences and is used with permission. Copyright and all rights are reserved by said council.*

#### 4.1.2 Local geology

##### 4.1.2.1 Introduction

The borehole logs of BH002-D and BH005-D are included in this section (Figure 16 and 17) as typical examples of the geology found on the SNP site (for the logs of all eight boreholes, see Appendix D). The site is situated on a quartzitic outcrop, and the quartzitic top layer indicated in the borehole log figures may appear strange to the reader, but it provides a good indication of the amount of quartzite present and the extent of the variation found on the site. As illustrated in these figures, the variation in depth of the overlying highly weathered and fractured quartzitic rock/soil layer fluctuates in thickness between ca. 11 - 21m. The whole SNP site is underlain by this layer. BH002-D is situated on the western side of the site and BH005-D on the eastern (see Figure 15).



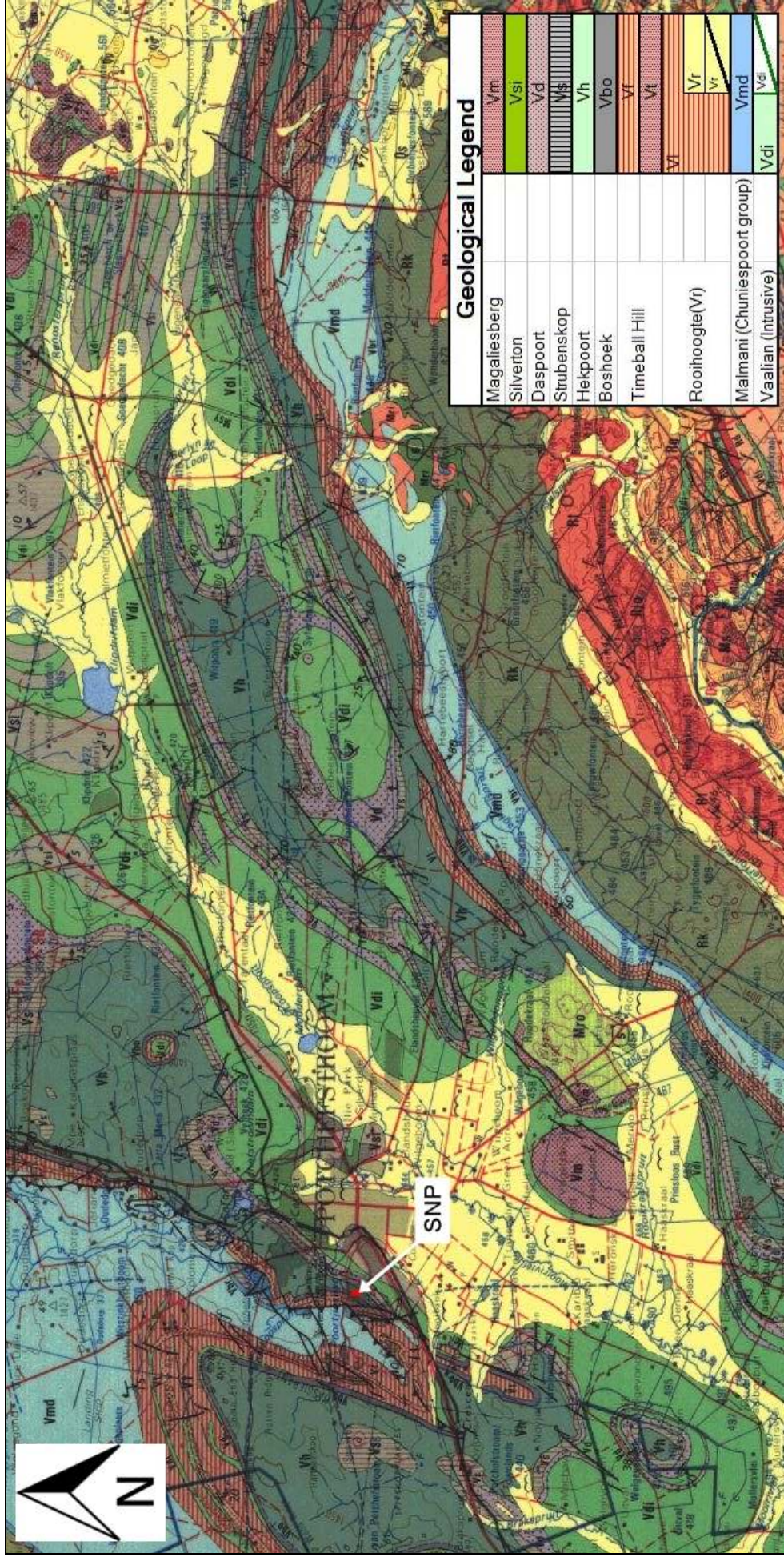


Figure 14: Geological map of the Potchefstroom area.





Figure 15: Aerial map of the SNP site indicating the locations of the boreholes.

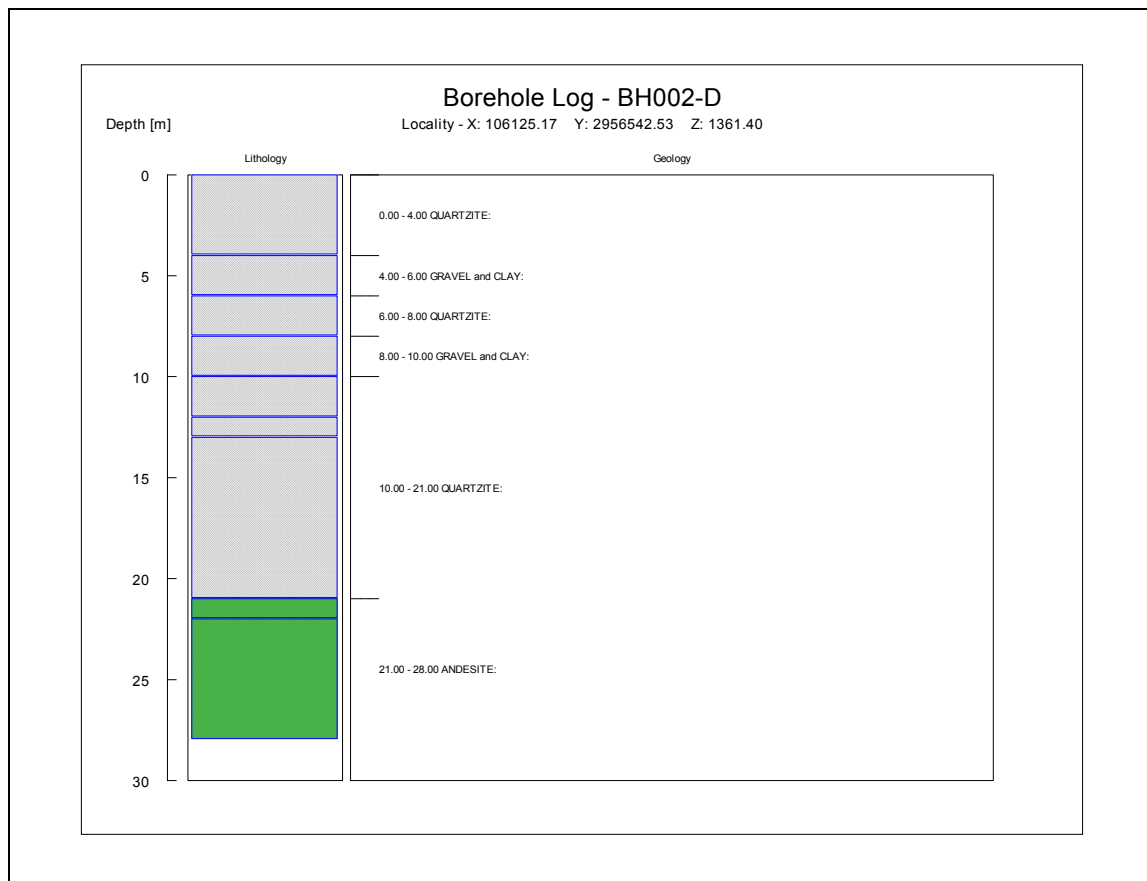


Figure 16: Borehole log of BH002-D. Coordinates; lat (S°): 26.71542, lon (E°): 27.06651.

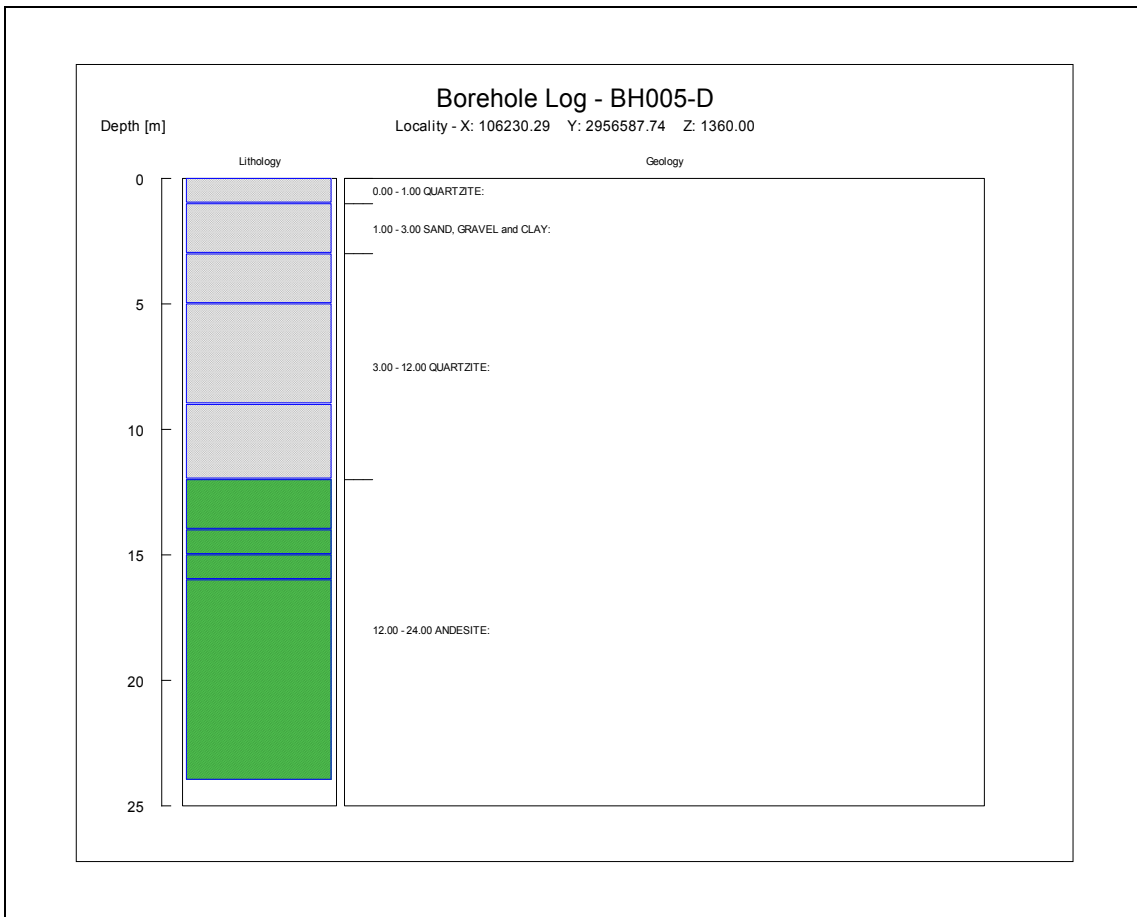


Figure 17: Borehole log of BH005-D. Coordinates; lat (S°): 26.71582, lon (E°): 27.06757.

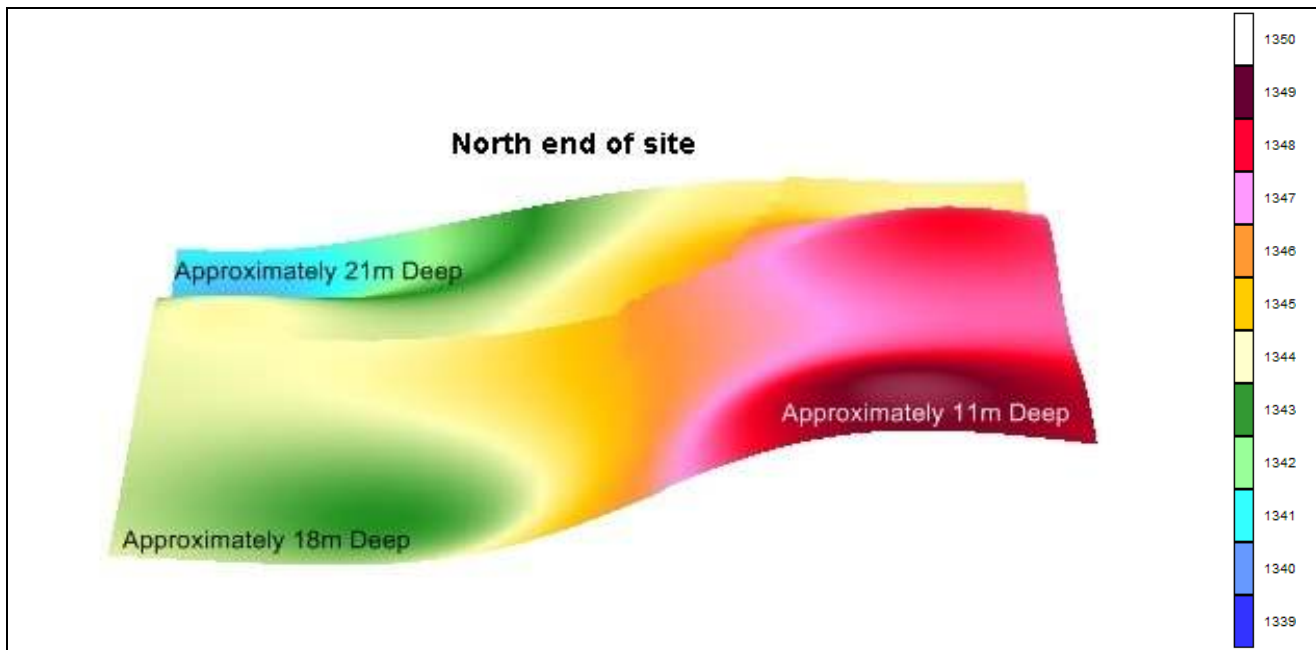


Figure 18: Three dimensional contour map of the lava formation under the SNP site (Elevation in mamsl).

The Hekpoort lava is identified by a characteristic dark green colour of the rock, also indicated as green in Figure 16 and 16. Figure 18 is a three dimensional contour map of the Hekpoort lava formation directly underlying the SNP site. The overlying weathered and fractured quartzitic layer show huge variation in sand, silt, and clay content, and also the quantity and size of the quartzite

rocks. There is a mixed sand, gravel, and clayey layer varying in depth between 2 and 10m over the whole site, with areas of the same constituency penetrating into layers with less clay content. In general, the deeper layers of rock/soil with a higher clay content occur on the western and north western side of the SNP site, with rock showing very little or no clay content to the south western side of the SNP site.

#### 4.1.2.2 Soil profiling

Figure 20 is a picture of the profile of a hole dug, ca. 1.2m deep, at AC1 (see Figure 19). There were five holes dug in total and they all (except for a layer of rubble ca. 0.6m deep at AC2) share the same characteristics. Table 11 is a description of the profile pit dug at AB10 at SNP provided by the Department of Soil Sciences at the University of the Free State. The top layer of soil of this pit (AB10) differs slightly from the others due to the fact that it is located in an area of grass, and hence has a higher organic constituency.



Figure 19: Aerial map of the SNP site indicating the locations of soils samples, auger points, and profile pits.

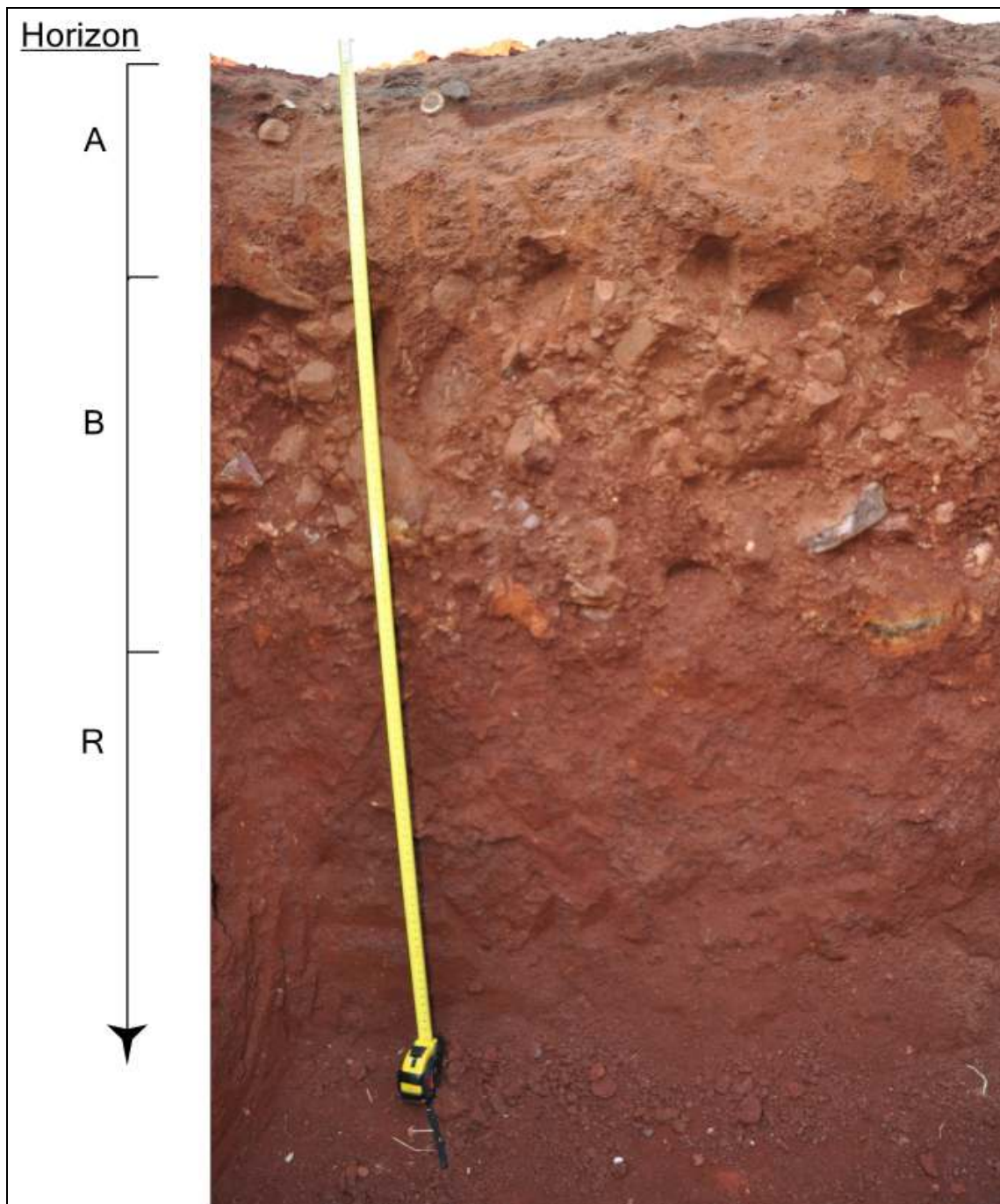


Figure 20: Photograph of profile pit (AC1) (approximately 1.2m deep) showing a weathered quartzitic layer over a more compacted zone (The Department of Soil Sciences, University of the Free State).

Table 11: Description of profile pit AB10 at SNP (The Department of Soil Sciences, University of the Free State).

<i>Horizon</i>	<i>Depth (m)</i>	<i>Description</i>	<i>Diagnostic horizon</i>
A	0.3	Colour: red; Texture: 35% clay, fine sand grade; No signs of wetness; Strong fine crumb structure; Friable consistency; No mottles; No stones; No Concretions; No free lime; Diffuse transition; Quartzite parent material.	Orthic A
B	0.9	Colour: red; Texture: 55% clay, fine sand grade; No signs of wetness; Strong fine crumb structure; Slightly firm consistency; No mottles; No stones; No Concretions; No free lime; Diffuse transition; Quartzite parent material.	Red structured B
R		Quartzite rock pieces.	Saprolite



### 4.1.2.3 Particle size distribution analysis

Table 12 indicates the results of particle size distribution analysis done on 60 soil samples. The Bouyoucos (Rapid) method was used, which allows particle size distribution analysis to be done rapidly with a hydrometer in non-destructed soil sample suspensions undergoing settling.

Soil suspensions are not homogeneous throughout, and the concentrations in the suspensions vary according to a logarithmic function with depth and time. The hydrometer reads the density (R) at a certain depth, called the “effective depth” (S). Day, P.R. developed a formula in 1952 to calculate the effective depth, and it is necessary to establish the relationship between R and S.

S is calculated using the formula;  $\log S = \frac{H_2 \log H_2 - H_1 \log H_1}{H_2 - H_1} - \log \alpha e$ , where,  $H_1 = \alpha h_1$ ,  $H_2 =$

$H_1 + L$ ,  $\alpha = \frac{A}{A-a}$ , and  $e = 2.7183$ . A = surface diameter of the sedimenting cylinder, a = surface diameter of the ball of the hydrometer, L = length of the hydrometer,  $h_1$  = distance from the top of the hydrometer ball to the point R (reading) of the hydrometer stem.

According to Stoke's Law,  $d = K\sqrt{s/t}$  can be deduced, where  $K = 1000 \sqrt{\frac{30\eta}{G(\rho_s - \rho_w)}}$ , d = particle size diameter in microns, t = time in minutes,  $\eta$  = viscosity of water, s = effective depth of the hydrometer,  $G = -981\text{cm/s}^2$ ,  $\rho_s$  = density of particles ( $2650\text{kg/m}^3$ ),  $\rho_w$  = density of water, at  $30^\circ\text{C}$ : 12.18.

The procedure involves the dispersion of the sample, separation of sand fractions, determination of clay, and the calculations of particle size. To determine the fractions of sand, clay, and silt, the following equations are used; percentage sand =  $\frac{A \times 100}{M}$ , percentage clay =  $\frac{E \times 50}{M}$  (a blank hydrometer reading is subtracted from the sample reading (C - B), and the percentage of clay is determined under the appropriate temperature in the provided table), percentage silt =  $100 - (\% \text{sand} + \% \text{clay})$ , where, A = mass (g) of sand fraction ( $>0.53\text{mm}$ ), B = hydrometer reading of blank, C = hydrometer reading of sample, E = C - B, T = temperature of suspension, and M = mass (g) of soil used.

Table 12: Particle size distribution results using the Bouyoucos (Rapid) method (%).

Sample	Clay	Silt	Clay and silt	Sand	Sample	Clay	Silt	Clay and silt	Sand
BH001-S (0-1)	30	20	50	50	AB0	16	16	32	68
BH001-D (0-1)	40	10	50	50	AB2	10	8	18	82
BH002-D (0-1)	64	16	80	20	AB6	16	10	26	74
BH003-D (0-1)	40	14	54	46	AB8	14	16	30	70
BH004-D (0-1)	64	16	80	20	AB16	18	12	30	70
BH005-S (0-1)	22	12	34	66	AB20	12	14	26	74
BH005-D (0-1)	22	10	32	68	AB27	12	14	26	74
BH006-D (0-1)	52	12	64	36	AB28	18	22	40	60
A01 (10cm)	14	18	32	68	AB30	8	6	14	86
A01 (30cm)	14	18	32	68	AB32	10	12	22	78
A01 (50cm)	12	16	28	72	AB33	20	10	30	70
A02 (0cm)	14	12	26	74	AB34	20	14	34	66
A02 (30cm)	20	18	38	62	AB10 (0-30)	22	12	34	66
A03 (10cm)	12	18	30	70	AB10 (30-60)	36	16	52	48
A03 (50cm)	20	22	42	58	AB10 (30-90)	40	10	50	50
A04 (10cm)	12	18	30	70	AC1 (30cm)	30	10	40	60
A04 (20cm)	6	4	10	90	AC1 (60cm)	40	8	48	52
A04 (30cm)	10	2	12	88	AC1 (90cm)	62	10	72	28
A05 (10cm)	26	2	28	72	AC1 (120cm)	60	16	76	24
A05 (30cm)	24	4	28	72	AC1 (135cm)	72	14	86	14
A050 (50cm)	20	0	20	80	AC3 (30cm)	28	14	42	58
A06 (10cm)	36	18	54	46	AC3 (60cm)	48	10	58	42
A06 (50cm)	32	18	50	50	AC3 (90cm)	48	14	62	38
A07 (10cm)	20	20	40	60	AC3 (120cm)	40	12	52	48
A07 (50cm)	20	20	40	60	AC2 (30cm)	22	18	40	60
A08 (10cm)	26	16	42	58	AC2 (60cm)	28	12	40	60
A09 (10cm)	30	16	46	54	AC2 (90cm)	38	16	54	46
A09 (30cm)	20	20	40	60	AC2 (120cm)	46	14	60	40
A10 Topsoil	16	16	32	68	AC4 (30cm)	22	20	42	58
A11 Topsoil	12	18	30	70	AC4 (60cm)	14	16	30	70

As indicated in Table 12, the clay, silt, and sand content of the soil samples taken from SNP vary considerably. The clay content vary from 6 - 72%, the silt content from 0 - 22%, and the sand content from 14 - 90%. As mentioned earlier, soil samples taken from the western and north-western side of the site have generally higher clay content than those taken from the south-eastern side of the site. The clay content has a significant influence on the transmissivity values, as indicated through the geohydrological tests conducted on the six deep boreholes. A full discussion of these results follows in section 4.3.

#### **4.1.3 Aquifers in the area**

There are three aquifers of concern in the SNP and KFPF area, viz.:

- The Malmani dolomitic aquifer, which is a regional groundwater source and is classified as a Major Aquifer,
- A secondary, confined fractured rock aquifer (referred to as the “minor” aquifer) formed by Transvaal sedimentary and igneous rocks, and,
- A perched (non-aquifer; shallow backfill aquifer), formed as a result of effluent from the KFPF site. This aquifer underlies only the KFPF site to the north, but is relevant to this study due to its seepage into the groundwater of the general area (and possibly into the Spitskopspruit). Seepage from this aquifer does not flow in the direction of the SNP site due to the general direction of the flow of groundwater (discussed in the following paragraphs) (Skinner, 2007).

The Malmani dolomitic aquifer (Major aquifer) (of the Chuniespoort Malmani dolomites) comprises of a weathered permeable zone of a thickness of between 3 – 20m and is underlain by solid/fractured dolomite to depths >100m. The minor confined fractured rock aquifer is comprised of weathered and fractured rock (5 – 15m) and fractured rock deeper than 15m. It has an estimated thickness of 8 – 40m. The weathered and fractured rocks of the minor aquifer are of the Transvaal sedimentary and igneous rocks, which include quartzites, shale, diabase and andesite. The perched aquifer is located within permeable asphalt, compacted fill, clayey residual shale, and gabbro. It is constrained to some extent by a discontinuous clay layer comprising of residual shale and quartzite.

The Major aquifer is located westward of the SNP plant and underlies the gypsum tailings dam area, which is ca. 2km away from SNP. A diabase sill also underlies the gypsum tailings dam and constrains seepage to some extent. There is however a suspected “weak zone” (the meaning of the term is undefined in the SRK Consulting report) on the northern side of the gypsum tailings dam, which means that contaminants are seeping relatively freely into the Spitskopspruit. The Major aquifer is bounded by the minor confined fractured rock aquifer to the east. The SNP and KFPF sites are located on this minor aquifer.



The major aquifer is classified as a very high yielding aquifer (>20l/s) and the minor aquifer as moderate yielding (0.1 – 2l/s). The major aquifer recharges the minor aquifer, which means that contaminants seeping into the major aquifer from the tailings dam seep into the minor aquifer. This is due to the direction of the flow of the groundwater which is in a general easterly direction. As mentioned above, the seepage from tailings dam into the major aquifer is constrained to some extent by a diabase sill underlying the tailings dam. (Skinner, 2007).

The perched aquifer is located north west of SNP at the north end of the KFPF site. The general direction of groundwater flow means that the seepage from this aquifer into the subsurface is not expected to impact the subsurface of the SNP site.

The general direction of flow of the groundwater is not the only factor influencing the migration of contaminants in the subsurface of the SNP site (and most likely the wider the area as well). The Hekpoort lava formation under the SNP site slopes towards the west and the north west (see Figure 18). Due to the very low porosity of the lava formation compared to the overlying weathered quartzitic layer, it is expected that contaminants would tend to collect and flow on its surface towards the west and north-west. This is confirmed by the results of the chemical analysis of water samples and EC profiles obtained from the boreholes on the SNP site.

The potential main KFPF contaminant contributing factors of concern for the SNP site come from the Tippler and Broadfields scrubber sump on the eastern boundary, and the waste deposits, coal wash bay, and granulation plant on the southern and south eastern boundary of the KFPF plant. Possible contaminants of concern to expect for from these facilities are high concentrations of ammonium, nitrate, sulphate, chloride, phosphate, and metals (Al, Co, Zn, Ni, and Mn). The southern end of the KFPF plant is, in general, not as polluted as the northern part, and nitrate, sulphate, and chloride are the main contaminants found in high concentrations in that area (Skinner, 2007).

## **4.2 Drilling (SNP)**

### **4.2.1 Drilling targets**

The drilling targets were determined by the researcher at the beginning of the investigation. The factors taken into account when determining the borehole positions were;

- That it is a relatively small site with many areas taken up by buildings, storage facilities, and machinery. Hence areas had to be selected where it was physically possible to drill without having to destroy any existing structures,
- That there were no previous data available of the site, and/or existing pollution plumes that might be significant, and,

- That it was not possible to conduct a thorough geophysical survey that might have indicated underlying geological structures and/or existing pollution plumes of significance, the knowledge of which may have indicated suitable locations for drilling. This was due to the amount of structures on the site which would have caused too much interference with the data collection (a geophysical investigation was conducted at a later stage. See section 4.4).



Figure 21: Example of drilled borehole (BH003-D) and information plate.

Given these restraints, the most practical and evenly distributed positions were selected to provide the most comprehensive data for the site. The positions decided upon are indicated in Figure 15. Table 13 indicates the coordinates of the drilling positions.

The boreholes to be drilled at the SNP site could serve to:

- Obtain information on the current groundwater quality,
- Obtain information about the chemical constituency of the soil/rock at various depths,
- Investigate the hydraulic properties of the intersected aquifer system, and,
- Act as monitoring boreholes to evaluate impacts of contaminants from SNP operations on the groundwater for future regulatory compliance.

Table 13: Coordinates of proposed drilling positions.

<i>Targets</i>	<i>Coordinates</i>	
	<i>Lat(S°)</i>	<i>Lon(E°)</i>
<i>BH001-S</i>	26.7158	27.0665
<i>BH001-D</i>	26.7158	27.0665
<i>BH002-D</i>	26.7154	27.0665
<i>BH003-D</i>	26.7165	27.0668
<i>BH004-D</i>	26.7166	27.0675
<i>BH005-S</i>	26.7158	27.0676
<i>BH005-D</i>	26.7158	27.0676
<i>BH006-6</i>	26.7154	27.0676

## 4.2.2 Boreholes

Boreholes were drilled at the positions indicated on Figure 15. Boreholes BH001-S and BH005-S are shallow boreholes located less than 3m away from BH001-D and BH005-D respectively. They were drilled to allow for observation of differences of the shallow and deeper zones in the subsurface. Table 14 and Table 15 specify the basic dimensions and construction information of each borehole. The boreholes were drilled on the 15<sup>th</sup>, 16<sup>th</sup>, 18<sup>th</sup>, 19<sup>th</sup>, and 20<sup>th</sup> of April 2010.

All the boreholes, except BH001-D (and the shallow boreholes), which has a blow yield of ca. 1000 l/h, have a blow yield of ca. 2500 l/h. All have a diameter of 215mm up to 18m, after which they have a diameter of 165mm. All the boreholes have been equipped with casing, varying in depth, type, and diameter, due to the location of fractured zones, seepage depths, and the vicinity of shallow boreholes. All the casing information is provided in Table 15.

**Table 14: Basic borehole dimensions.**

<i>Borehole Name</i>	<i>Depth (m)</i>	<i>Collar Height (m)</i>	<i>Water Level (m)</i>	<i>Blow Yield (l/d)</i>	<i>Fractures (m)</i>	<i>Water Seepage (m)</i>
BH001-S	10	0.485	4.59			
BH001-D	34	0.485	4.6	1000	20 - 23, 24 - 34	6
BH002-D	30	0.82	5.15	2500		12
BH003-D	22	0.587	4.29	2500	16 - 20, 21, 22	12
BH004-D	24	0	3.75	2500	11 - 22, 23, 24	5
BH005-S	10	0.22	3.64			6
BH005-D	24	0.22	3.64	2500		
BH006-6	24	0.22	3.69	2500	11, 21, 22	

## 4.3 Pumping tests and geohydrological parameter estimations (SNP)

The constant rate pumping test is performed to assess the yield of the aquifer according to its response to the abstraction of water, and/or to determine the aquifer parameters. This response can be analyzed to provide information with regard to the hydraulic properties of the groundwater system. With this information, it is possible to determine an optimum yield for the long- and medium-term utilization of the borehole, and to determine the ease with which contaminants are expected to migrate through the subsurface.

A pumping test is performed by pumping water from a borehole at a single rate, which is kept constant for an extended period of time. It is critical that the pumping rate during the entire duration of the test be as constant as possible.

**Table 15: Borehole construction, depth, diameter, casing-, gravel pack-, and sanitary seal data.**

Borehole Name	*Depth from Top (m)	*Depth to Bottom (m)	Diameter (mm)	Casing Diameter (mm)	Casing Type	Gravel Pack (m)	Sanitary Seal (m)
BH001-S	0	1	215	113	PVC Plain	1 - 10	0 - 1
BH001-S	1	9	215	113	PVC Screens		
BH001-D	0	18	215	165	Steel Plain	18 - 34	1 - 18
BH001-D	0	18		113	PVC Plain		
BH001-D	18	34	165	113	Screens		
BH002-D	0	1	215 (0 - 18m)	113	PVC Plain	1 - 30	0 - 1
BH002-D	0	18	165 (18 - 30m)	165	Steel Perforated		
BH002-D	1	30		113	PVC Screens		
BH003-D	0	1	(Hand cleared)	113	PVC Plain	1 - 22	0 - 1
BH003-D	0	18	215 (1 - 18m)	165	Steel Perforated		
BH003-D	1	22	165 (18 - 22m)	113	PVC Screens		
BH004-D	0	1	(Hand cleared)	113	PVC Plain	1 - 24	0 - 1
BH004-D	0	18	215 (1 - 18m)	165	Steel Perforated		
BH004-D	1	24	165 (18 - 24m)	113	PVC Screens		
BH005-S	0	1	215	113	PVC Plain	1 - 10	0 - 1
BH005-S	1	10	215	113	PVC Screens		
BH005-D	0	18	215	165	Steel Plain	18 - 24	0 - 18
BH005-D	0	18		113	PVC Plain		
BH005-D	18	24	165	113	PVC Screens		
BH006-D	0	1	(Hand cleared)	113	PVC Plain	1 - 24	0 - 1
BH006-D	0	17	215 (1 - 17m)	165	Steel Perforated		
BH006-D	1	24	165 (17 - 24m)	113	PVC Screens		

\*“Depth from Top” and “Depth to Bottom” indicate the starting- and end depth of a specific section in each borehole, e.g. borehole BH001-D has a diameter of 215mm from 0 - 18m and 165mm from 18 - 34m, etc. All PVC screens are slotted.

Pumping tests were done on the six deep boreholes, i.e., BH001-D, BH002-D, BH003-D, BH004-D, BH005-D, and BH006-D, in order to determine the general geohydrological parameters (especially the sustainable yield and late T ( $m^2/d$ ) values) for the whole area underlying the SNP site. Due to pump availability and budget constraints, only a low pumping rate (ca. 0.5l/s) could be obtained. The same pumping rate was used for all the boreholes. The pump was fixed at approximately 5m from the bottom of each borehole. The pumping tests varied in length from 105 - 150min, and the recovery was measured for ca. 30min for each borehole. The relatively short pumping tests and recovery measurements were due to time constraints.

The pumping tests were conducted on the 18<sup>th</sup> - 20<sup>th</sup> of May 2010. Figure 22 is a summary of the estimated Transmissivity values ( $m^2/d$ ) obtained using the Flow Characteristics (FC) program to analyze the data. Table 16 indicates the results obtained using the FC program.

The transmissivity values are higher than expected, and this is due to the fact that the upper layer of soil/rock (overlying the Hekpoort lava formation) consists of highly fractured and weathered quartzitic rock which provides ample pathways for water to migrate through (except where there are interspaced perched clayey layers which would serve as water and contaminant traps). Generally speaking, the western side of the SNP site shows much lower values for transmissivity than the eastern side (see Figure 22). This is attributed to the fact that soil with a higher clay was found on the western side of the site.



Figure 22: Map showing the approximate transmissivity values of different zones of the SNP site (values shown are in  $m^2/d$ ).

Table 16: Summary of the yield and transmissivity of the pump-tested boreholes. "N/A" indicates values that were excluded due to too large variation from the T-value estimation using the recovery data.

<b>BH001-D</b>		
<b>Method</b>	<b>Sustainable Yield (l/s)</b>	<b>Late T (m<sup>2</sup>/d)</b>
Basic FC	0.21	10
FC Inflection Point	0.2	
Cooper-Jacob	0.2	20
Recovery		14
<b>Average Q-sus (l/s)</b>	<b>0.2</b>	

<b>BH002-D</b>		
<b>Method</b>	<b>Sustainable Yield (l/s)</b>	<b>Late T (m<sup>2</sup>/d)</b>
Basic FC	0.29	14
FC Inflection Point	0.21	
Cooper-Jacob	0.18	9
Recovery		7
<b>Average Q-sus (l/s)</b>	<b>0.23</b>	

<b>BH003-D</b>		
<b>Method</b>	<b>Sustainable Yield (l/s)</b>	<b>Late T (m<sup>2</sup>/d)</b>
Basic FC	0.25	15
FC Inflection Point	0.18	
Cooper-Jacob	0.16	10
Recovery		5
<b>Average Q-sus (l/s)</b>	<b>0.21</b>	

<b>BH004-D</b>		
<b>Method</b>	<b>Sustainable Yield (l/s)</b>	<b>Late T (m<sup>2</sup>/d)</b>
Basic FC	0.4	78
FC Inflection Point	0.38	
Cooper-Jacob	0.22	45
Recovery		38
<b>Average Q-sus (l/s)</b>	<b>0.31</b>	

<b>BH005-D</b>		
<b>Method</b>	<b>Sustainable Yield (l/s)</b>	<b>Late T (m<sup>2</sup>/d)</b>
Basic FC	0.38	44
FC Inflection Point	0.39	
Cooper-Jacob	0.16	11
Recovery		32
<b>Average Q-sus (l/s)</b>	<b>0.27</b>	

<b>BH006-D</b>		
<b>Method</b>	<b>Sustainable Yield (l/s)</b>	<b>Late T (m<sup>2</sup>/d)</b>
Basic FC	0.4	*N/A
FC Inflection Point	0.4	
Cooper-Jacob	0.19	*N/A
Recovery		11
<b>Average Q-sus (l/s)</b>	<b>0.3</b>	

## **4.4 Geophysical investigation**

### **4.4.1 Introduction**

A geophysical study was conducted in the concerned area (SNP) in order to determine if any structural anomalies, or flow paths exist. This was done in conjunction with Orpheus Geophysics.

The purpose of the geophysical investigation was two-fold, namely:

- Investigate the possible presence of geological structures that could act as preferential pathways for the migration of contaminants in the subsurface, and,
- Determine whether there is a pollution plume present in the subsurface of the SNP site.

Two traverses were selected for two-dimensional resistivity on the SNP site (indicated in Figure 23). The reasons for choosing the specific locations of these traverses are that the site is mostly back-filled or covered with concrete leaving very little available open space. The results of the geophysical investigation were used to confirm conclusions made from analyzing drilling and chemical data.

### **4.4.2 Approach to the geophysical investigation**

As part of the geophysical investigations, the following actions were taken:

- A geological map covering the area under investigation was obtained from the Council for Geosciences and studied to determine the geological conditions that can be expected, and to ascertain whether any large-scale geological features have been mapped in the immediate vicinity of the site under investigation.
- Aerial photographs of the area under investigation were studied to determine the areas where investigations could be possible due to the built up nature of the area. Such features could include visible changes in vegetation, the presence of rock outcrops, site features (e.g. machinery, storage tanks, etc.), and prominent topographical changes.
- A site visit was conducted to determine the site layout and orientation.
- Only resistivity data was recorded on the selected traverses, as Magnetometer and EM readings would have been of no use due to interference from all the machinery and storage tanks (especially metal) on the site.
- All the geophysical data recorded during the survey were processed and interpreted in terms of the local geological and geohydrological conditions.
- Based on the results of the geophysical investigations, interpretations were made which included the geological features of the subsurface and the location of contaminants.





Figure 23: Two Dimensional Resistivity Traverses at the SNP Site.



Figure 24: Photo of traverse 1.





Figure 25: Photo of traverse 1.

#### 4.4.3 Geophysical investigation of SNP

##### 4.4.3.1 Introduction

###### *Description of the resistivity method.*

The resistivity method is a non-invasive geophysical tool that can provide cost-effective answers to geological questions. The method is based on the fact that different geological units are more or less resistive to electrical current flow. A DC or slowly varying AC current is injected into the earth by means of pairs of grounded current electrodes. The voltage drops between pairs of grounded potential electrodes are then measured at selected positions. These voltage drops are dependent on the resistivities of the materials through which the electrical currents flow.

By assuming that the earth is homogeneous and isotropic, measurements of the injected electrical current and measured voltage drops, as well as the distances between the different electrodes, may be used to calculate an apparent resistivity for the earth at a specific position and (pseudo-) depth. The apparent resistivities recorded during a survey may be inverted to obtain a model of the resistivity distribution within the subsurface. The model resistivity distribution may now be interpreted in terms of the local geological conditions by incorporating known information of the geology of the site.

The resistivity surveys on the SNP site were conducted using the Lund Imaging System with a Schlumberger geometry and unit electrode spacings of 1m (Traverse 1) and 2m (Traverse 2), in order to record resistivity data with a high spatial resolution and a maximum depth of investigation of approximately 23m.

#### 4.4.3.2 Ground geophysical investigations

Two-dimensional resistivity data was recorded along two traverses, viz. **Traverse 1** at the south end and **Traverse 2** on the western border of the SNP site, on 9 May 2010. The positions and orientations of the geophysical traverses are shown in Figure 23 - Figure 25.

It had rained the day before the two-dimensional resistivity tests were conducted, and some areas were completely covered in water and/or mud. The investigation was further hampered by a very hard layer of topsoil (clay) and rock along Traverse 2. These difficulties were overcome however, and sufficient data were collected to produce excellent results. Figure 26 and Figure 27 show the modeled resistivity profiles along the respective traverses after five iterations (Orpheus Geophysics).

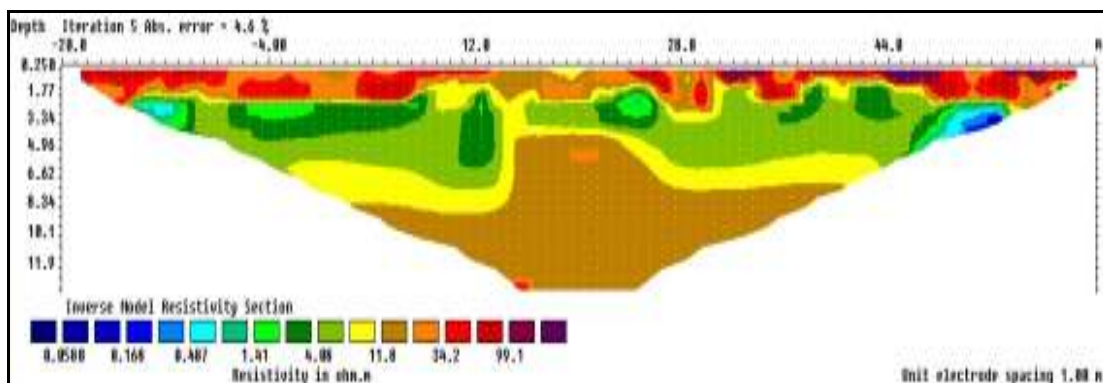


Figure 26: Two-dimensional resistivity profile along Traverse 1 (1m unit electrode spacing).

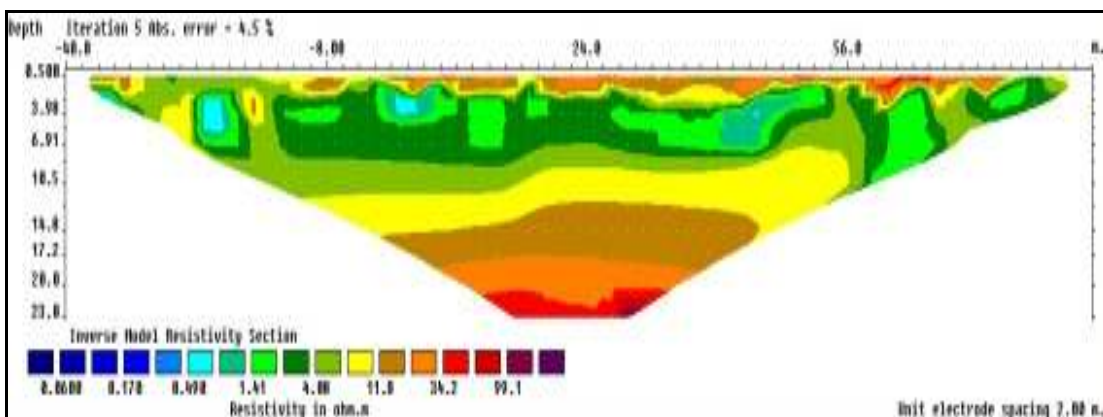


Figure 27: Two-dimensional resistivity profile along Traverse 2 (2m unit electrode spacing).

Traverse 1 was laid along the south end of the SNP site with unit electrode spacings of 1m. As previously mentioned, the location and orientation of traverses depended on the areas of the site not built up or covered with concrete. At the south end of the site there is a spacing of ca. 2m wide

between a concrete driveway and a concrete wall. On the eastern side of the traverse there is a small brick building and on the western side the concrete wall juts about 10m into the site and then returns in its original direction towards the western wall. In about the middle of traverse 1 there is a thorn bush, which made it difficult to get the unit electrodes into the ground.

Traverse 2 was laid out along the western boundary of the SNP site with unit electrode spacings of 2m. The southern end of the traverse started adjacent the concrete wall jutting into the SNP site and the northern end of the traverse went as far as the railway entrance gate. Traverse 2 was laid out just west of a small patch of grass located around the middle of the traverse. The area just north of the patch of grass was extremely wet and muddy. It was in the area between the patch of grass and the southern wall that there were difficulties inserting the unit electrodes due to a layer of extremely hard soil (clay) and quartzitic rock.

Both resistivity profiles (Figure 26 and Figure 27) were calculated with five iterations.

#### **4.4.3.3 Results of the ground geophysical investigations**

##### *Traverse 1:*

Profile 1 (Figure 26) reaches a maximum depth of ca. 12m in the middle, which is not enough to provide information about the depth, profile, and possible water and/or contaminant constituency of the Hekpoort lava formation at that point. On the left of the profile (south east corner of SNP), the lava formation has a depth of about 11m, but the V-shape (due to the Schlumberger geometry used) of the profile only allow for shallow depths to be reached at the ends of the traverse.

As can be seen in Figure 26, there is a layer of ca. 2m thick on top showing high resistivity. This could be due to the layer being dry, leached of salts/ions and/or the formation itself showing a high resistivity in this zone. Although it had rained before we arrived on site, the open ground of the SNP plant is covered in intermittent areas of clayey soil which acts as traps for moisture and would slow down the movement of water through the subsurface. This could be a likely explanation for this layer showing high resistivity values.

Just below this layer is a zone (indicated in green and blue) varying in depth between ca. 2 - 6m with much lower resistivity values. Below this layer the resistivity values increase again (shown in brown).

There are a few possible explanations for the zone of low resistivity (indicated in green and blue);

- The soil at this level may have a high clay content and act as a trap for moisture and/or salts/ions,

- The layer may be particularly weathered and fractured and serve as a preferential pathway for groundwater flow,
- The constituency of the soil/rock itself may have a low resistivity, and/or
- There may be a manmade structure (e.g. pipeline) in this zone in the subsurface.

The most likely explanation might be that the soil in this zone has the highest constituency of contaminants. This corresponds and is illustrated by the chemical analysis done on samples at various depths across the site (fully discussed in Chapter 5). This is due to the fact that certain contaminants, e.g. phosphate, do not dissolve in water and accumulate in the upper regions of the rock/soil layer. These contaminants do not enter, and are not transported by the groundwater, and if they do, only to a limited extent.

### *Traverse 2.*

**Traverse 2** reaches much deeper into the subsurface, with the maximum depth being ca. 23m. The deeper depth reached is due to the doubling of the unit electrode spacing. Again, the nature of data collection (Schlumberger geometry) causes a V-shape of the data presentation and do not allow for observation deeper into the subsurface at the ends of the traverse. The depth reached in the middle of the traverse is where the depth of the Hekpoort lava formation is ca. 17m, which allows observation of the profile and water and/or contaminant constituency at this depth.

As illustrated in the resistivity profile (Figure 27), a zone of high resistivity starts from around 17m, with a zone of very high resistivity >20.5m. The very high resistivity indicated in the profile may confirm the notion that the Hekpoort lava formation holds little water and/or salts/ions, and may act as an impenetrable boundary on which groundwater and/or contaminants collect and flow. The zone of slightly less resistivity between ca. 17 and 20.5m can be attributed to the partial weathering of the lava formation in this zone.

As with Traverse 1, there is a layer of roughly 2m thick near the surface of the resistivity profile showing high resistivity values. The same possible explanations given for Traverse 1 apply here.

Also, as with Traverse 1, there is a layer of lower resistivity below this layer of high resistivity, but here with a thickness of between ca. 2 - 8m. Again the same potential explanations given for Traverse 1 apply here.

Unlike Traverse 1, which shows regions of lower resistivity at its ends, the profile for Traverse 2 is relatively uniform, with the exception of a zone on the right (north west corner of site) which



indicates a region of low resistivity penetrating to an unknown (due to the V-shape of the profile) depth.

#### 4.5 Topography, water levels, and drainage

Figure 29 and Figure 31 are contour and vector maps, and Figure 30 and Figure 32 three dimensional contour maps of the surface- and water table elevations (mamsl) respectively of the Potchefstroom area. As illustrated in these figures, water drains into the Mooi River basin and from here flow into the Vaal River catchment. The water table elevation corresponds with the surface elevation, i.e. the direction of groundwater flow in the SNP and KFPF area is in a general easterly direction.

The water table elevation data were obtained by using Bayesian interpolation on the water level measurements taken in February 2009 by SRK Consulting on all their observation boreholes in the area. This data was preferred due to the fact that SRK Consulting's boreholes are spread out over a larger area than those on the SNP site (see Figure 28 for the location of these boreholes). In addition, the water level data of the boreholes on the SNP site were not used in conjunction with KFPF water level data, due to the fact that water levels here were measured more than one year after those at KFPF. Historical data of the KFPF site indicated significant variations in water levels over time.

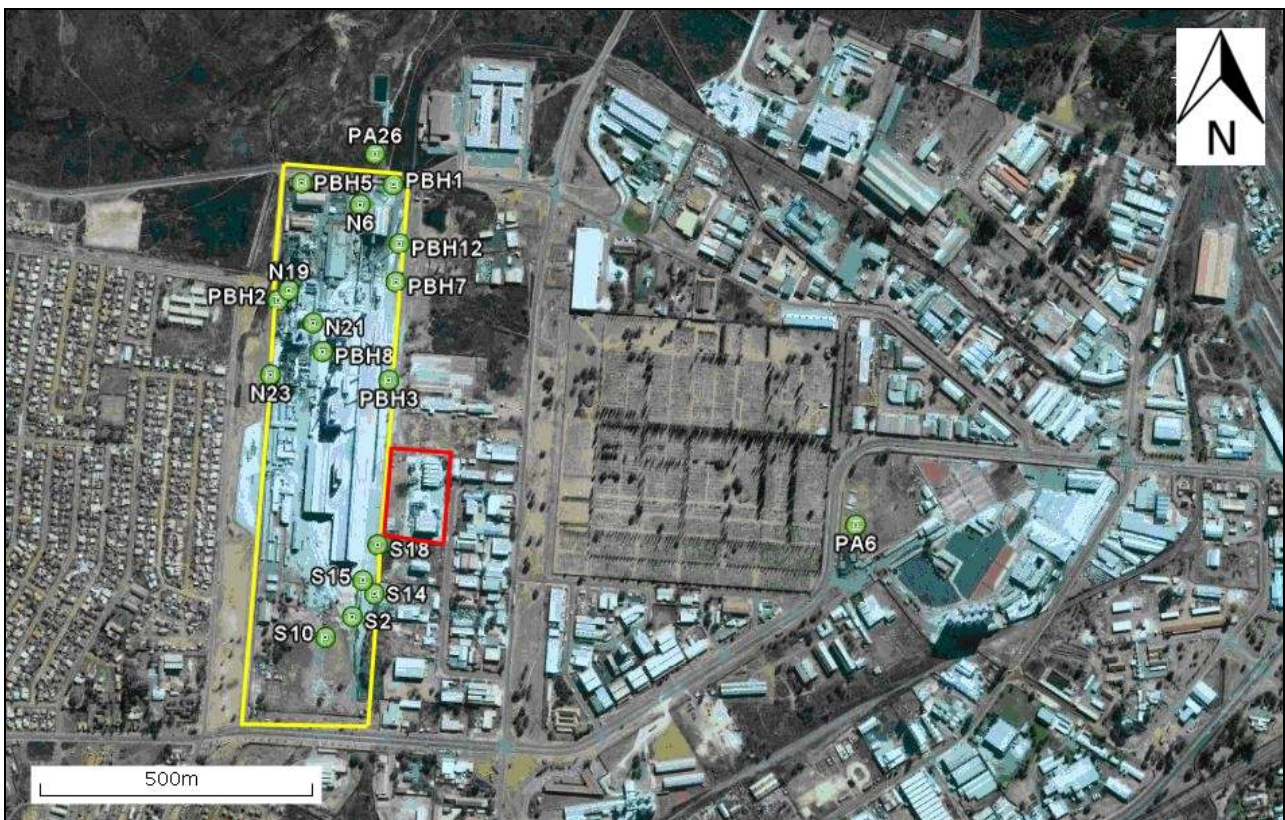


Figure 28: The boreholes used for water elevation contours. KFPF is delineated in yellow and SNP in red.



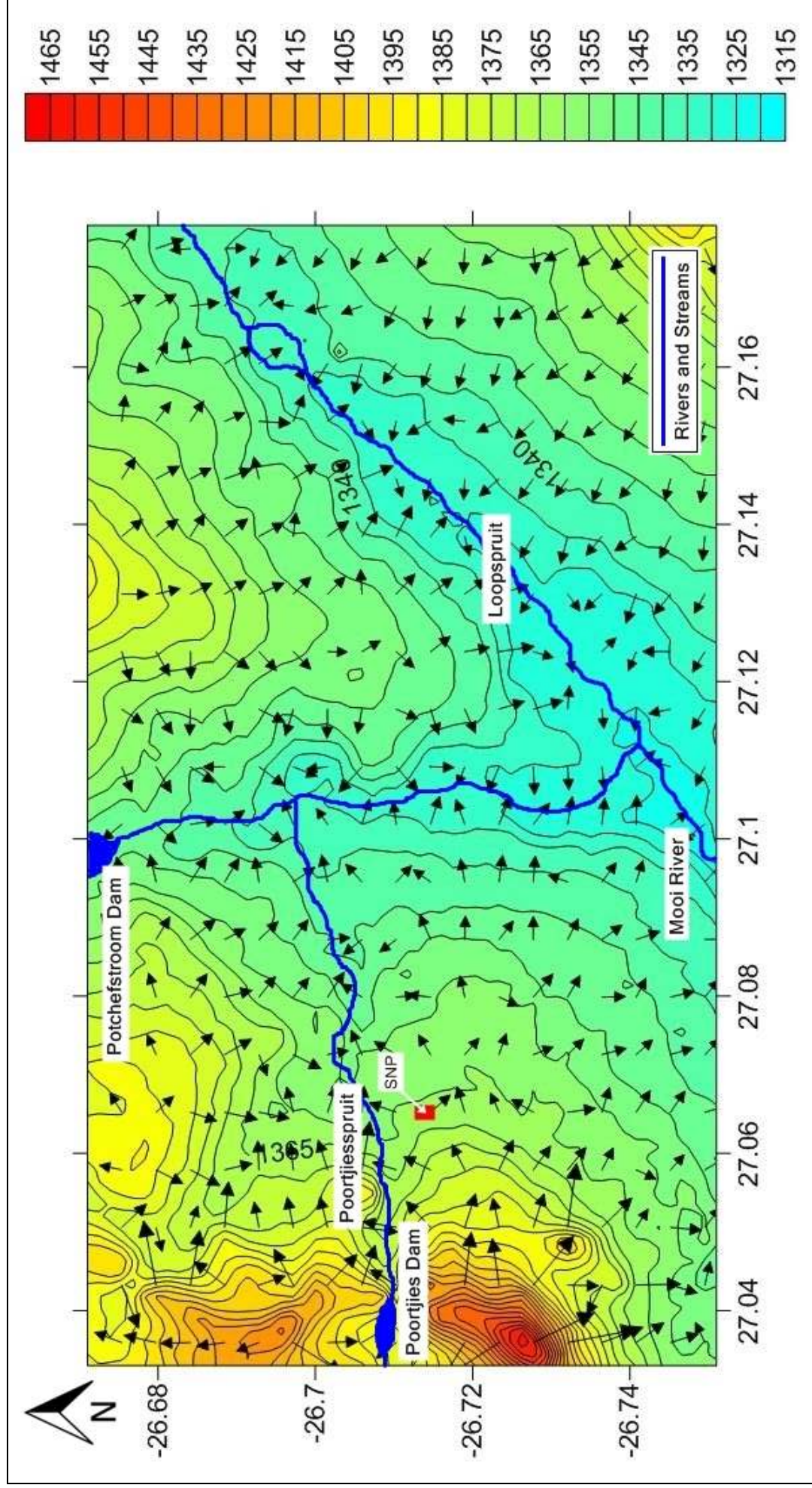


Figure 29: Contour and vector map of the surface elevation of the Potchefstroom area. The location of SNP is indicated in red (elevation values in mamsl and coordinates in lat/lon).

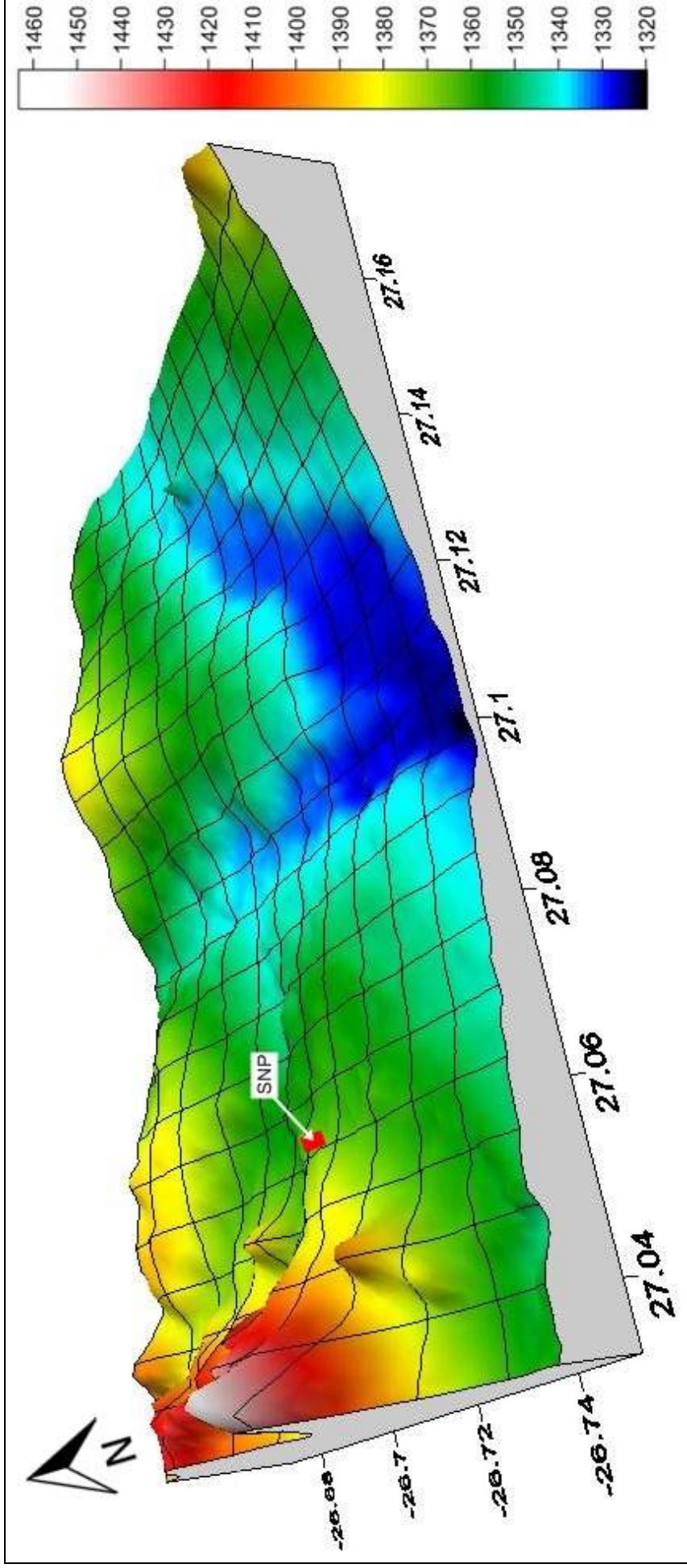


Figure 30: Three dimensional contour map of the surface elevation of the Potchefstroom area. The location of SNP is indicated in red (coordinates in lat/lon and elevation values in mams!).



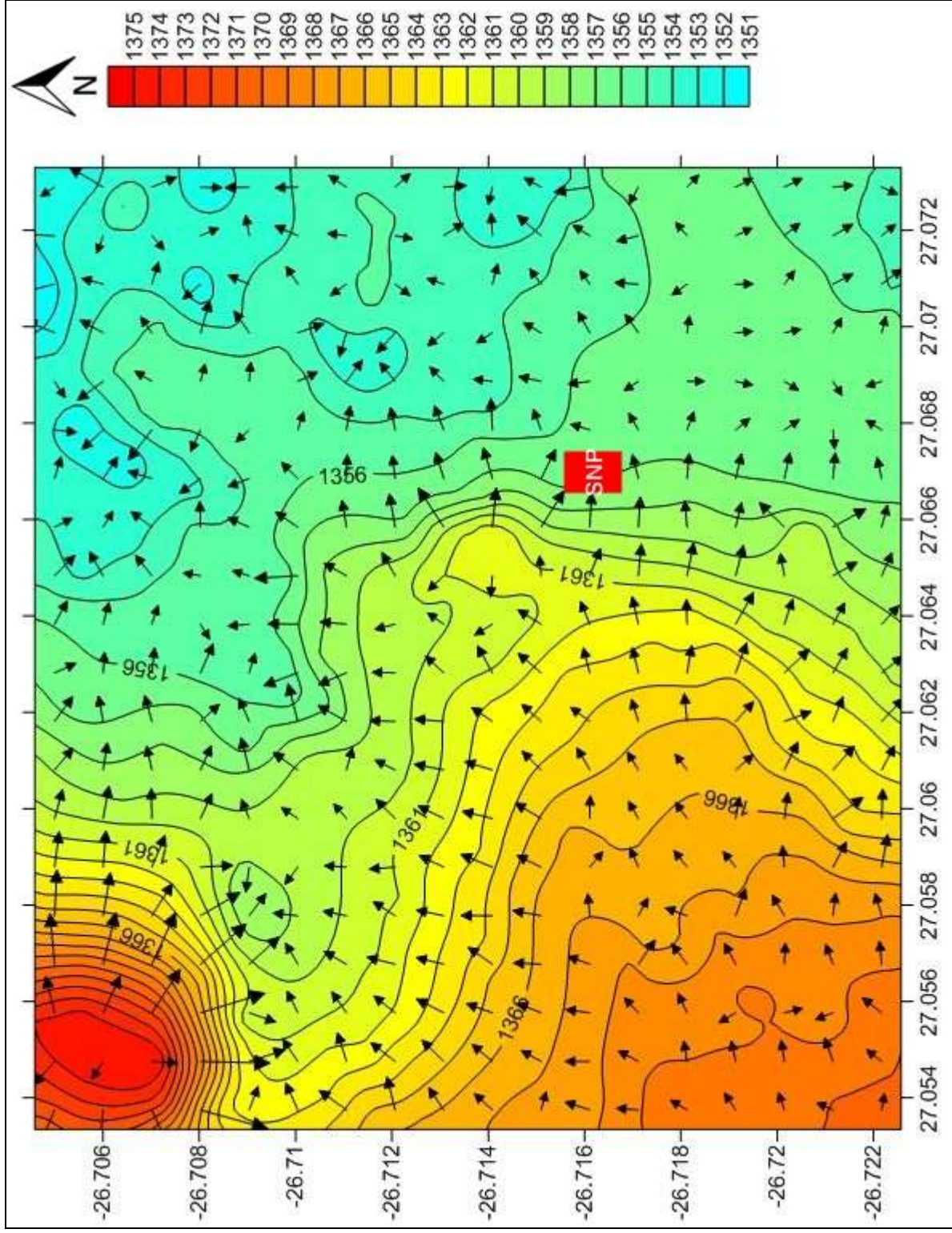


Figure 31: Contour and flow vector map of the water level elevation of the Potch Industria area. The location of SNP is indicated in red (coordinates in lat/lon and elevation values in mams!).



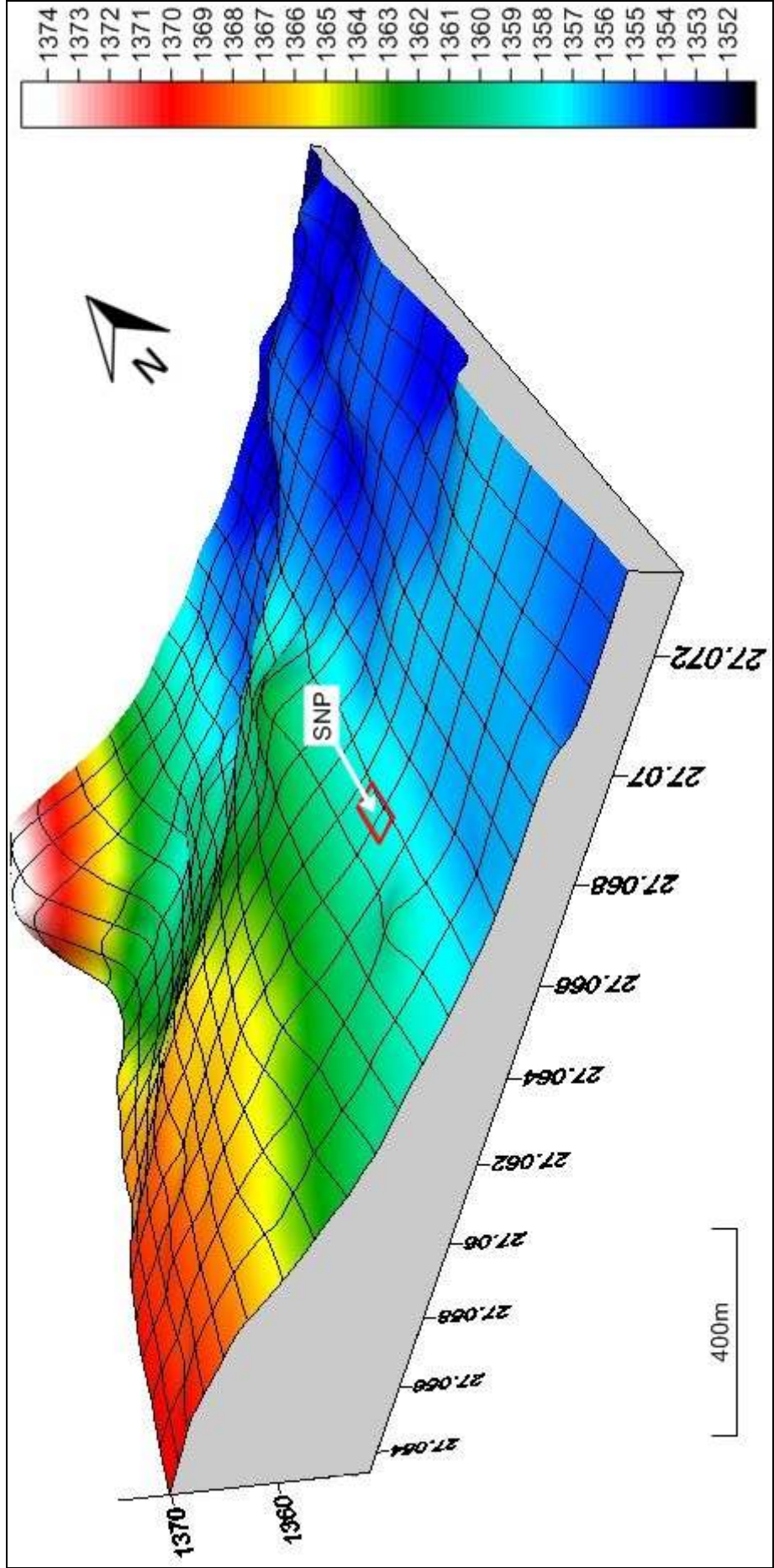


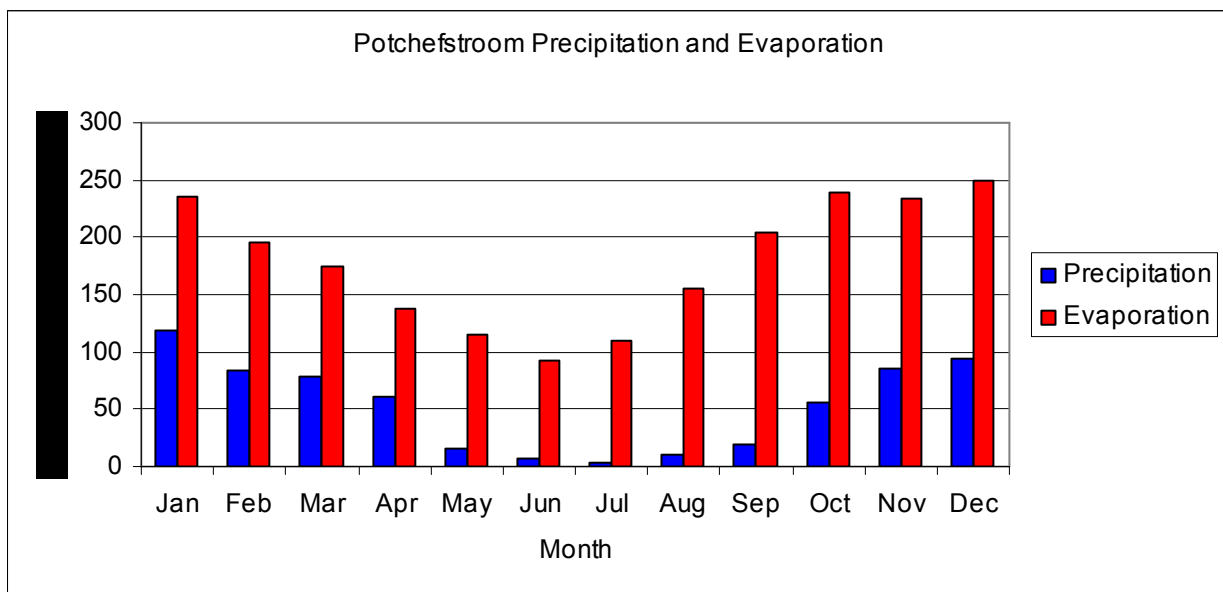
Figure 32: Three dimensional contour map of the water level elevation of the Potch Industria area. The location of SNP is indicated in red (coordinates in lat/lon and elevation values in mams!)

Surface water runoff is not a major problem from either the KFPP or the SNP site. The KFPP site is practically completely bounded by a concrete wall, especially along its border with SNP. This means that contaminants found in the unsaturated zone on the SNP site does not originate from KFPP and that the migration of contaminants occur almost exclusively in the saturated zone, and to a very limited extent, the unsaturated zone.

SNP has seven sumps on site, the location of which is indicated in Figure 13. Any runoff that may occur due to spillages are captured in these sumps and reused in fertilizer products. SNP is also mostly bounded by a concrete wall, and hence runoff from the site does not pose a significant danger to the adjacent sites.

#### 4.6 Climate

Potchefstroom has a typical highveld climate, i.e. warm summers during which most of the precipitation occurs, and dry, cold, and frosty winters. It has a long term average annual rainfall of 613mm, and high evaporation rates, which means that the area has a water deficit during the whole year. Figure 33 indicates the monthly average precipitation and evaporation rates.



**Figure 33: The Potchefstroom monthly average precipitation and evaporation (A-pan equivalent) rates (Aucamp, 2000).**

Figure 34 indicates the monthly average minimum and maximum temperatures. Potchefstroom has an average maximum temperature of ca. 27°C in summer and 21°C in winter. The average minimum temperature ranges between ca. 15°C in summer and 5°C in winter (Aucamp, 2000).

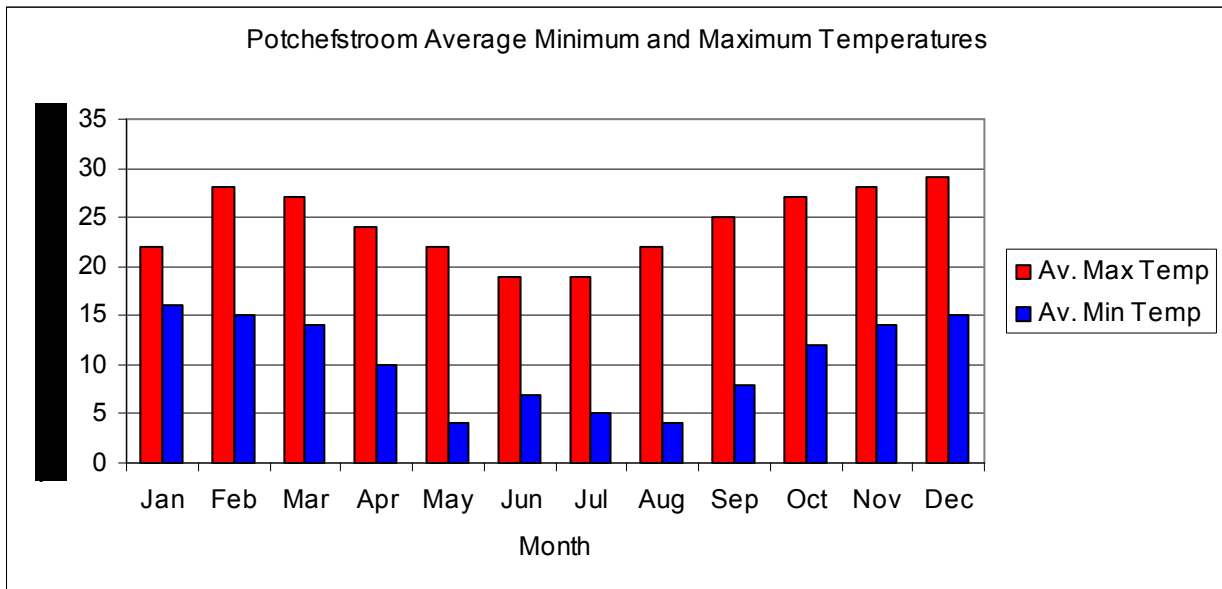


Figure 34: The Potchefstroom monthly average minimum and maximum temperatures (Aucamp, 2000).

#### 4.7 Recharge

Figure 35 illustrates the groundwater mean recharge values for the North West Province, South Africa. Knowledge of the recharge of an area gives the researcher an idea of how much water infiltrates into and flows in a groundwater system. As indicated on the map, the groundwater mean recharge for Potchefstroom ranges between 31.1 - 65.0mm/a, i.e. between 5.07 - 10.6% (Geography Department, Potchefstroom University (North West University), Date unknown). Due to the excessive chloride contamination of the groundwater caused by fertilizer manufacturing and mixing operations on the KFPF and SNP sites, the chloride method to calculate recharge could not be used.

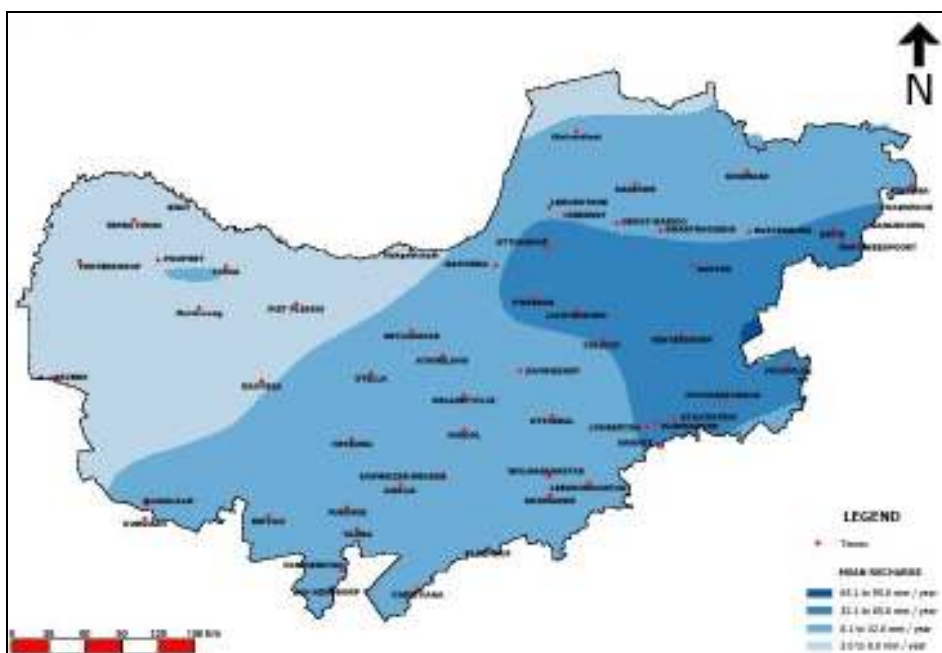


Figure 35: The groundwater mean recharge values for the North West Province (Geography Department, Potchefstroom University (North West University), Date unknown).

## Chapter 5: Chemistry

### 5.1 Natural groundwater quality and contamination

#### 5.1.1 Introduction

“The chemical composition of groundwater mainly depends on the composition of the initial pore water; the composition of infiltrating water and subsurface inflow that replaces the pore water; the composition and physical properties of the soil and rock; the chemical interaction between rock, pore water, and infiltrating water; and microbiological processes. From the moment rain falls on the ground and begins to infiltrate and pass through the soil and rock, the water dissolves the host materials, and minerals are added to the groundwater flowing through. In general, the amount of total dissolved solids (TDS) increases with the residence time of groundwater.” (Romijn, 2002)

Constituents dissolved in groundwater take part in the geochemical cycle. This process starts with the weathering of rocks. Weathering breaks up rock minerals which enter into solution in the groundwater. Weathering is more intense in hot and humid weather than in dry and cold. Mineral substances and organic material are also released into soil and groundwater by vegetative litter which forms part of the biochemical cycle. There are two types of weathering, viz. physical (e.g. frost action) and chemical (e.g. hydrolysis) weathering. Chemical weathering is most active in the unsaturated zone.

**Table 17: Constituents normally occurring in groundwater (Romijn, 2002).**

<i>Major constituents</i>	<i>Secondary constituents</i>	<i>Selected minor and trace constituents</i>	
Calcium (Ca)	Potassium (K)	Aluminium (Al)	Molybdenum (Mo)
Magnesium (Mg)	Iron (Fe)	Arsenic (As)	Nickel (Ni)
Sodium (Na)	Manganese (Mn)	Barium (Ba)	Phosphate (PO <sub>4</sub> )
Bicarbonate (HCO <sub>3</sub> )	Strontium (Sr)	Cadmium (Cd)	Radium (Ra)
Chloride (Cl)	Boron (B)	Chromium (Cr)	Selenium (Se)
Sulphate (SO <sub>4</sub> )	Fluoride (F)	Cobalt (Co)	Silver (Ag)
Silica (SiO <sub>2</sub> )	Carbonate (CO <sub>3</sub> )	Copper (Cu)	Uranium (U)
	Nitrate (NO <sub>3</sub> )	Lead (Pb)	Zinc (Zn)
		Mercury (Hg)	Sulphide (H <sub>2</sub> S, HS)

Groundwater differs considerably from place to place due to the variations mentioned above. Although these differences exist, groundwater is still made up of quite a limited number of constituents, which is unexpected considering the great differences in mineral and organic material through which the water had passed. Of the 22 elements that comprises 99.8% of the mass of the upper lithosphere, oceans, and atmosphere, only seven elements occur normally in groundwater above concentrations of 1mg/l and constitute 95% of all the constituents of groundwater. Besides these seven, groundwater can normally contain eight secondary constituents in lesser amounts (0.01 - 10 mg/l) and 40 minor constituents in still lesser amounts (<1mg/l), the occurrence of which depends on the local situation. Table 17 indicates the constituents normally occurring in

groundwater, and Table 18 examples of constituents in groundwater in relation to different rock types (Romijn, 2002).

**Table 18: Examples of various compositions of groundwater in relation to rock type (mg/l) (Romijn, 2002).**

<i>Constituent</i>	<i>Granite water, North Carolina, USA</i>	<i>Thermal soda spring, Lýsuhóll, Iceland</i>	<i>Karst spring, Areuse, Switzerland</i>	<i>Quartz-sand water, Veluwe Heath, 1927 (1979), The Netherlands</i>
pH	6.5	6.7	7.2	8.5 (4.5)
Na	7	451.2	1.3	3.5 (4.3)
K	Incl. in Na	34.2	0.8	Incl. in Na (1.2)
Mg	2	20.7	3.5	1.4 (0.5)
Ca	5	86.8	82.8	8.2 (1.4)
Sr			0.3	
Fe	0.2		0.1	0.6 (-)
HCO <sub>3</sub> total	34	1500	257	17.0 (0.0)
H <sub>4</sub> SiO <sub>4</sub>	48	350	3.4	18.2 (-)
NO <sub>3</sub>	0.9		2.7	2.4 (20.3)
SO <sub>4</sub>	2	41.2	5.3	6.5 (28.8)
H <sub>2</sub> S total		0.1		
F	0.1	5		
Cl	2	80	2.4	5.0 (8.2)

### 5.1.2 The expected natural composition of groundwater in relation to rock type

The types of rock found on the SNP site and surrounding area fall into these four main categories;

1. *Coarse and medium-grained crystalline silicate rocks*: This group of rock includes igneous and metamorphic rocks like granite, gneiss, and amphibolite, and has an interconnected system of fractures which makes them porous and permeable. Their primary permeability is negligible. Weathered granitic rock in warm and humid conditions often form good aquifers because of a layer of disintegrated rock in the upper regions and underlying fractured rock. Except in arid conditions where the salt content of water is usually higher, the natural chemical quality of water in igneous plutonic and metamorphic rocks are almost always very good. In warm and humid conditions the TDS value is reported to be less than 500mg/l and in semi-arid conditions it can easily be more than 3000mg/l.
2. *Fine-grained schistose silicate rock*: Rocks in this group include metamorphic rocks like slates and phyllites which have a low primary permeability, but high secondary permeability and porosity forming during deformation. Slates and phyllites are generally composed of alumino-silicates, mica, iron oxides, and quartz, which means that weathering will cause only a few cations to go into solution. Carbonate-rich layers involved in metamorphism have a larger amount of calcium that dissolves and precipitates in cation-exchange processes. Where there is pyrite included in the slate, ferrous iron and sulphate is brought into solution during weathering which causes the groundwater to be rich in iron and to become acidic.
3. *Volcanic rocks*: Volcanic rocks usually have a high primary porosity caused by their vesicular or block structures. Cooling fractures may cause secondary permeability and porosity. Basic volcanic rocks often contain zeolites as alteration products and influence the

chemical composition of the groundwater due to its high exchange capacity for both cations and anions. Table 18 gives an example of the chemical composition of groundwater from a thermo-mineral spring in volcanic rock in Iceland

4. *Carbonate rocks and evaporites*: These rock types develop secondary permeability due to the dissolution of rock material along fractures, and hence have a typical “dual-porosity” structure with a total porosity ranging between 15 - 40%. Dolomite and gypsum frequently occur together. The quality of the groundwater depends on the composition of the carbonates and evaporites in the rock. Groundwater that have circulated through soluble halite and gypsum deposits usually contain elevated TDS levels. Anhydrite and gypsum layers bring calcium, magnesium, and sulphate ions into solution. The rock salt forms brines. Table 18 gives an example of groundwater quality found in a karst spring (Romijn, 2002).

### 5.1.3 The expected pristine groundwater quality in the Potch Industria area

The major constituents expected to be found in most pristine groundwater samples, are; calcium (Ca), magnesium (Mg), sodium (Na), bicarbonate ( $\text{HCO}_3$ ), chloride (Cl), sulphate ( $\text{SO}_4$ ), and silica ( $\text{SiO}_2$ ).

Potchefstroom is situated in a semi-arid region, and hence pristine groundwater TDS (total dissolved solids) levels are expected to be naturally high.

The underlying volcanic rock (Hekpoort lava formation) may contain zeolites, which has a high chemical exchange capacity for both cations and anions. This may result in contaminants being adsorbed: contaminants are contained in the rock and not easily released. This may be beneficial in reducing the migration of contaminants to other regions.

Due to the dolomite formation lying to the west of SNP and KFPPF, and the groundwater moving in a general easterly direction, the groundwater will undoubtedly show characteristics of water that have circulated through these types of rock. The result may be elevated TDS levels and higher concentrations of calcium-, magnesium-, and sulphate ions.

Table 18 gives a general idea of the expected ranges of concentrations of the constituents that may have been found in groundwater in the Potch Industria area prior to human interference.

The DWA database provides very little groundwater data for the study area. Chemistry results of the nearest borehole to the study area (ca. 30km away; coordinates -26.7 lat, 26.7 lon) are (in mg/l); pH: 7.49,  $\text{SO}_4$ : 13.1, DMS: 332, Total alkalinity as calcium carbonate: 164.1, K: 3.04, EC: 41.5 (mS/m),  $\text{NH}_4\text{-N}$ : 0.02,  $\text{PO}_4$ , 0.003, Ca: 25.3, Mg: 12.8, Na: 37.5, Cl: 11.3, F: 0.48, and Si: 24.22. Due to the distance of this borehole from the study area, and the unknown nature of

operations in the vicinity of this borehole, this data is not recommended to be used as a very accurate representation of the ambient conditions of the study area.

### 5.1.4 Mechanisms of contamination

When a contaminant enters into the soil-rock-groundwater system, it will only spread if there is a transport mechanism available, e.g. a flowing liquid. As soon as the contaminant reaches the subsurface water various processes determine what happens to it, viz.;

1. *Physical Processes*: advection, dispersion, evaporation, filtration, and degassing.
2. *Geochemical Processes*: acid-base reactions, adsorption-desorption, ion exchange, oxidation-reduction, precipitation-dissolution, retardation, and complexation.
3. *Biochemical Processes*: transpiration, bacterial respiration, decay, and cell synthesis.

These processes influence each other and interact, and may either attenuate or worsen the effects of contamination (Romijn, 2002).

The soil zone is the most reactive part of the system as a result of the soil-water-air environment, soil-plant behavior, and the microbiological activity, and bypassing this system makes the soil-rock-groundwater system much more vulnerable. See Figure 36 for the processes affecting contaminant transport.

Contaminants are transported by the groundwater (advection) and travel at more or less the same rate as the average linear velocity of the groundwater. Dispersion causes a dilution of the contaminant and is accelerated by groundwater velocity and aquifer heterogeneity. For the removal of bacteria and viruses by filtration, however, a fine-grained and homogeneous material is needed.

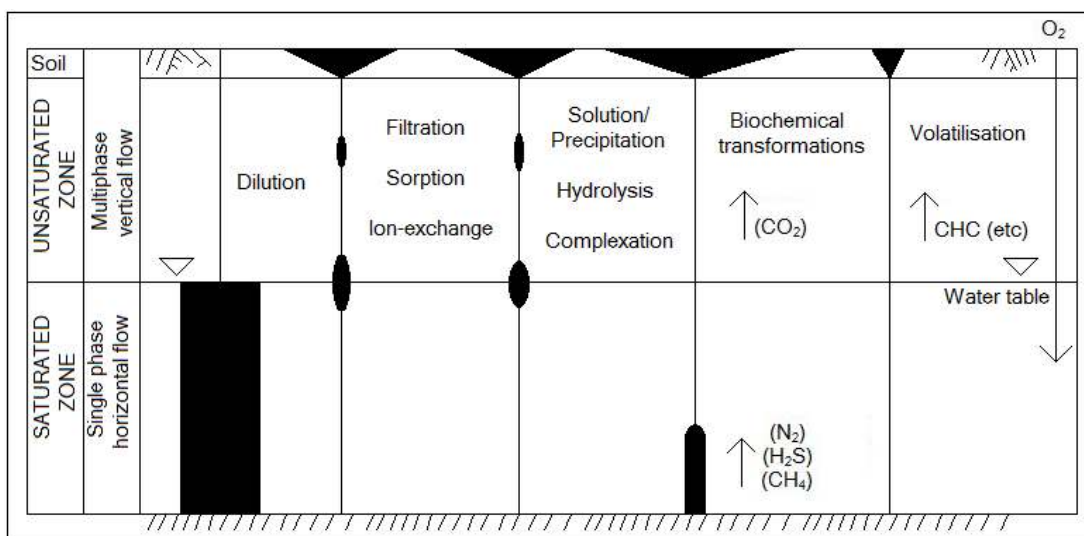


Figure 36: Processes affecting contaminant transport. The thickness of the corresponding line indicates typically the relative importance of the process in the soil and above, at, and below the water table (Romijn, 2002).

Degassing can be used to remove volatile bacterial products, such as carbon dioxide, nitrogen, or methane, and volatile organic compounds. Bacteria use the reaction energy of redox reactions for their metabolism. Contaminant movement can be retarded by chemical reactions such as adsorption, desorption, and ion exchange. Once oxygen is depleted, anaerobic respiration may successfully reduce nitrate, sulphate, and even carbon dioxide, and decompose organic compounds (Romijn, 2002).

When in the anaerobic saturated zone, nitrate may be reduced by pyrite according to;  $2\text{FeS}_2(\text{s}) + 6\text{NO}_3^- + 4\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_3(\text{s}) + 3\text{N}_2(\text{g}) + 4\text{SO}_4^{2-} + 2\text{H}^+$ . Pyrite may release heavy metals during oxidation, viz. bivalent Cd, Ni, and/or Zn, which become mobile under acidic conditions or by complexation with organic substances and may contaminate the groundwater (Romijn, 2002).

### **5.1.5 The subsurface transport of contaminants in the Potch Industria area**

The water levels in the Potch Industria area is not very deep and hence contaminants enter the transport mechanism (flowing groundwater) very early on. From here it undergoes the various processes described in section 5.1.4 (see section 3.1.5.2 for a description of the behaviour of nitrogen in the subsurface).

The SNP site has a thick top layer of soil/rock which provides a buffer for the movement of contaminants into the deeper groundwater. This top layer ranges in thickness between 11 and 22m, and is highly heterogeneous, consisting of interspersed layers of clay, gravel, soil, and highly fractured and weathered silicate rocks.

There are three aquifers of concern in the SNP and KFPF area through which groundwater flows, viz. the Malmani dolomitic aquifer, which is a regional groundwater source and is classified as a Major Aquifer, a secondary, confined fractured rock aquifer formed by Transvaal sedimentary and igneous rocks, and a perched (non-aquifer; shallow backfill aquifer), formed as a result of effluent from the Kynoch Fertilizer Production Facility.

The major dolomitic aquifer is located westward of the SNP site, and underlies the gypsum tailings dam area, which is approximately 2km away from SNP. The major dolomitic aquifer is bounded by the minor confined fractured rock aquifer to the east, and the SNP and KFPF sites are located on this minor aquifer. The major dolomitic aquifer is classified as a very high yielding aquifer and the minor aquifer as a moderate yielding aquifer. The major aquifer recharges the minor aquifer, which means that contaminants seeping into the major aquifer from the tailings dam migrate into the minor aquifer. The perched aquifer is located north west of the SNP site at the north end of the KFPF site. Water in this aquifer is of a very poor quality and some of it seeps into the minor fractured rock aquifer. Due to the general direction of groundwater flow (easterly direction), this aquifer does not pose an immediate risk to the pollution of the SNP site.



The seepage from the tailings dam into the major aquifer is constrained to some extent by a diabase sill underlying the tailings dam. There is however a suspected “weak zone” (the meaning of the term is undefined in the SRK Consulting report) in the diabase sill on the northern side of the gypsum tailings dam, which means that contaminants are seeping relatively freely into the Spitskopspruit.

The groundwater moves towards the Spitskopspruit and Potch Industria (east), as evidenced from topographical data and results in the SRK Consulting report. Most of the groundwater eventually reaches the Mooi River, and from here it flows into the Vaal River catchment (Skinner, 2007).

## **5.2 The Kynoch Fertilizer Production Facility (KFPF)**

Only a limited quantity of data obtained by SRK Consulting through their study on KFPF in 2007 was made available to the researcher. It was however sufficient for the purpose of this study. These were the findings in regard to the contaminants, their concentrations, and their location on the site.

Figure 37 indicates the predominant groundwater contaminants on the KFPF site and their general location. The main KFPF contaminant contributing factors of concern for the SNP site come from the Tippler and Broadfields scrubber sump on the eastern boundary, and the waste deposits, coal wash bay, and granulation plant on the southern and south eastern boundary of the KFPF plant. Possible contaminants of concern to look out for from these facilities are high concentrations of ammonia, nitrate, sulphate, chloride, phosphate, and metals (aluminium, cobalt, zinc, nickel, and manganese). The southern end of the KFPF plant is, in general, not as polluted as the northern part, and nitrate, sulphate, and chloride are the main contaminants found in high concentrations in that area.

Groundwater with a very low pH (<2.5) were found in the middle-north-western area of the site. This area was also found to have high concentrations of nitrate (NO<sub>3</sub>) (120 - 700mg/l), ammonium (NH<sub>4</sub>) (300 - 1500mg/l as N), fluoride (F) (0.1 - 4100mg/l), sulphate (SO<sub>4</sub>), phosphate (PO<sub>4</sub>) (3000 - 110102mg/l), iron (Fe), nickel (Ni), chromium (Cr), and zinc (Zn). Radionuclide contamination was indicated in the acid plant area and has been rehabilitated. In the far north-western corner of the factory, groundwater with a pH of ca. 4.5 was found, and elevated concentrations of nitrate (<10 - 40mg/l) and sulphate (70 - 2240mg/l).

Moderately acidic groundwater (pH between 3 and 4.5) was found in the north-eastern corner of the site. The major contaminants found in high concentrations here, were; nitrate (52 - 510mg/l), ammonia (310 - 1100mg/l as N), sulphate (2700 - 7600mg/l), chloride (Cl) (311 - 788mg/l), and phosphate (41 - 128mg/l). On the eastern boundary, groundwater has a pH of ca. 4.3, and nitrate

(<1000mg/l), sulphate (<1000mg/l), chloride (<300mg/l), and phosphate (<10mg/l) were found in significant concentrations.

The southern area of the site has slightly acidic to neutral groundwater, and is contaminated with mainly nitrate (20 - 450mg/l) and sulphate (30 - 900mg/l). An emergency dam (delineated in red in Figure 37) is located ca. 200m north-north-west of the KFPF plant. Water here was found to be neutral to slightly alkaline, with nitrate (<6050mg/l), sulphate (<500mg/l), and chloride (<360mg/l) present in significant concentrations.

Radionuclides (Th and Ra) were found in the boreholes just east of the gypsum tailings dam, but the doses were consistently below the recommended dose to members of the public (South Africa), i.e. <0.25mSv/a. The WHO prescribes a recommended reference dose level (RDL) of the committed effective dose of 0.1mSv/a.

The study conducted by SRK Consulting on KFPF in 2007 showed that the “Gypsum Tailings dam and the Factory [KFPF] both contribute to contamination in the Spitskopspruit” (Skinner, 2007).

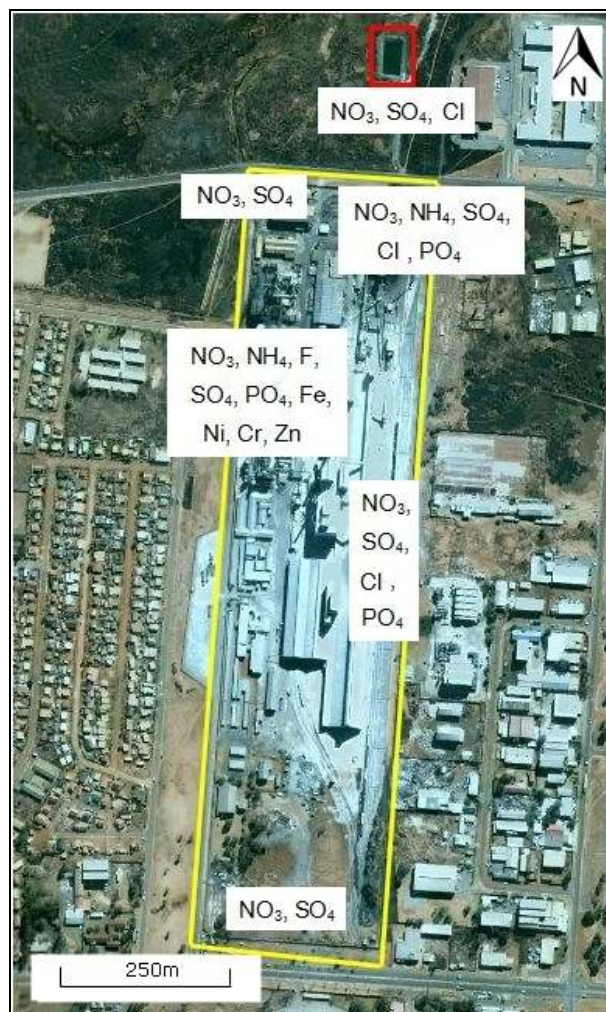


Figure 37: Map indicating the predominant groundwater contaminants and their general location on the KFPF site. KFPF is delineated in yellow and the emergency dam in red (Skinner, 2007).

## 5.3 Sasol Nitro Potchefstroom (SNP)

### 5.3.1 Soil- and water sampling targets

#### 5.3.1.1 Soil sampling targets

Soil sampling targets are divided into four groups (see Figure 38);

- A01 - A11: Shallow auger holes under the storage tanks in the centre of the site (On request from SNP).
- AB1 - AB35: Surface samples scattered randomly across the site (except position AB10, which is where a profile hole was dug 0.9m deep, and AB2, where two extra samples were taken, viz. a sample paving brick and a sample 0.3m deep. The extra samples taken from AB2 are due to the fact that chemical damage to the pavement and building (see Figure 39) at the north side of the SNP site was observed.
- AC1 - AC4: Profile holes dug varying in depth between 0.6 - 1.35m, to collect soil samples at varying depths and gain further insight into the soil profile of the site.
- BH001-D (x) - BH006-D (x): Samples taken during the drilling of the boreholes. x = the depth of the sample taken.



Figure 38: Proposed soil sampling targets and position of boreholes.

The specific targets for soil sampling were selected in order to obtain the optimum amount of data for the whole site, not just on the surface, but at various depths. This is important for a good understanding of the location and movement of contaminants in the subsurface.

SNP indicated that they were concerned about the area under the storage tanks in the centre of the site in particular, and consequently the first set of samples taken were A01 - A11 at the end of April 2010, using a manual auger. It was hoped to reach depths of 2m, but the high content of rock in the subsurface made this impossible. The deepest samples were taken at 0.5m. The researcher was informed that this area in particular has been rehabilitated in the past, viz. the area was dug up, a concrete wall was built to contain any future contaminants from migrating, and it was refilled with poor grade fill. This was evident from the amount of waste bricks come across during drilling.

Surface samples at AB1, AB2, AB6, AB8, AB16, AB20, AB27, AB28, AB30, AB32, AB33, and AB34 were taken on the 13<sup>th</sup> of May 2010.

The option of profile holes were chosen due to the fact that the quartzitic constituency of the soil/rock, which makes it extremely hard, made it impossible to auger (even with a motorized auger). Five profile holes were dug. The first one was dug at position AB10 on the 10<sup>th</sup> of May 2010 (See Table 11 for a description of the soil profile). A further four were dug on the 18<sup>th</sup> (AC1 and AC3) and 19<sup>th</sup> (AC2 and AC4) of May 2010. AC1 - AC4 have respective depths of 1.35, 1.2, 1.2, and 0.6m. The shallow depth reached at AC4 was due to the extremely high content of quartzitic rock in this particular area. Samples were taken at every 0.3m from each of these holes.

The 0.3m deep and paving brick samples were taken on the 19<sup>th</sup> of May 2010. The reason it was decided upon to take these extra samples at this particular location was due to the suspected presence of high concentrations of phosphates at this point, which were beginning to crystallize in the subsurface, lift the area, and cause damage to the buildings (see Figure 39).

Soil samples at 1m intervals were analyzed for the first 10m of every borehole. Between 10 - 20m, a sample was analyzed every second meter. Then, for boreholes deeper than 20m, only one or two samples were analyzed, e.g., for a borehole 24m deep, one sample was analyzed, and for a borehole 30m deep, two samples were analyzed. The names of the samples are given as the name of the borehole, including the depth of the sample in brackets, e.g. BH001-D (8m) and BH006-D (20 - 24m).

All soil samples taken were placed in individual plastic bags, appropriately marked, and then sent to the IGS laboratory for analysis. The analysis of samples included determining the concentrations of various contaminants and also the determination of the clay, silt, and sand content of the soil.

As mentioned in section 4.5, SNP has seven sumps on site, the location of which is indicated in Figure 13. Any runoff that may occur due to spillages during operations are captured in these sumps and reused in fertilizer products. SNP is also mostly bounded by a concrete wall, and hence runoff from the site does not pose a significant danger to the adjacent sites. There is a concrete wall separating KFPF and SNP, which means that surface runoff from KFPF towards SNP also doesn't pose a significant problem. For these reasons, and due to their inaccessibility, surface soil samples were not collected from adjacent sites.



Figure 39: Photo indicating the chemical damage to the pavement and building on the northern side on the SNP plant.

### 5.3.1.2 Water sampling targets

Water sampling targets are divided into three groups (see Figure 40);

- BH001-D (x) - BH006-D (x): "x" indicates the depth below water level of the sample taken using a Bailer,
- BH001-D (y) - BH006-D (y): "y" indicates the time after the pumping test started of the sample taken, and,
- ROSS6 and SAB1; viz. the samples taken outside the SNP site during the hydro census.



The first set of water samples were taken using a Bailer on the 12<sup>th</sup> of May 2010. Standard depths of ca. 2m below the water level and 5m above the bottom of the borehole were used for all the boreholes. Extra samples were also taken where EC profiles showed anomalies, which might indicate possible fractures and/or zones of preferential flow. The EC profiles were done on the same day.

The location of the samples taken outside the SNP site during the hydro census is indicated on Figure 40. ROSS6 is owned by Mighty Products Company and is located at 6 Ross Street, and SAB1 is owned by South Africa Breweries (SAB) and is located in Promosa Ave. Both boreholes are fitted with a pump, and samples were taken from the outlet of these pumps. These samples were taken on the 12<sup>th</sup> of May 2010.

The second set of water samples were taken during the pumping tests (18 - 19 May). These water samples were necessary in order to ascertain the migratory characteristics of the contaminants in the subsurface, i.e., to determine whether there are zones in the subsurface that would yield contaminants after the extraction of water in a specific area.

All water samples taken were placed in plastic bottles, appropriately marked, and then sent to the IGS laboratory for analysis.



Figure 40: Location of boreholes ROSS6 and SAB1, and boreholes on the SNP site (delineated in red).

## 5.3.2 Soil- and water sample results

### 5.3.2.1 Introduction

The criteria used for inorganic sampling are the SANS241:2006 standards for drinking water. The soil and water samples will be classified as:

- Class I - acceptable (colour coded **green**),
- Class II - allowable (colour coded **yellow**),
- Class III - not allowable (colour coded **red**).

(The analysis units are mg/l (for water samples), kg/ton (for soil samples), and mS/m for EC). See the attached CD for the full results of the chemical analysis of samples taken from the SNP site, SAB1, and ROSS6.

### 5.3.2.2 Soil chemistry

Figure 41 illustrates the general location of the predominant contaminants found in soil samples.

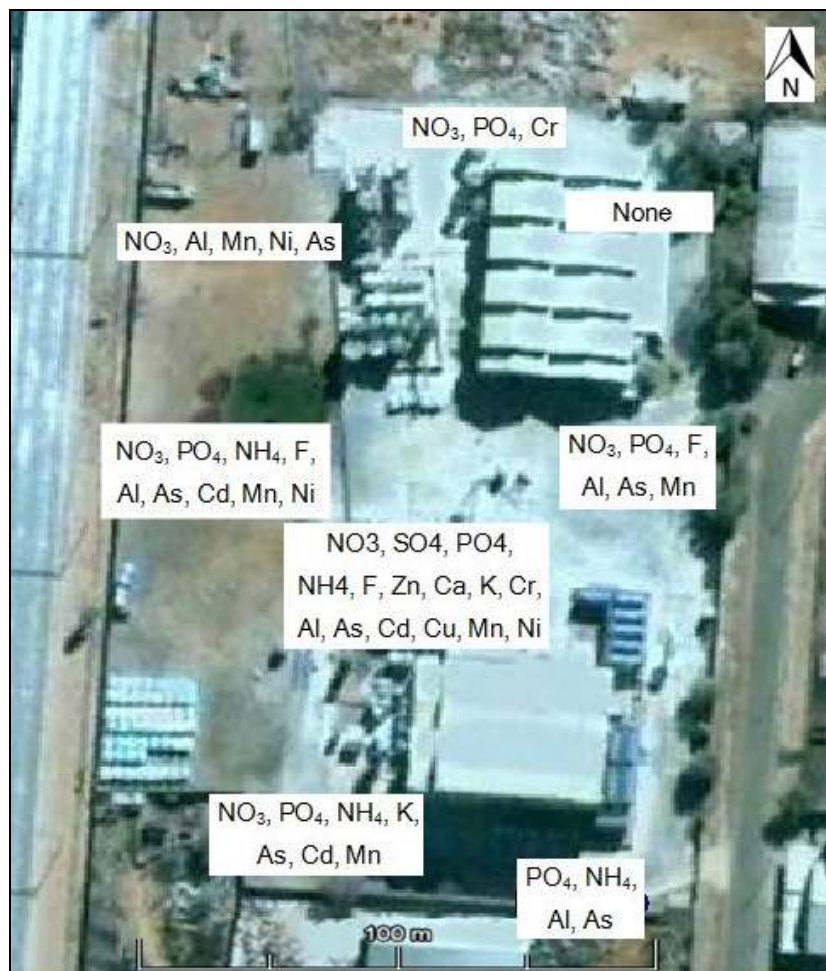


Figure 41: The general location of contaminants found in soil samples.

Figure 43 - Figure 45 illustrate the distribution, classification, and quantity of selected contaminants found in soil samples at various depths. The depths indicated are either "Shallow" (0 - 1.2m),

“Middle” (9 - 14m), or “Deep” (ca. 18 - 24m). Each rectangle represents the entire SNP site (see Figure 41). In total, 172 soil samples were taken and analyzed. Figure 42 indicates the main problem area. This is under storage tanks located in the centre of the site.

The following conclusions can be made from analyzing the contaminants and their location on the SNP site (see Figure 43 - Figure 45);

- As indicated, the upper layer of soil is generally the most contaminated, with very little contaminants occurring in depths >9m.
- The most predominant contaminant occurring throughout the site is Nitrate ( $\text{NO}_3$ ) (0.00034 - 1.546kg/ton). Nitrate occurs mostly at depths <7m. This is due to nitrate not easily being adsorbed by soil, i.e. nitrate occurring in the saturated zone is predominantly found in water samples (this is also true for Ca, Mg, Cl, and Mn).
- The biggest problem area is the storage tank area in the middle of the site, where excessive concentrations of nitrate (0.0264 - 1.451kg/ton), sulphate ( $\text{SO}_4$ ) (0.07 - 20.84kg/ton), phosphate ( $\text{PO}_4$ ) (0 - 5.45kg/ton), ammonium ( $\text{NH}_4$ ) (0.00084 - 3.7kg/ton), fluoride (F) (0.0057 - 0.2862kg/ton), potassium (K) (0.001 - 2.72kg/ton), chromium (Cr) (0.0003 - 0.00046kg/ton), zinc (Zn) (0.002 - 9.6kg/ton), calcium (Ca) (0.01456 - 2.07518kg/ton), aluminium (Al) (0.0001 - 0.10359kg/ton), arsenic (As) (0.00017 - 0.011kg/ton), cadmium (Cd) (0.00002 - 0.003kg/ton), copper (Cu) (0.00045 - 0.04399kg/ton), manganese (Mn) (0.00085 - 0.05623kg/ton), and nickel (Ni) (0.00006 - 0.00377kg/ton) are present (see Figure 42).
- Heavy metal pollution occurs throughout the site, with the exception of the north-eastern corner (see Figure 41). These heavy metals include cadmium (0 - 0.0004kg/ton), chromium (0 - 0.00102kg/ton), aluminium, (0.00005 - 0.05706kg/ton), manganese (0.00000233 - 0.23684kg/ton), nickel (0 - 0.00432kg/ton), and arsenic (0 - 0.02077kg/ton).
- Phosphate and ammonium is present in high concentrations at shallow depths throughout the site, and throughout the depth of the site at the southern end of SNP. Phosphate is highly immobile in the subsurface (and also  $\text{NH}_4$ , but to a lesser extent), and was expected to be found only in the uppermost layer of soil/rock. Phosphate does not have drinking water standards.
- Cobalt (Co) was found in significant concentrations in the profile holes AC1 - AC4 (0 - 0.0067kg/ton).
- There were excessively high fluoride (F) concentrations found at shallow depths in most areas of the site, and in a deep sample taken from the south-eastern corner of the site (0.000017 - 0.2862kg/ton). Fluoride is present in lower concentrations throughout the entire site.



- Chromium (Cr) was found in concentrations between 0.0003 and 0.00045kg/ton at A03 and in the paving brick analyzed at AB2 (see Figure 38). To find chromium only on the brick and not in the samples taken directly underneath it (on the surface and at 0.3m) suggests that it was either a once off small spill of a chromium containing substance, or that there are traces of chromium inherent in the paving brick, i.e., some form of chromium is used during the manufacturing of the brick. Chromium was found at various depths at A03 and an investigation into the source of this is advised, as no chromium is used in SNP products or their manufacturing processes.
- Class II concentrations of Iron (Fe) (ca. 0.002kg/ton) were found at deep levels in the middle region of the western border of the site (BH001-D).
- In general, the upper 2m of soil is mildly acidic, with pH values increasing with depth to approximately neutral levels. pH values for soil samples taken from the storage tank area range between 3.44 - 5.61, and soil samples taken from the profile holes (AC1 - AC4) have pH values ranging between 3.46 - 5.31. pH values for soil samples taken during drilling range between 3.09 - 6.24 for the first 2m, and then quickly increase with depth to near neutral values. The only alkaline pH was measured in the crushed brick sample taken from position AB2. The solubility of many heavy metal contaminants increase with a decrease in pH, which explains the distribution of contaminants on the SNP site, i.e. most contaminants collect in the zone of soil/rock where the pH starts to increase (see Figure 56 and Figure 57). They leach through the first layer of soil (ca. 2m deep) as a result of the acidity.
- The little or no contaminants found in the north-eastern region of the site is attributed to the fact that there is a flourishing garden. The plants phytoremediate the contaminants, i.e. contaminants are extracted from the soil and groundwater, and then stored in the plant tissue.
- As expected, many of the major contaminants associated with the fertilizer industry, i.e.  $\text{NO}_3$ ,  $\text{PO}_4$ ,  $\text{SO}_4$ ,  $\text{NH}_4$ , F, and Cd, were found in excessive concentrations on the SNP site.



Figure 42: Photos of storage tank area in the centre of the site.

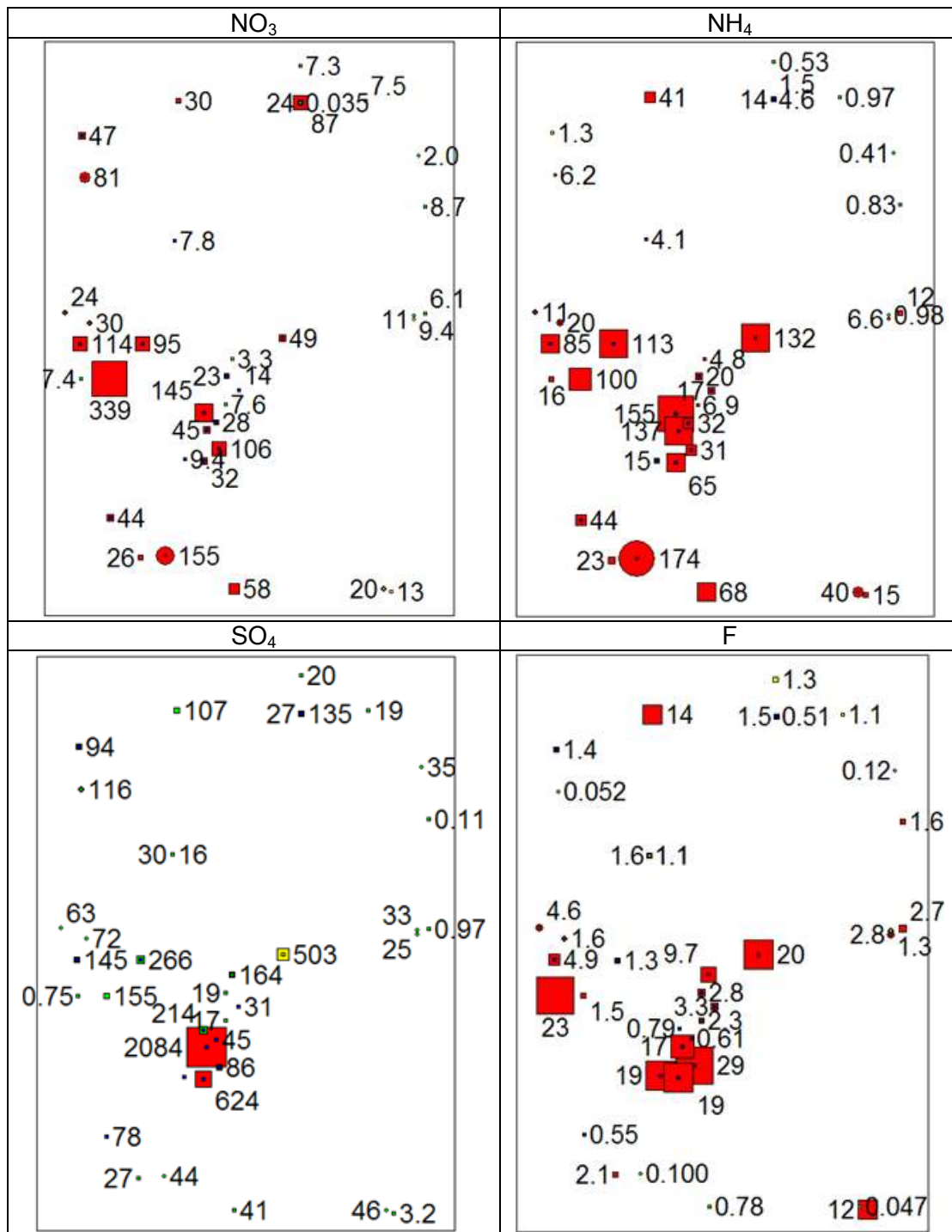


Figure 43: Distribution, classification, and proportionality of contaminants of concern found in soil samples at “Shallow” depth (0 - 1.2m). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption), **Blue**: no standards (according to SANS241:2006) (mg/l).

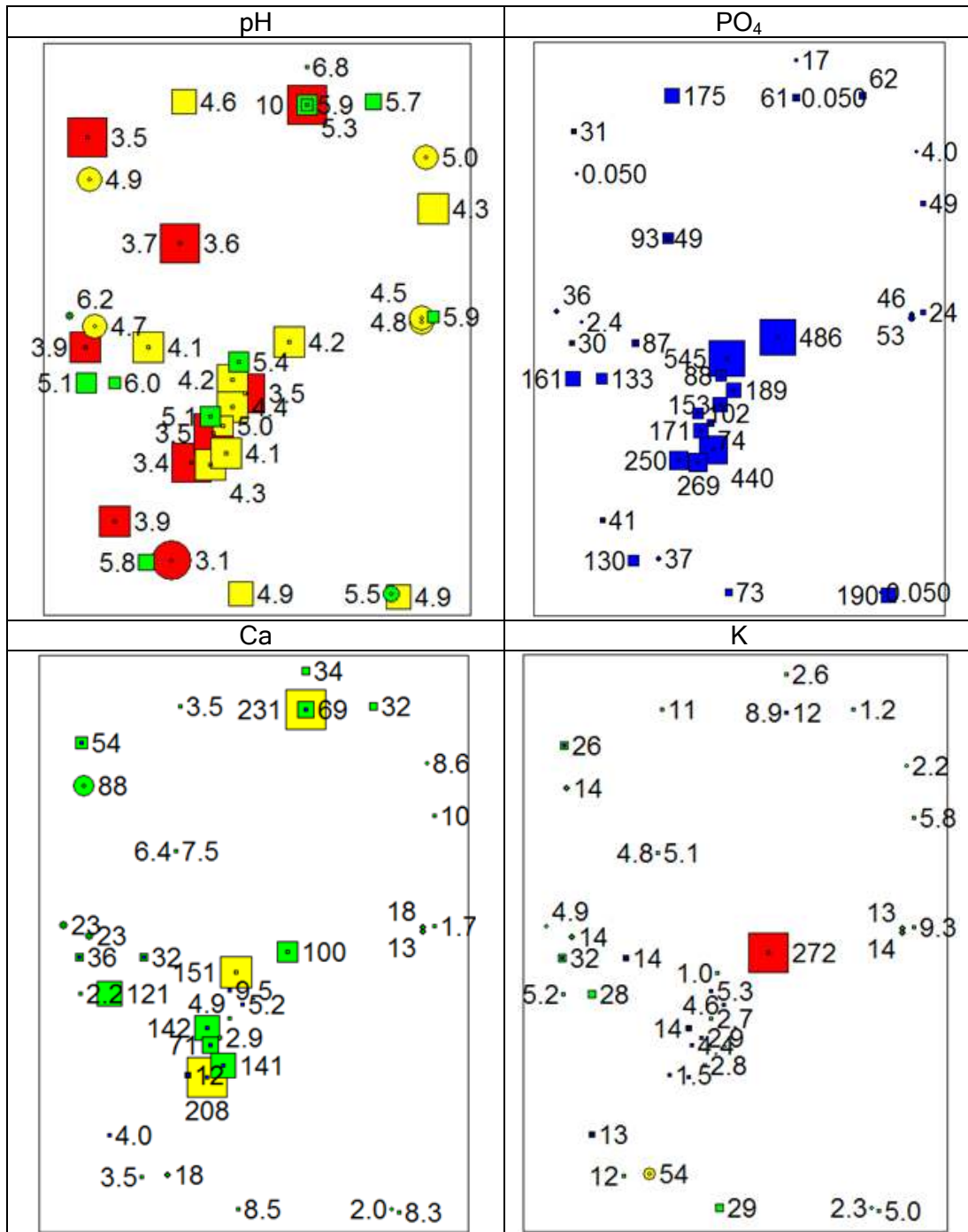


Figure 43 (continued): Distribution, classification, and proportionality of contaminants of concern found in soil samples at “Shallow” depth (0 - 1.2m). **Red:** not allowable concentrations, **Yellow:** allowable concentrations (short term), **Green:** allowable concentrations (lifetime consumption), **Blue:** no standards (according to SANS241:2006) (mg/l).

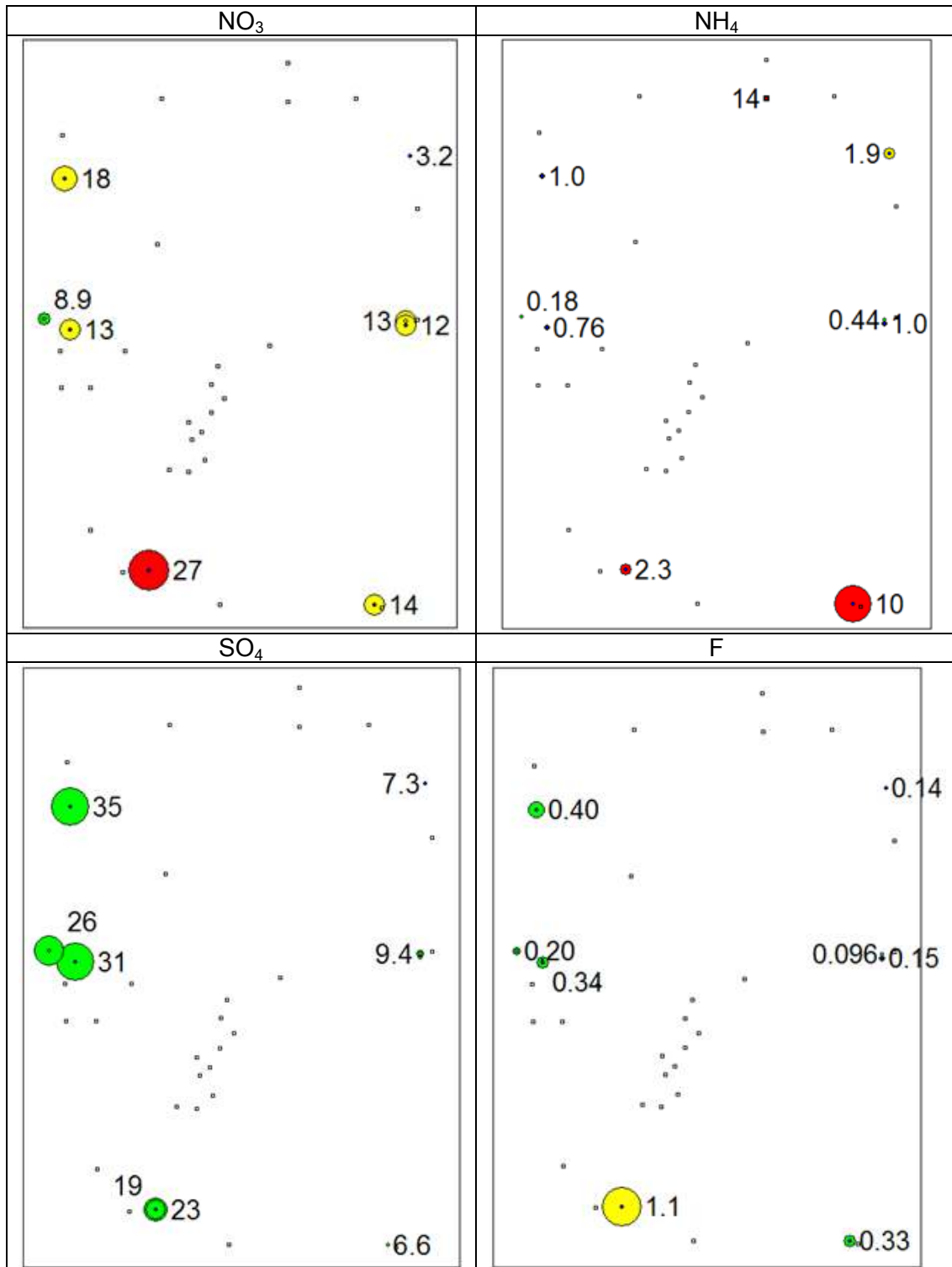


Figure 44: Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Middle" depth (9 - 14m). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption), **Blue**: no standards (according to SANS241:2006) (mg/l).

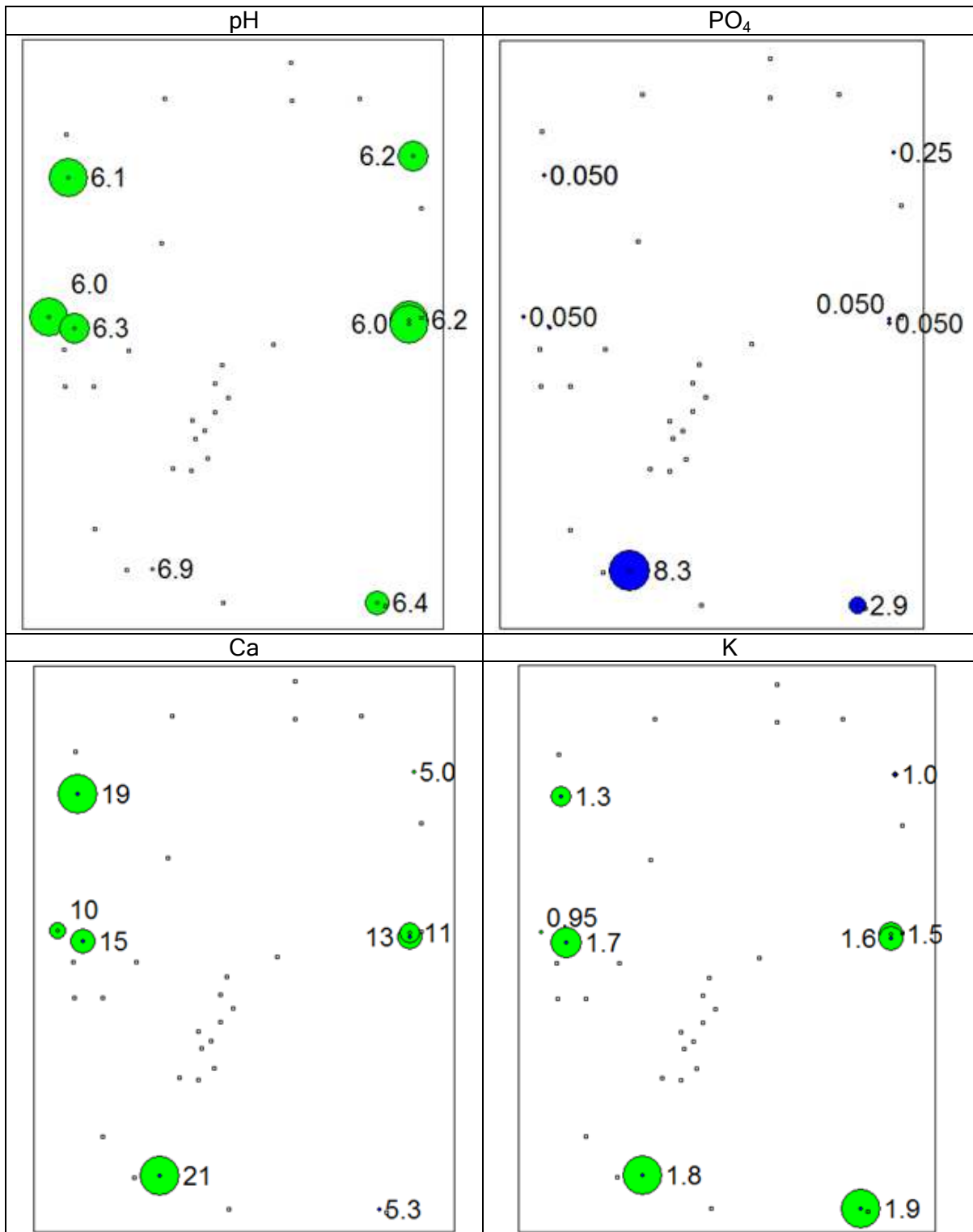


Figure 44 (continued): Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Middle" depth (9 - 14m). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption), **Blue**: no standards (according to SANS241:2006) (mg/l).

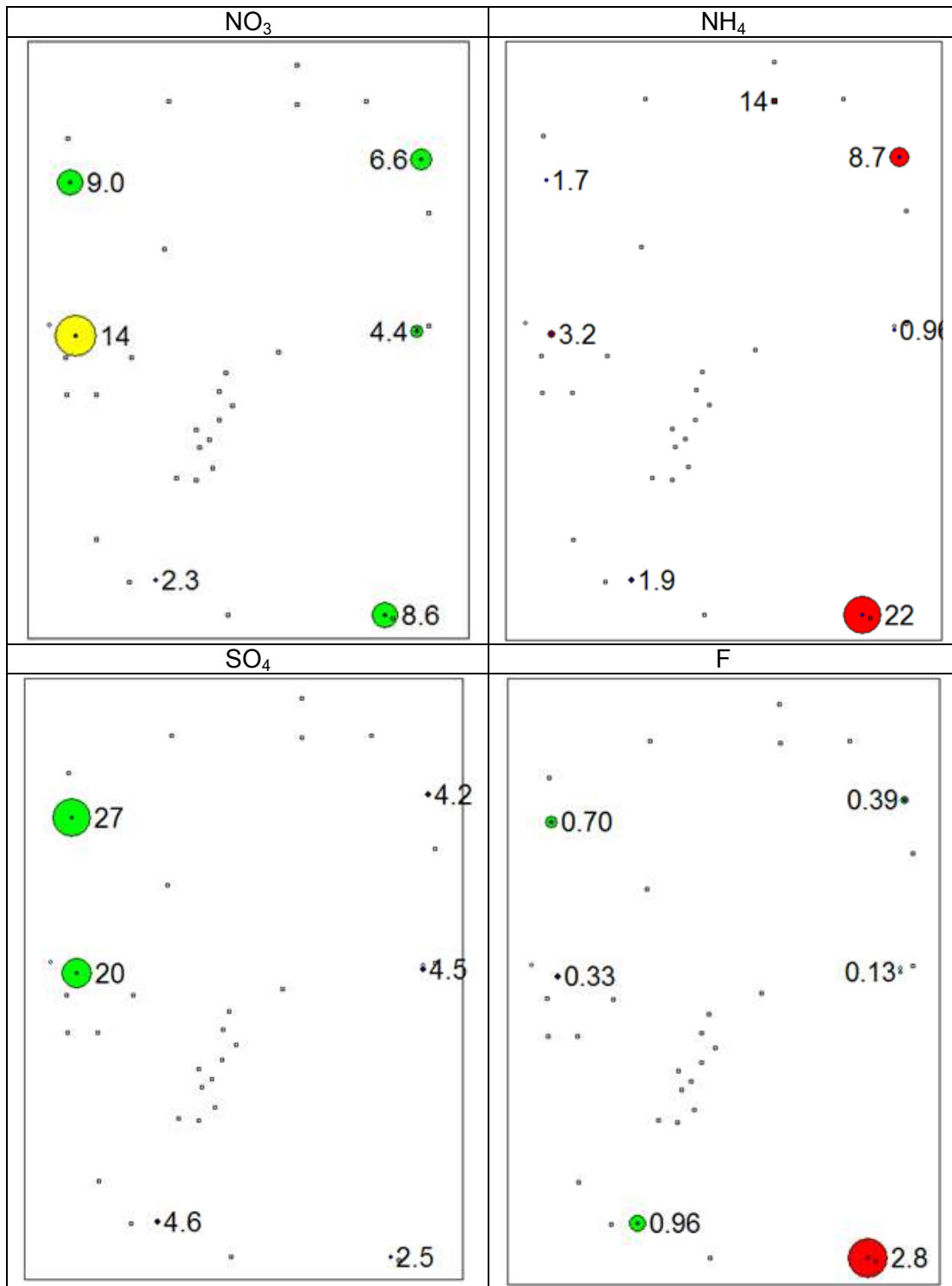


Figure 45: Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Deep" depth (ca. 18 - 24m). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption), **Blue**: no standards (according to SANS241:2006) (mg/l).

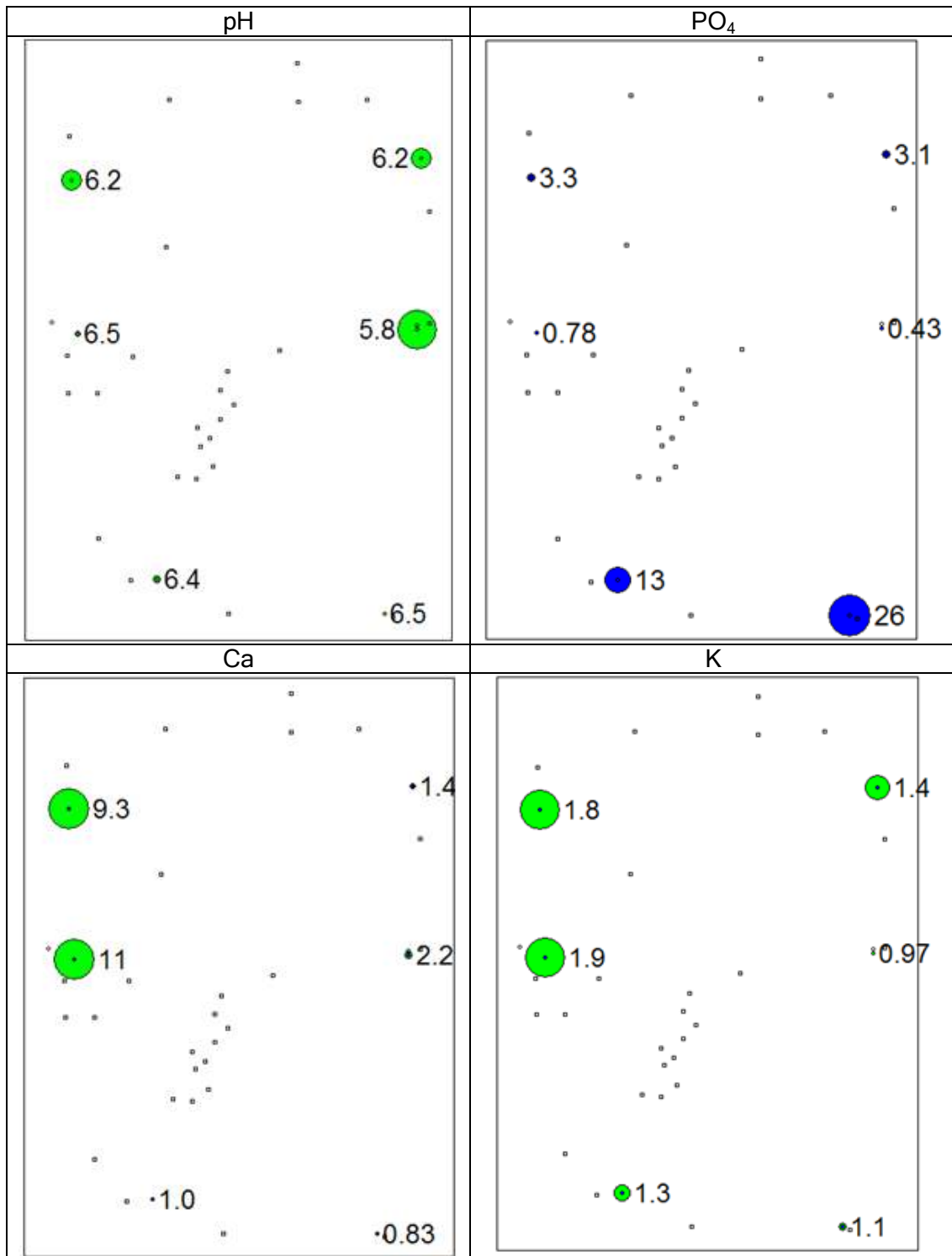


Figure 45 (continued): Distribution, classification, and proportionality of contaminants of concern found in soil samples at "Deep" depth (ca. 18 - 24m). **Red:** not allowable concentrations, **Yellow:** allowable concentrations (short term), **Green:** allowable concentrations (lifetime consumption), **Blue:** no standards (according to SANS241:2006) (mg/l).

### 5.3.2.3 Groundwater chemistry

Figure 50 - Figure 52 illustrate the distribution, classification, and quantity of contaminants found in groundwater samples at various depths. Three different depths are used for illustrative purposes, viz. “Shallow” (ca. 2m below water levels), “Middle” (ca. 10 - 13m below water levels), and “Deep” (ca. 15 - 19m below water levels). Each rectangle represents the entire SNP site (see Figure 46). In total, 71 water samples were taken and analyzed. Only water qualities within Class II (yellow) and Class III (red) (according to SANS241:2006) are included, in order to identify problem areas (except F, which is included due to it being considered a predominant contaminant in the fertilizer industry). Figure 46 illustrates the general location of the predominant contaminants found in the groundwater samples.



**Figure 46: The general location of predominant contaminants found in the groundwater samples.**

The following conclusions can be made from analyzing the contaminants and their location on the SNP site (see Figure 50 - Figure 52);

- The most predominant contaminants occurring in excessive concentrations are nitrate (NO<sub>3</sub>) (144.2 - 938mg/l), ammonium (NH<sub>4</sub>) (0.064 - 32.394mg/l), calcium (Ca) (189.3 - 1011.1mg/l), and magnesium (Mg) (141.4 - 625.6mg/l). NO<sub>3</sub> and NH<sub>4</sub> concentrations were expected to be high, as they are used in large quantities in SNP products.
- Nitrate, calcium, and magnesium occur in high concentrations throughout the site, with the exception of the south east corner (in the area of BH004-D).
- Sulphate (SO<sub>4</sub>) and chloride (Cl) also occur in high, but not excessive, concentrations (276 - 779 and 136.3 - 476.9mg/l respectively).



- Significant concentrations of manganese (Mn) were also found in groundwater samples (<0.001 - 2.703mg/l), and not in soil samples from the saturated zone.
- Nickel (Ni) concentrations ranging from <0.006 - 0.05mg/l were found in groundwater samples.
- Mn and Ni are some of the expected contaminants originating from the KFPF site (as mentioned in section 5.2). It is not used in any of the SNP products, but may be present in trace concentrations in their liquid products, depending on the content of the phosphate rock used in the manufacturing process.
- Cadmium (Cd), a common heavy metal pollutant in the fertilizer industry, was not found in any of the water samples in significant concentrations. The reason for this may be the relatively neutral pH values in the deeper layers (>6m deep), which causes the heavy metals to precipitate in the upper layer of soil/rock.
- The pH values for all the water samples tested ranged between 6.5 - 7.45. This corresponds to the general pH levels of soil samples taken below the static water level.
- As expected, mobile contaminants, e.g. nitrate, chloride, and chromium were found in significant concentrations in the water samples analyzed and not in the soil. This is due to their high solubility in water.
- There were high concentrations of chromium (Cr) (0.4 - 1.925mg/l) found in all the boreholes on the eastern side of the SNP site. An investigation was conducted in order to find the source of the chromium, as SNP does not use chromium in any of its products or processes. It was discovered that a tannery was operated in the past on the premises on the southern border of SNP. Tanneries are known to use large quantities of chromium in its processes (to soften leather). A further indication that the chromium does not originate on the SNP site is that it occurs exclusively on the eastern border, and one would expect a more distributed occurrence of a mobile contaminant like chromium if it originated on the SNP site. A few other possible contributing sources may include; the weathering of the andesite formation (which may contain chromium), scrap metal industries, and a sewage pipe passing along the eastern side of the SNP site carrying chromium containing effluent.
- During the pumping tests the concentrations of chromium increased with time (see Figure 47 - Figure 49). Only BH005-D did not show an increase in the concentration of chromium). This is a further indication that the source of chromium contamination lies outside the SNP border, and is being drawn into the subsurface underlying the SNP site.
- A significant concentration (0.023mg/l), of chromium was also found in the water sample taken from ROSS6.
- It would be valuable to determine whether the chromium is Cr(III) or Cr(VI) in future.

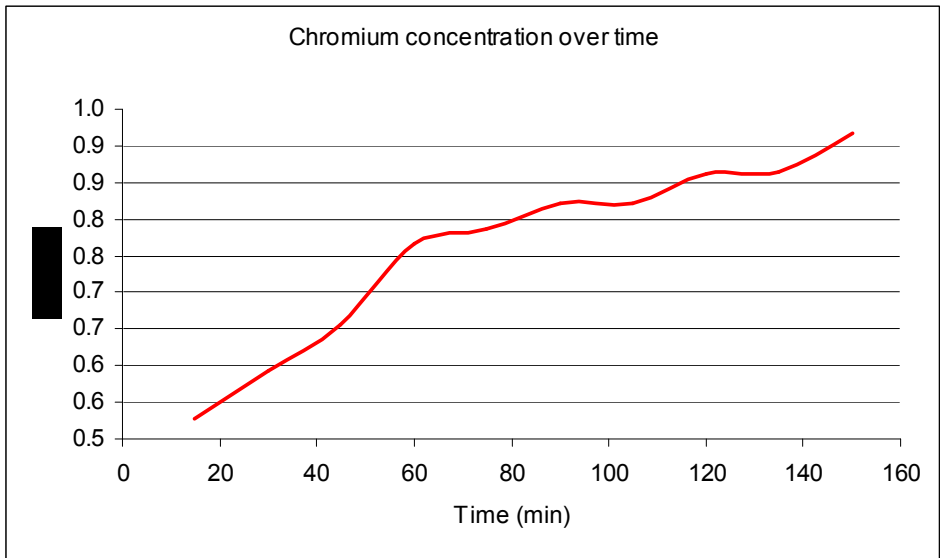


Figure 47: Chromium concentration over time during pump test (BH004-D).

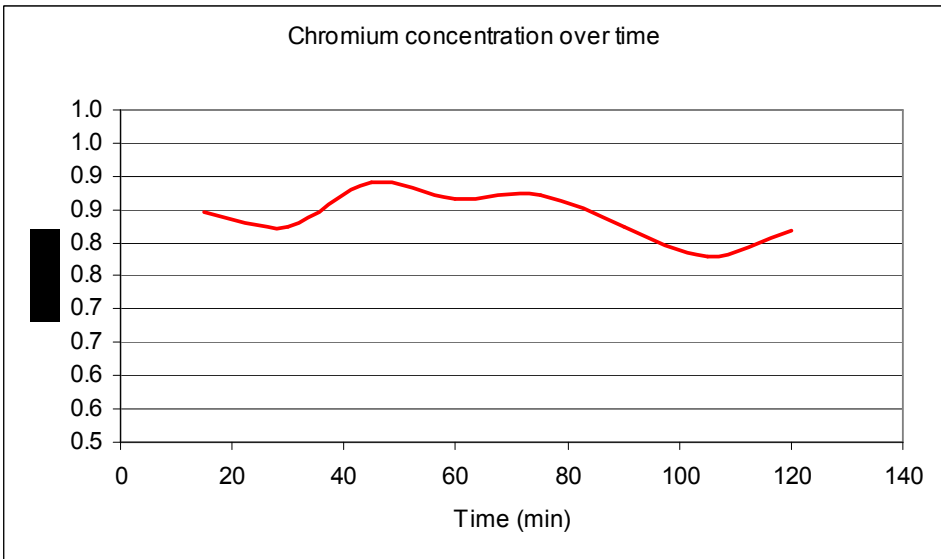


Figure 48: Chromium concentration over time during pump test (BH005-D).

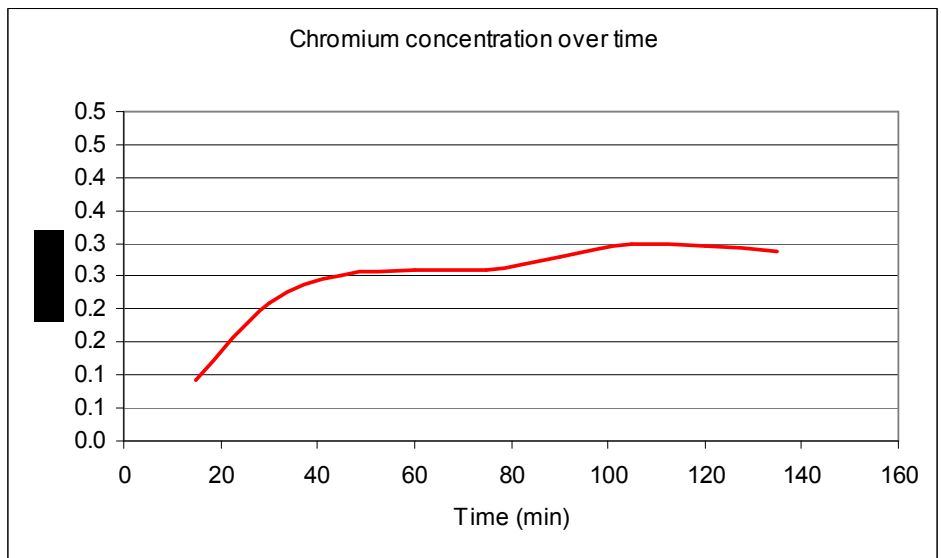


Figure 49: Chromium concentration over time during pump test (BH006-D).

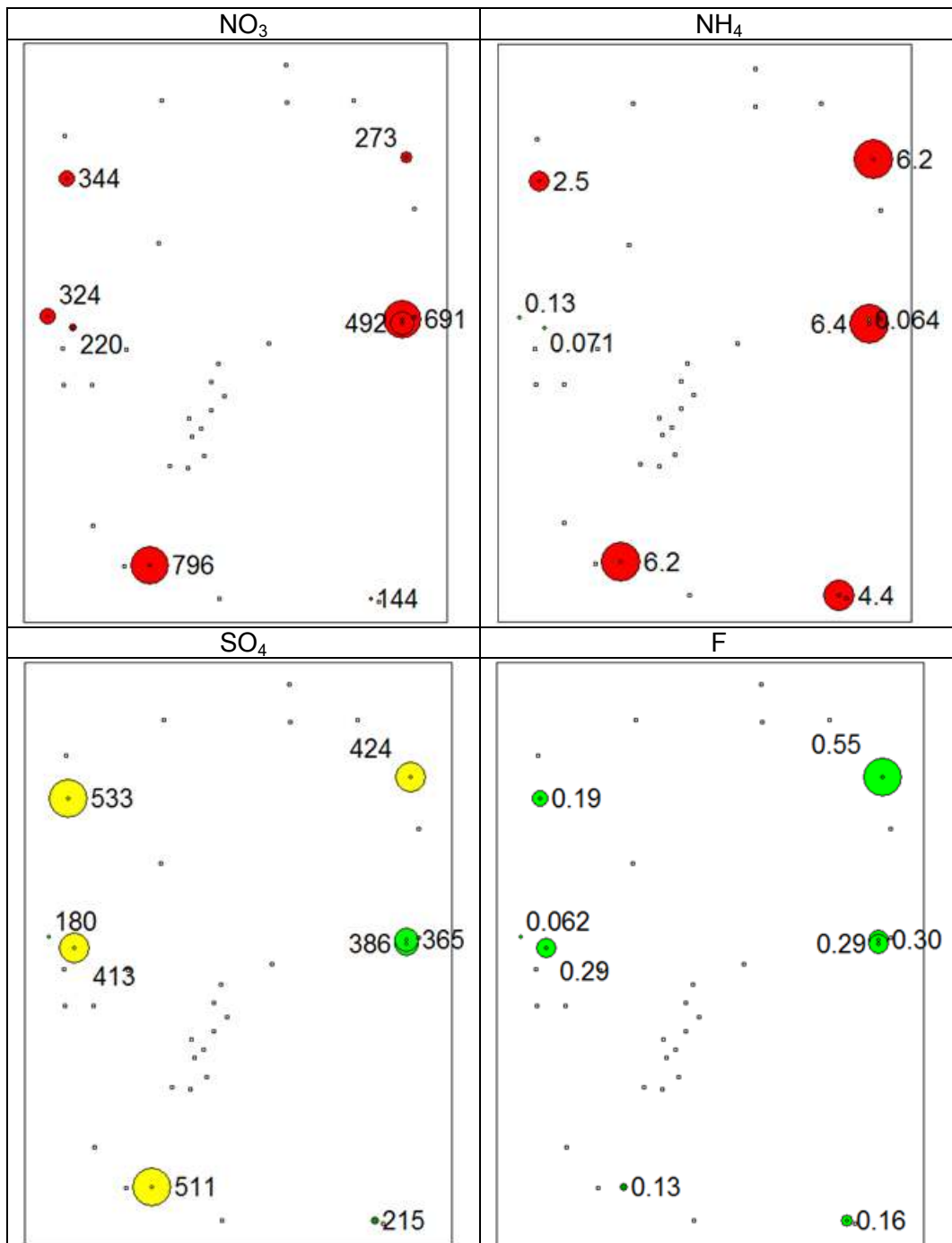


Figure 50: Distribution, classification, and proportionality of contaminants of concern found in water samples at "Shallow" depth (ca. 2m below water levels). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l).

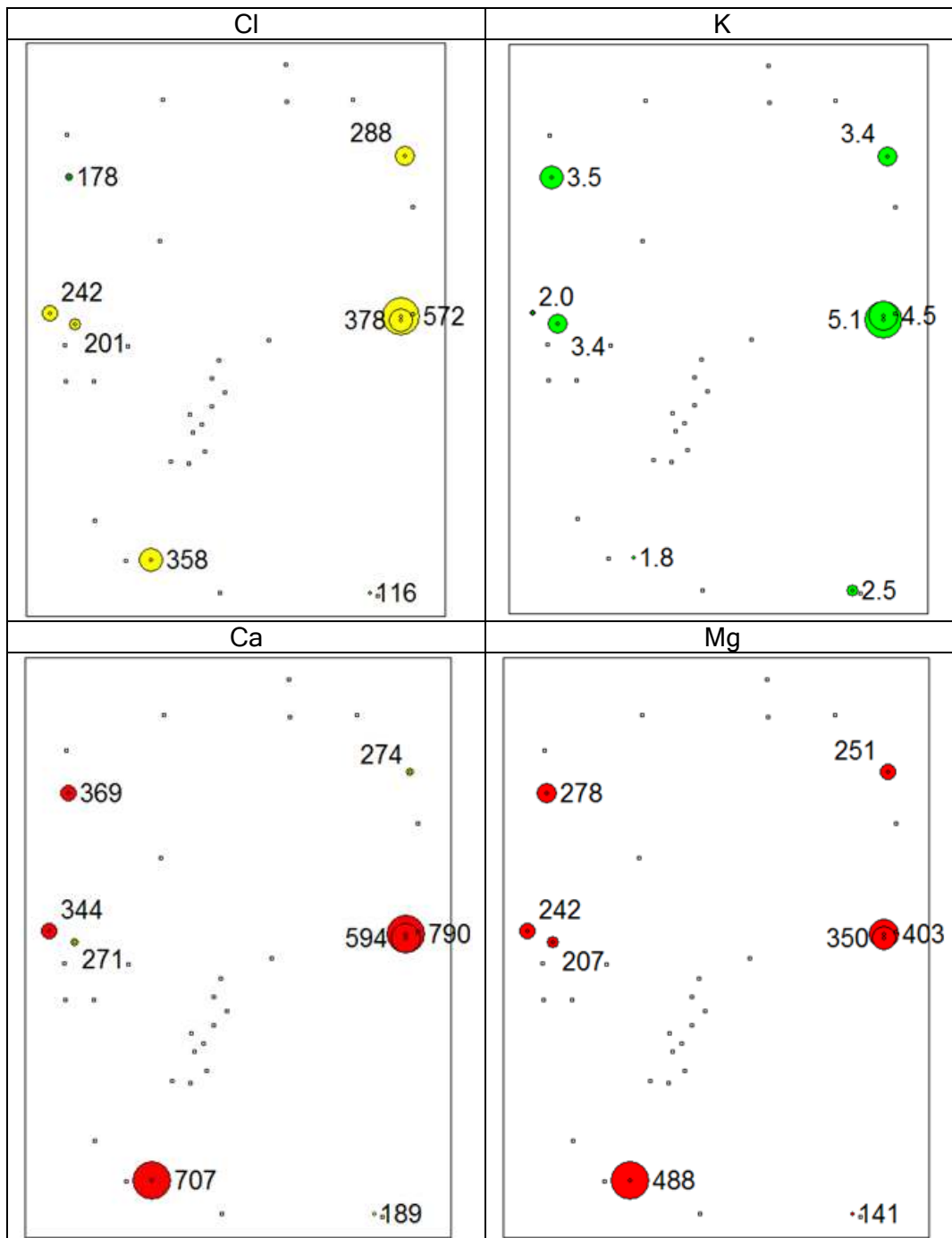


Figure 50 (continued): Distribution, classification, and proportionality of contaminants of concern found in water samples at “Shallow” depth (ca. 2m below water levels). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l).

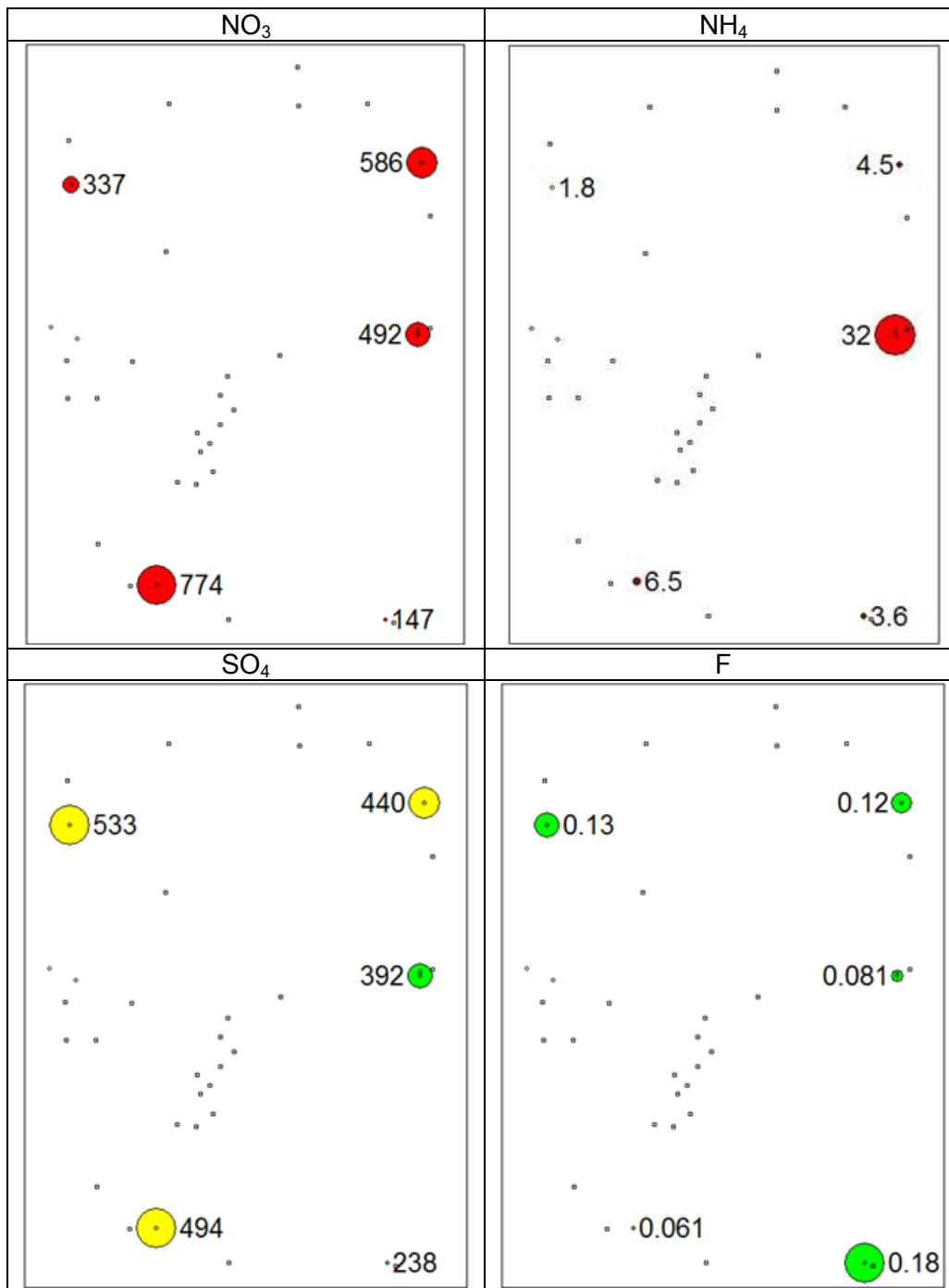


Figure 51: Distribution, classification, and proportionality of contaminants of concern found in water samples at "Middle" depth (ca. 10 - 13m below water levels). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l).

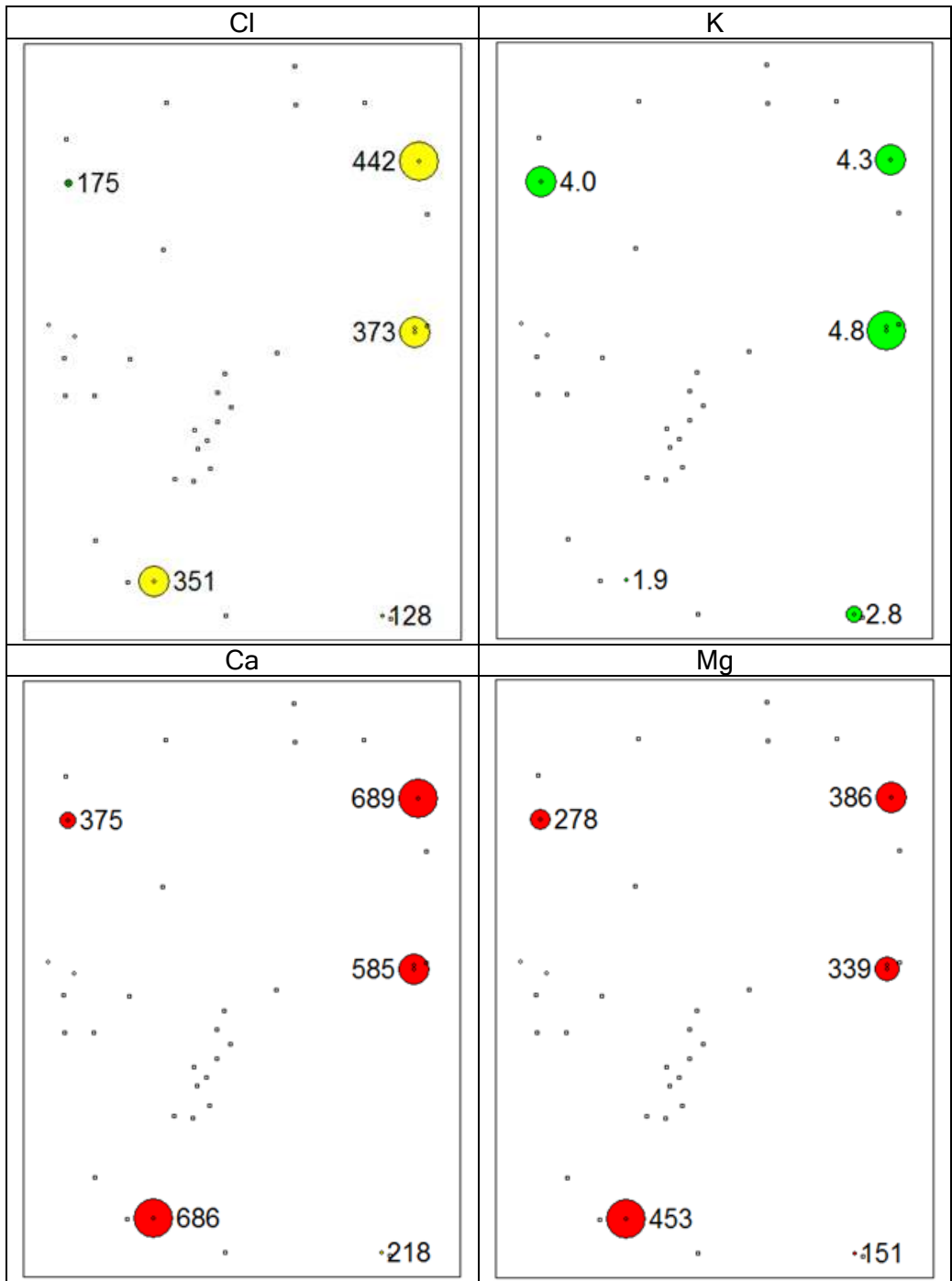


Figure 51 (continued): Distribution, classification, and proportionality of contaminants of concern found in water samples at "Middle" depth (ca. 10 - 13m below water levels). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l).

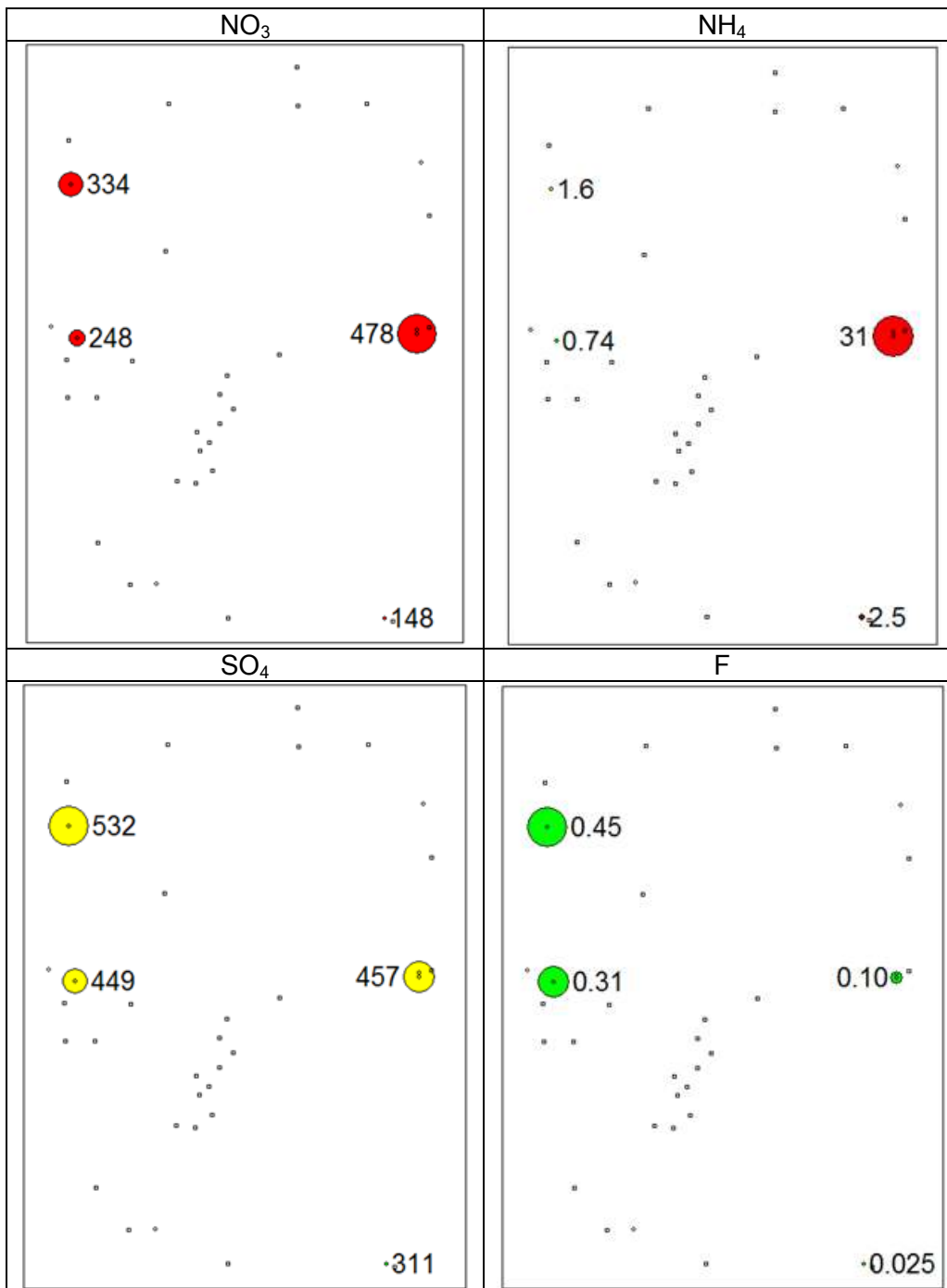


Figure 52: Distribution, classification, and proportionality of contaminants of concern found in water samples at "Deep" depth (ca. 15 - 19m below water levels). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l).

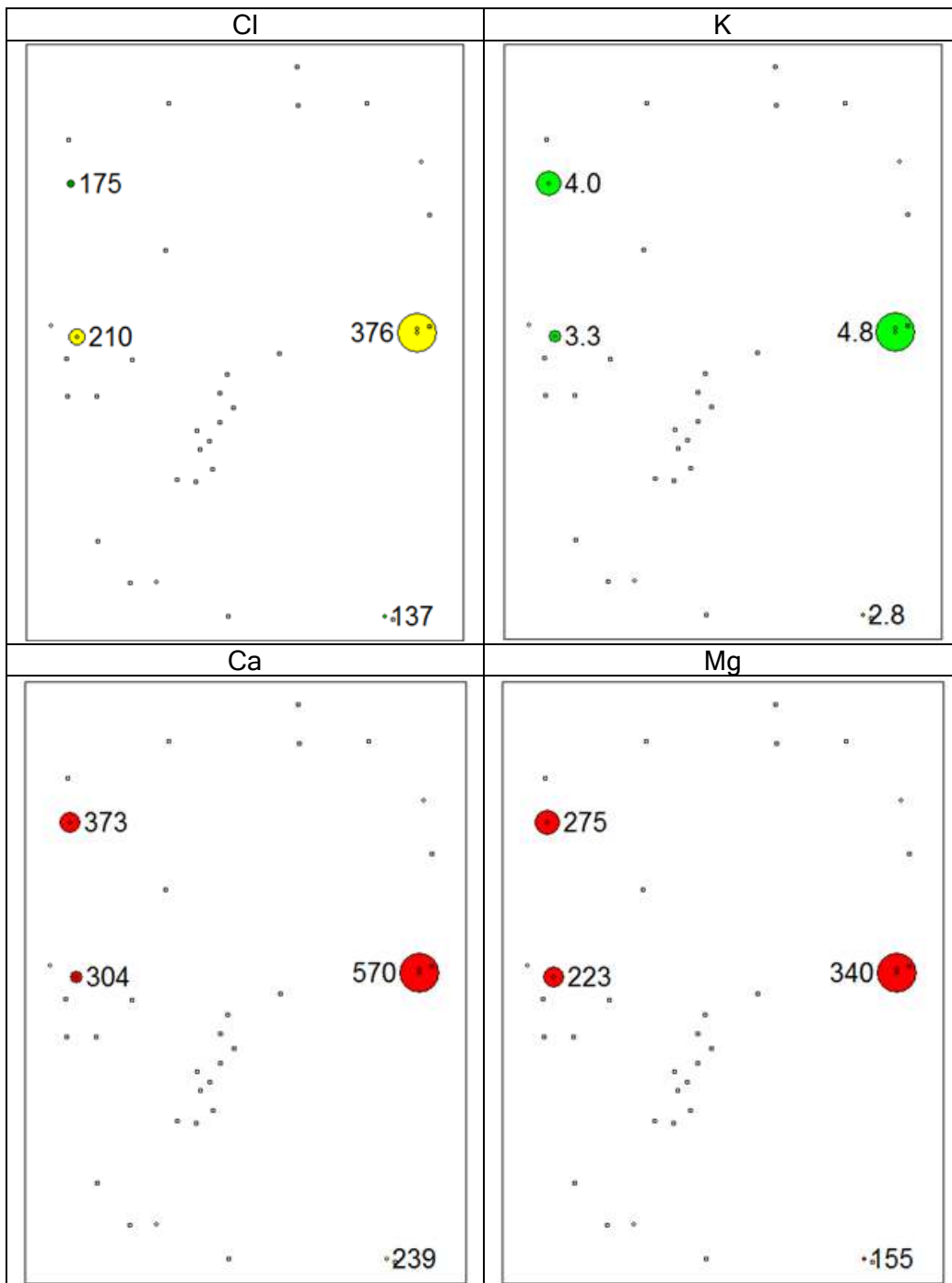


Figure 52 (continued): Distribution, classification, and proportionality of contaminants of concern found in water samples at "Deep" depth (ca. 15 - 19m below water levels). **Red**: not allowable concentrations, **Yellow**: allowable concentrations (short term), **Green**: allowable concentrations (lifetime consumption) (according to SANS241:2006) (in mg/l).



Figure 53 - Figure 55 are stiff diagrams of the groundwater samples taken from the boreholes on the 12<sup>th</sup> of May 2010. STIFF diagrams compare milli-equivalent concentrations of macro elements, which make them more appropriate, in certain respects, than piper diagrams. A “pattern” is formed, which can be used to identify the source of water samples relatively simply and accurately (as with Piper diagrams). These water samples were divided into three groups to indicate three different sample depths (as in Figure 53 - Figure 55).

As illustrated in these diagrams, most of the water samples show the same general “signature”/“pattern”, with only variations in the amounts of macro elements found in each. This means that there are strong correlations between groundwater samples, and indicate pathways connecting all the boreholes through which groundwater moves, i.e. there are no singular fractures connecting certain boreholes.

The trend shown in each groundwater sample, is; high Cl content, low Na + K content, a moderate and relatively the same concentrations of Ca and Mg, and a low and relatively the same concentrations of alkalinity (alk) and SO<sub>4</sub> (except in deep levels at BH001-D and BH002-D, which show higher concentrations of SO<sub>4</sub>).

As expected, water samples taken from the same boreholes show the highest correlation, with the correlation decreasing with an increase in distance.

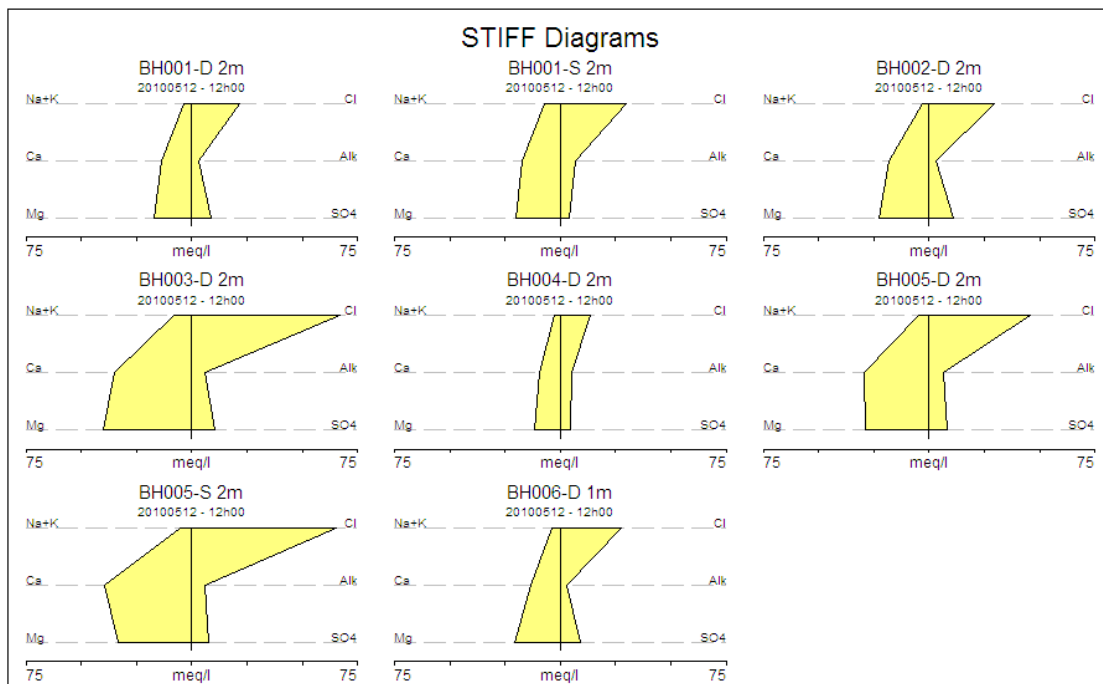


Figure 53: STIFF diagrams of "shallow" water samples (water samples taken ca. 2m below water levels).

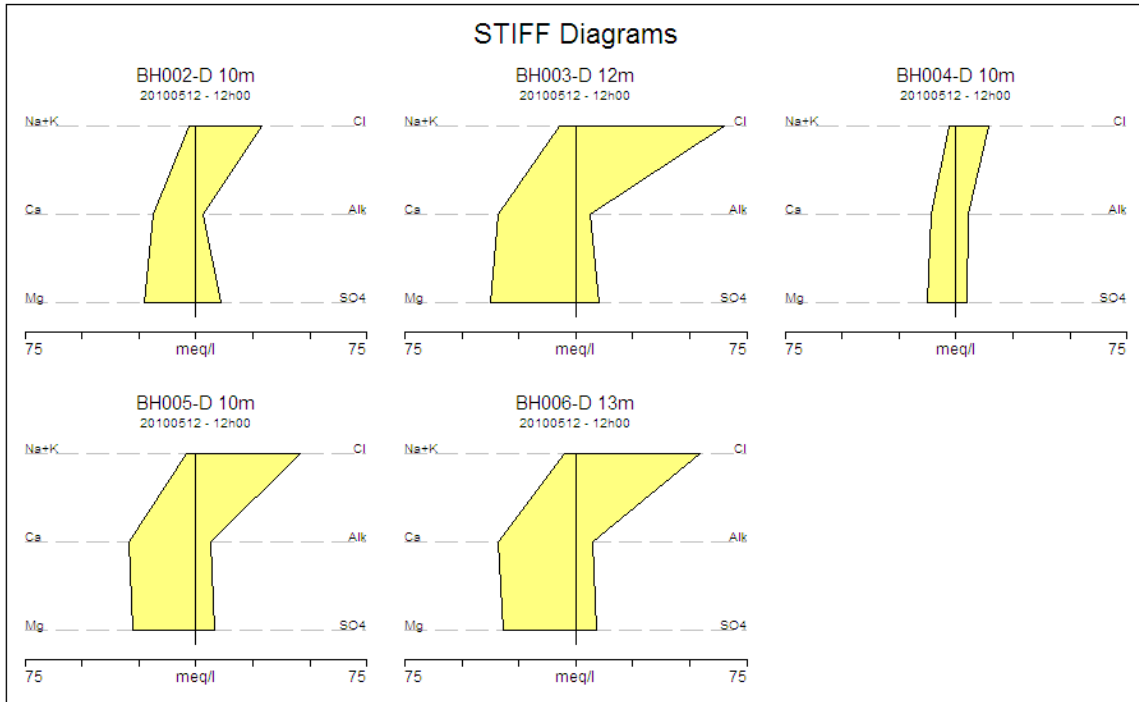


Figure 54: STIFF diagrams of "medium" depth water samples (water samples taken ca. 10 - 13m below water levels).

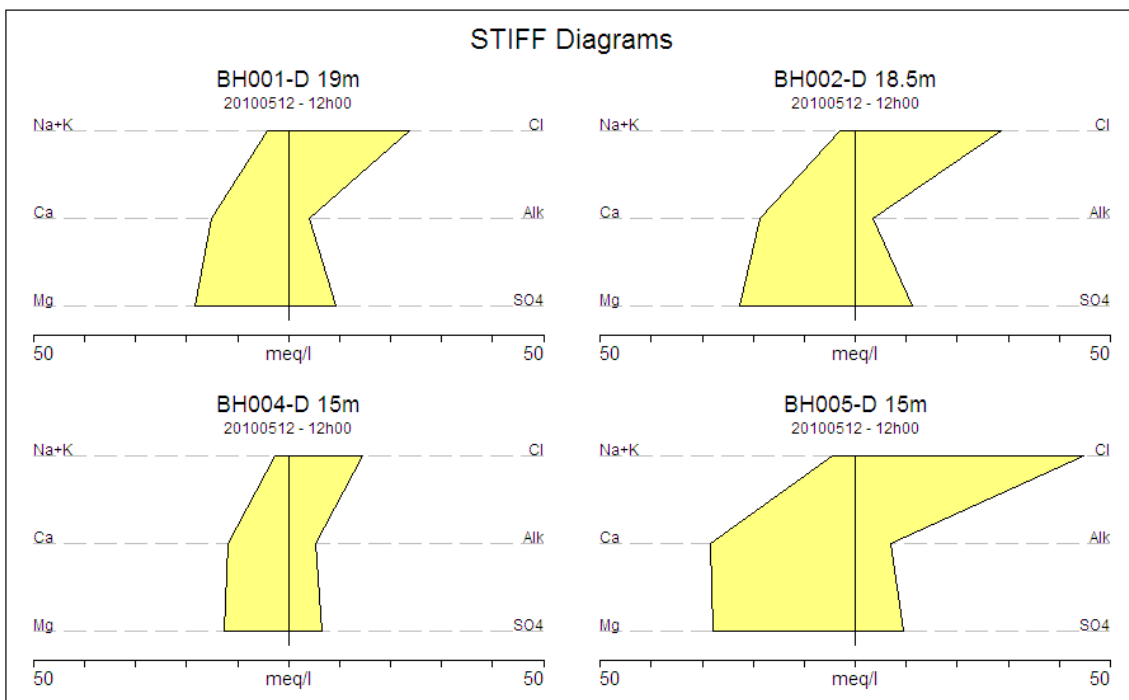


Figure 55: STIFF diagrams of "deep" water samples (water samples taken ca. 15 - 19m below water levels).

### 5.3.3 Borehole geology, electronic conductivity (EC), and soil chemical results as profiles in relation to depth

Electric conductivity (EC) is a measure of the amount of total dissolved salts/ions in water. EC is a good indicator of the presence and quantity of possible contaminants, and anomalies in EC profiles are good markers of the flow of water in a borehole, possible fractured zones, and zones where contaminants might collect.

Figure 56 - Figure 57 show the EC profiles (groundwater), borehole geology, and soil sample chemistry results of boreholes BH001-D and BH003-D. These two boreholes were chosen, because they show the general trends found in all eight boreholes very well. Figure 58 illustrates the EC profiles of all eight boreholes put side by side. The depth for each profile was set at 35m.

Figure 56 - Figure 57 provides the following information;

- Most contaminants (especially those originating from fertilizer mixing and loading operations, i.e. nitrate, ammonium, and phosphate) are situated within the first few meters of the soil/rock layer.
- The contaminants;  $\text{NO}_3$ ,  $\text{SO}_4$ , Mg, Ca, and Cl, show a consistent peaking at ca. 6m deep, viz. BH003-D 5m, BH004-D 7m, BH005-S 7m, BH005-D 8m, and BH006-D 4m. This might suggest a horizontal zone of preferential groundwater flow caused by a weathered and/or fractured geological layer. This corresponds with the resistivity data.
- The pH level in the top layer (ca. 2m) of soil/rock is moderately acidic, after which it increases relatively quickly with depth and stabilise at approximately neutral levels. This could be due to the Fe-rich quartzites of the Transvaal group (which would lower the pH), the influence of Ca in the subsurface (see section B.1: Ca reduces the mobility of  $\text{PO}_4$ ,  $\text{SO}_4$ , and F), reducing conditions below a depth of ca. 2m, and/or oxidation of contaminants in shallower depths due to higher oxygen concentrations (oxygen enters shallower depths). Contaminants whose solubility is pH dependent (lower pH increases solubility) therefore dissolve more easily in the top layer of soil/rock. They consequently leach through the top layer of soil to depths of higher pH levels, where they precipitate. This might also explain the consistent peaking of concentrations at ca. 6m deep.
- After peaking, the concentrations of contaminants in soil samples show a decrease and general stabilization with depth, except for BH004-D and BH006-D. The general decreasing trend is confirmed by the EC profiles.
- It should be mentioned that certain contaminants (e.g.  $\text{NO}_3$ , Ca, and Mg) occur predominantly in solution in the saturated zone, and may not be easily adsorbed by soil/rock. The general trend of contaminant concentrations in soil samples decreasing with depth is hence misleading.

Comparing the EC profiles (Figure 58) provides the following information;

- There is a general trend of EC values gradually decreasing, which indicates the movement of contaminants in the upper regions of the geological formation.
- There is a spike in the EC values at BH004-D at around 12m (see B in Figure 58), which is approximately the depth of the start of the lava formation at that point. EC values spike at BH001-D and BH002-D at roughly 22m (see A in Figure 58), approximately the start of the lava formation in this area. The spike in EC values at these depths suggests that the lava formation acts as an impenetrable boundary on which contaminants collect and flow (as mentioned earlier). This fact was also confirmed by the resistivity findings.
- There is an anomaly in the EC values at BH006-D at around 7m, which is not the start of the lava formation. This might be due to pH values increasing with depth, i.e. contaminants leach through the first few meters of soil and precipitate at higher pH values. Another reason might be a zone of preferential flow.
- BH005-D is the only borehole showing a slightly increasing trend in EC values, which might indicate the cross contamination of different flow zones in the geological formation.

The two most important conclusions that can be drawn from the EC profiles of the boreholes is that the lava formation acts as an impenetrable boundary on which the contaminants flow and collect, and that contaminants leach through the top layer of mildly acidic soil and precipitate where pH values increase.

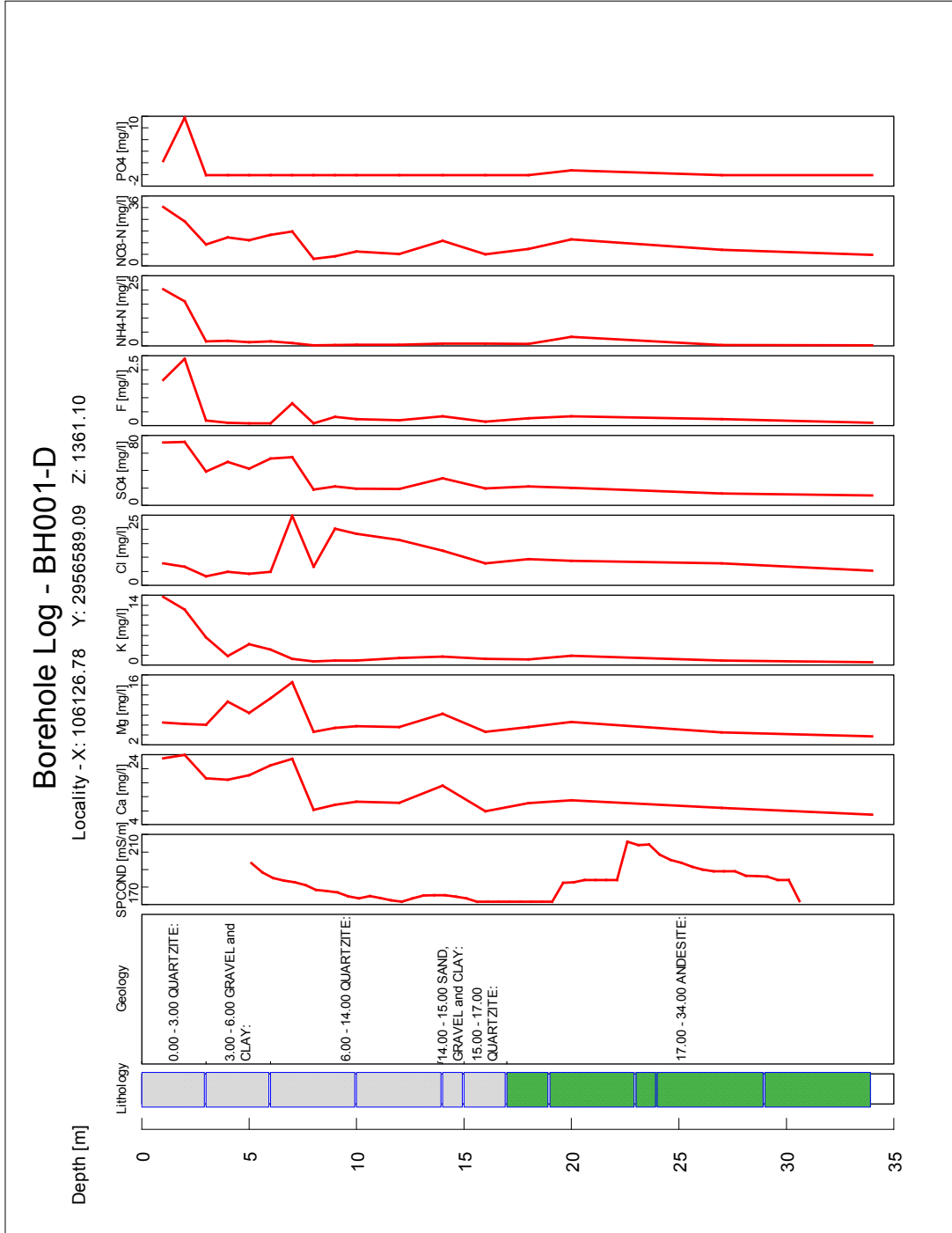


Figure 56: Borehole geology, EC, and chemical parameters (for soil samples) represented as profiles in relation to depth (BH001-D).

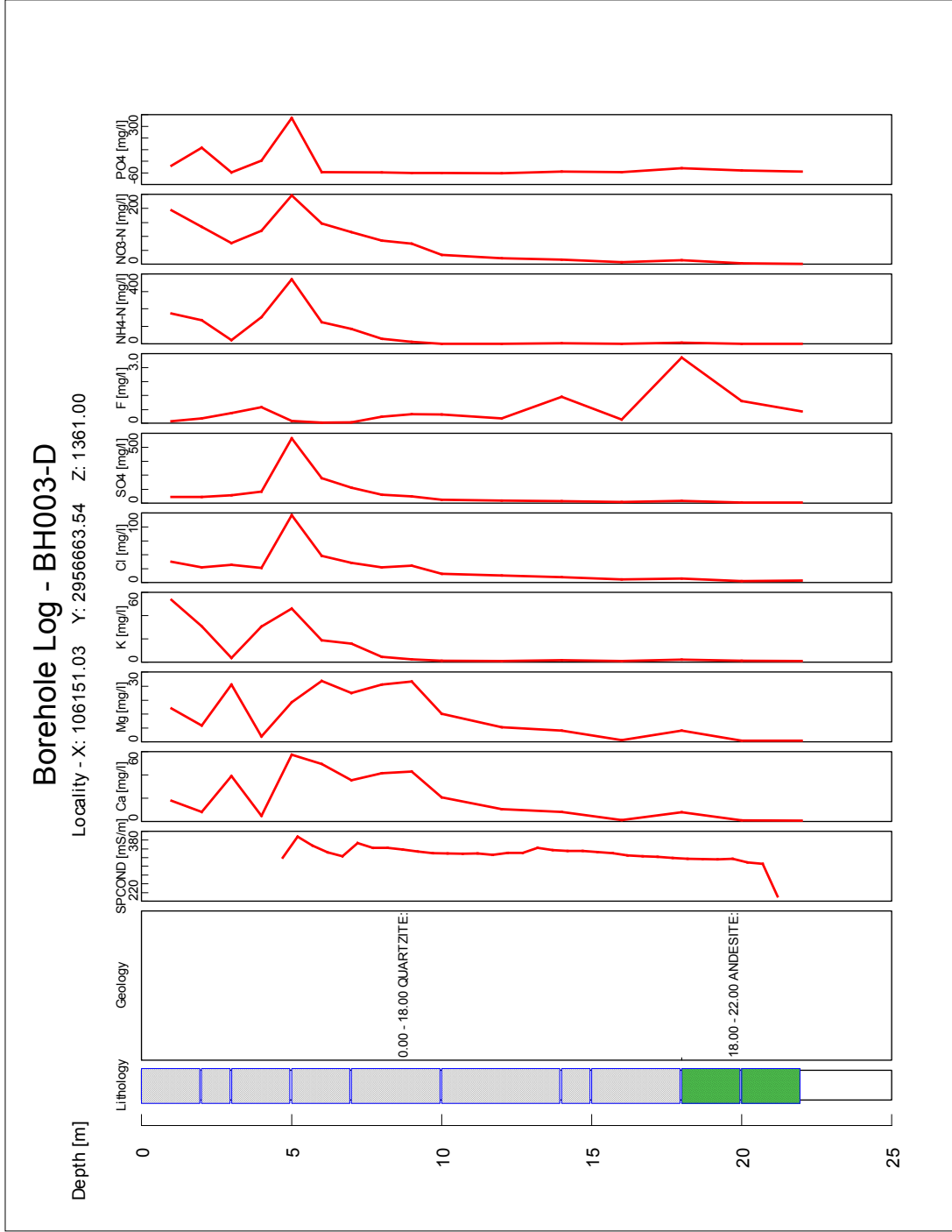


Figure 57: Borehole geology, EC, and chemical parameters (for soil samples) represented as profiles in relation to depth (BH003-D).

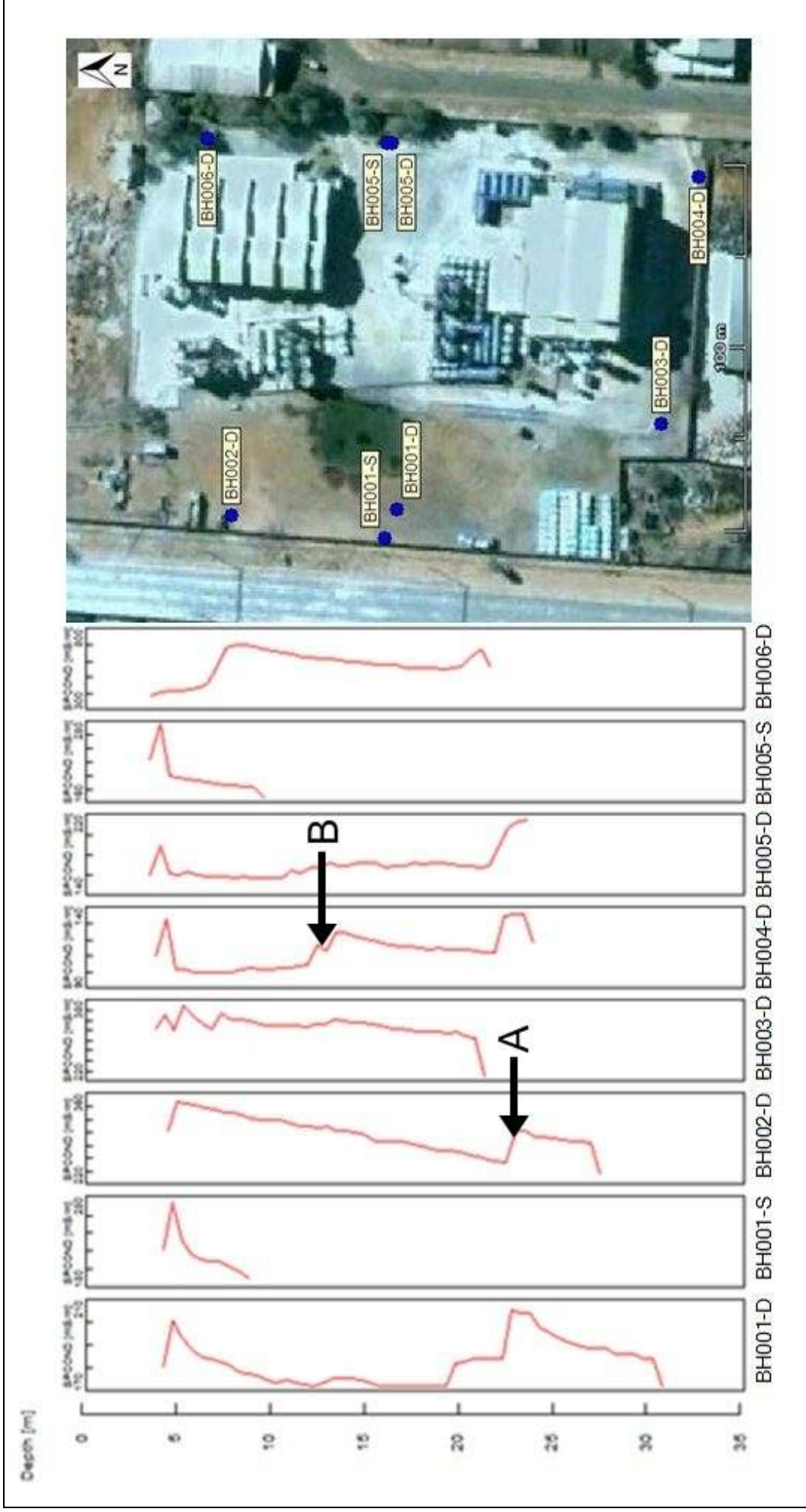


Figure 58: EC profiles of boreholes and the position of boreholes on map (EC measured in mS/m).

## 5.4 Statistical analysis of chemical data obtained from the SNP site

This section describes the chemical results obtained statistically, and aims to find relationships between the occurrence of different contaminants, and between the occurrence of contaminants and other variables, viz. distance from source and groundwater extraction.

Table 19 shows the descriptive statistical analysis of the chemical data of the auger, borehole soil- (obtained during drilling), and water samples respectively. Only the main contaminants of concern are included in these tables.

### *Description of statistical terms;*

- The *mean* values indicated in Table 19 are the arithmetic mean values, i.e. it is the sum of all the values divided by the number of values (samples).
- The *median* is the value separating the top half of the values from the lower half, i.e. if all the values are arranged from lowest to highest, the value in the middle of the arrangement will be the median. If there are an even number of samples, the median is the mean of the two values in the middle.
- *Standard deviation* is a measure of variability, i.e. it indicates the amount of variation from the mean. A low standard deviation indicates that values are close to the mean, and a high standard deviation indicates that values are spread out.
- *Sample variance* describes the distribution of values, i.e. it indicates how much values differ from the mean. It is a parameter describing the theoretical probability distribution.
- The *minimum* and *maximum* values are exactly that; the minimum and maximum value of each set of values.

The soil samples obtained during drilling have the lowest standard deviation and sample variance values, with both the other two sets of samples showing much higher values. This indicates that the values of the soil samples obtained during drilling are significantly less spread out, i.e. are much closer to the mean compared to the values of the other two sets and their respective means, and that there is less variation in the values, i.e. less values differing significantly from the mean.

Table 19 can also help in giving a general idea as to which contaminants are predominantly found in the groundwater, i.e. soluble and mobile, and which are mainly found in the soil, i.e. insoluble and



immobile in the subsurface. For example, the predominant contaminants found in the groundwater are Ca, Mg, Cl, and NO<sub>3</sub>, and those in the soil samples, F, NH<sub>4</sub>, PO<sub>4</sub>, and Zn.

Table 20 - Table 22 show the correlation coefficients of the chemical analysis of the auger-, boreholes soil-, and water samples respectively. The correlation coefficient is a measure of the probability of two contaminants occurring concurrently. A high value (close to one) indicates a high correlation, and a low value (close to zero) indicates a low correlation. High correlations are highlighted in **yellow**.

For illustrative purposes, the correlation between NO<sub>3</sub> and other contaminants are discussed (see Table 20 - Table 22);

- There were no real correlations between NO<sub>3</sub> and other contaminants found in the auger samples (storage area in the middle of the site), i.e. finding any one of the contaminants cannot predict the presence of NO<sub>3</sub>.
- There were strong correlations between NO<sub>3</sub> and TDS, EC, K, and NH<sub>4</sub> found in the soil samples taken during drilling, i.e. TDS and EC values, and the occurrence of K and NH<sub>4</sub>, are good indicators for the presence of NO<sub>3</sub>. (Please note that Cr and Zn are not included in the correlation table, as no tests were done for Cr and Zn in these samples).
- In the water samples, strong correlations were found between NO<sub>3</sub> and EC, Ca, and Mg, i.e. EC values and the presence of Ca and Mg are good indicators for the occurrence of NO<sub>3</sub>.

Figure 59 and Figure 60 show the chromium concentrations over time for the pumping tests done on boreholes BH004-D and BH006-D respectively, each fitted with a trend line. BH005-D was excluded, as an accurate fit of a trend line could not be achieved. The equations for the trend lines, are;  $y = 0.1716\ln(x) + 0.0378$  ( $R^2 = 0.9697$ ) for BH004-D, and  $y = 0.085\ln(x) - 0.1027$  ( $R^2 = 0.884$ ) for BH006-D, where x is the time elapsed in minutes and y the chromium concentration in mg/l. A constant extraction rate of 0.5l/s is assumed.

With these equations, very rough predictions can be made for short periods (assuming a constant extraction rate of 0.5l/s), e.g. the chromium concentration predicted to be found in BH004-D after 24 hours and pumping at 0.5l/s is 1.29mg/l. It has to be emphasized that these equations only provide very rough predictions for very short periods of time. The pumping tests were not performed long enough, the source concentration is not known, and extraction rates might vary, which make it impossible to predict the concentrations accurately.

**Table 19: Descriptive statistical analysis of the chemical results (major contaminants of concern only) of the soil and groundwater samples.**

	pH	EC	Ca	Mg	K	MALK	Cl	SO <sub>4</sub>	F	NH <sub>4</sub>	NO <sub>3</sub>	PO <sub>4</sub>	Cr	Zn
<i>40 Auger samples</i>														
Mean	5	102	48	9	16	3	16	218	5.223	45.2	48.31	120.6	0.003	58.78
Median	4	97	21	6	9	0	12	92	1.423	31.8	27.89	77.5	0	1.07
Standard Deviation	1	85	59	13	42	11	17	420	7.34	44.4	42.04	136	0.009	201.25
Sample Variance	1	7207	3505	164	1784	120	297	176507	53.869	1968	1767.27	18486.4	0	40500.43
Minimum	3	1	0	0	0	0	1	0	0.002	0.1	0.04	-1	0	0.01
Maximum	10	368	231	66	272	69	64	2084	28.625	155.5	145.1	544.9	0.046	960
<i>118 Soil samples obtained during drilling</i>														
Mean	6	29	16	8	4	9	10	38	0.39	12.68	21.2	7		
Median	6	21	13	6	1	7	7	24	0.18	1.01	12.3	0		
Standard Deviation	1	32	14	6	8	14	11	51	0.65	43.59	29.4	30		
Sample Variance	1	1011	207	41	65	203	117	2570	0.42	1900.07	867.2	902.4		
Minimum	3	0	0	0	1	0	1	2	0.02	0.08	1.6	0		
Maximum	7	244	88	26	54	146	97	464	4.59	370.22	197.4	283.8		
<i>71 Water samples</i>														
Mean	7	478	498	317	4	280	282	469	0.13	4.7	456.2		0.35	0.01
Median	7	381	369	275	4	287	239	457	0.1	2.5	339		0.02	0.01
Standard Deviation	0	185	228	131	1	82	145	148	0.1	6.8	234.1		0.44	0.01
Sample Variance	0	34295	52070	17096	2	6673	20980	21965	0.01	46.6	54785.4		0.2	0
Minimum	7	215	189	141	1	132	116	180	0.02	0.1	144.2		0	0.01
Maximum	8	827	1011	626	7	411	1005	798	0.55	32.4	938		1.93	0.05

**Table 20: The correlation coefficient of 40 auger samples.**

	pH	EC	TDS	Ca	Mg	Na	K	MALK	Cl	SO4	NO2	F	NH4	NO3	PO4	Cr	Zn
pH	1																
EC	0.006	1.00															
TDS	0.017	0.98	1														
Ca	0.554	0.40	0.50	1													
Mg	0.016	0.18	0.28	0.49	1												
Na	0.064	0.60	0.60	0.45	0.383	1											
K	-0.057	0.27	0.30	0.14	-0.097	-0.09	1										
MALK	0.882	0.03	0.05	0.52	-0.125	0.01	-0.04	1									
Cl	0.305	0.77	0.75	0.41	-0.003	0.39	0.36	0.42	1								
SO4	-0.138	0.85	0.85	0.19	0.006	0.33	0.09	-0.05	0.63	1							
NO2	0.827	0.03	0.05	0.50	-0.106	-0.06	-0.02	0.97	0.45	-0.03	1						
F	-0.233	0.27	0.39	0.19	0.296	0.13	0.26	-0.17	0.11	0.29	-0.10	1					
NH4	-0.068	0.81	0.75	0.18	-0.016	0.61	0.36	-0.11	0.56	0.53	-0.16	0.09	1				
NO3	0.246	0.45	0.40	0.36	0.191	0.67	0.10	0.21	0.42	-0.02	0.15	-0.18	0.61	1			
PO4	-0.112	0.22	0.36	0.36	0.628	0.13	0.33	-0.18	-0.01	0.13	-0.15	0.76	0.06	-0.156	1		
Cr	0.171	0.65	0.64	0.18	-0.063	0.18	-0.08	0.35	0.67	0.81	0.39	0.15	0.29	-0.017	-0.008	1	
Zn	-0.172	0.76	0.75	0.05	-0.026	0.29	-0.08	-0.07	0.53	0.97	-0.05	0.26	0.44	-0.073	0.076	0.85	1

**Table 21: Correlation coefficient of 118 borehole soil samples (obtained during drilling).**

	pH	EC	TDS	Ca	Mg	Na	K	MALK	Cl	SO4	NO2	F	NH4	NO3	PO4
pH	1														
EC	-0.0358	1													
TDS	-0.1417	0.901	1												
Ca	-0.2027	0.646	0.5881	1											
Mg	0.0051	0.571	0.5161	0.857	1										
Na	0.3844	-0.022	-0.066	0.009	0.1838	1									
K	-0.4079	0.666	0.8645	0.395	0.2594	-0.223	1								
MALK	0.252	-0.068	-0.025	-0.09	-0.0316	0.1184	-0.028	1							
Cl	-0.0051	0.791	0.8567	0.509	0.4892	0.3057	0.627	-0.051	1						
SO4	-0.251	0.857	0.8562	0.691	0.5299	-0.081	0.649	-0.153	0.782	1					
NO2	0.1813	-0.045	-0.056	-0.07	-0.0288	0.6804	-0.105	0.0777	0.202	-0.064	1				
F	0.0221	0.025	0.0179	0.004	-0.0237	0.0014	0.086	0.3554	-0.08	0.002	0.0116	1			
NH4	-0.1109	0.796	0.9307	0.271	0.2155	-0.158	0.853	-0.071	0.779	0.7419	-0.074	-0.02	1		
NO3	-0.1282	0.853	0.965	0.59	0.5604	-0.098	0.867	-0.081	0.779	0.7353	-0.1101	-0.04	0.887	1	
PO4	-0.077	0.697	0.7961	0.188	0.0743	-0.141	0.7	0.084	0.692	0.6938	-0.0621	0.169	0.858	0.668	1

**Table 22: Correlation coefficient of 71 water samples.**

	pH	EC	Ca	Mg	Na	K	MALK	Cl	SO4	NO2	F	NH4	NO3	Cr	Zn
pH	1														
EC	-0.0562	1													
Ca	0.0042	0.987	1												
Mg	-0.0443	0.984	0.9836	1											
Na	-0.1792	0.629	0.5423	0.566	1										
K	0.021	0.594	0.6694	0.625	0.1051	1									
MALK	0.3507	0.798	0.8202	0.76	0.4899	0.435	1								
Cl	-0.1111	0.808	0.7856	0.748	0.7796	0.541	0.625	1							
SO4	-0.1278	0.799	0.8185	0.845	0.4198	0.767	0.459	0.6648	1						
NO2	0.0106	0.021	-0.003	-0.011	0.1783	-0.024	0.074	0.0847	-0.171	1					
F	-0.1321	-0.193	-0.212	-0.177	-0.103	0.061	-0.38	-0.085	-0.094	0.1269	1				
NH4	0.2421	0.637	0.6467	0.633	0.3006	0.574	0.603	0.484	0.529	0.3873	-0.11	1			
NO3	-0.0357	0.98	0.977	0.984	0.5077	0.597	0.789	0.6835	0.8	-0.037	-0.22	0.6337	1		
Cr	0.411	0.133	0.1807	0.048	-0.085	0.066	0.383	0.2067	-0.19	0.1554	-0.09	0.0844	0.08	1	
Zn	-0.3494	-0.137	-0.18	-0.129	-0.027	0.042	-0.37	-0.015	-0.065	0.1055	0.634	-0.0514	-0.16	-0.2165	1

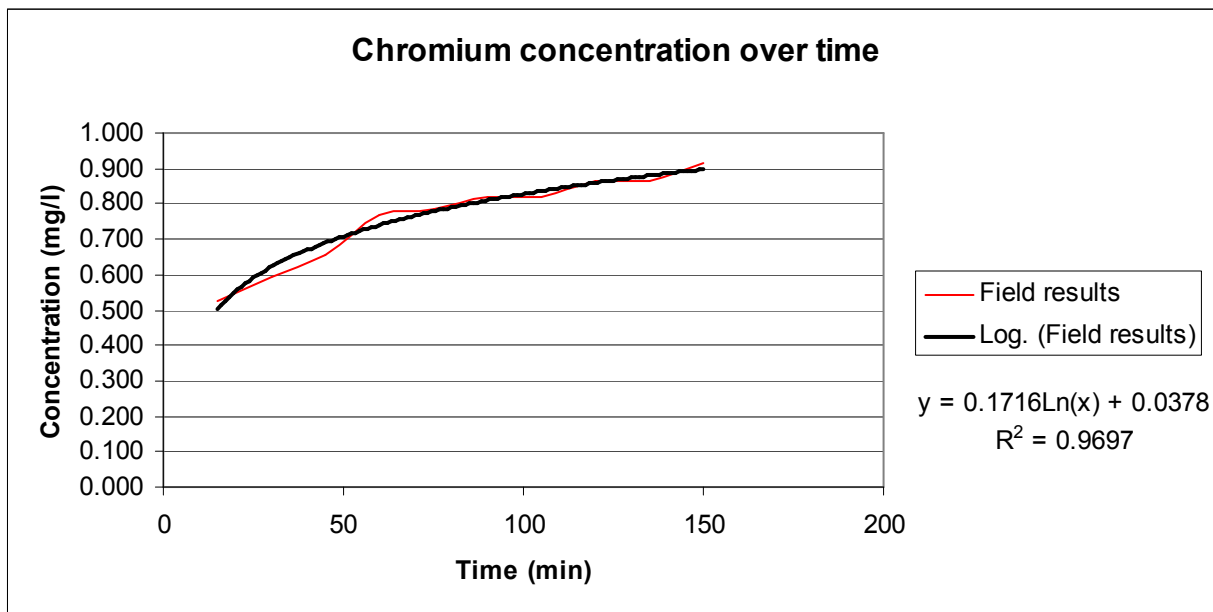


Figure 59: Chromium concentration over time for pumping test done on BH004-D with fitted trend line.

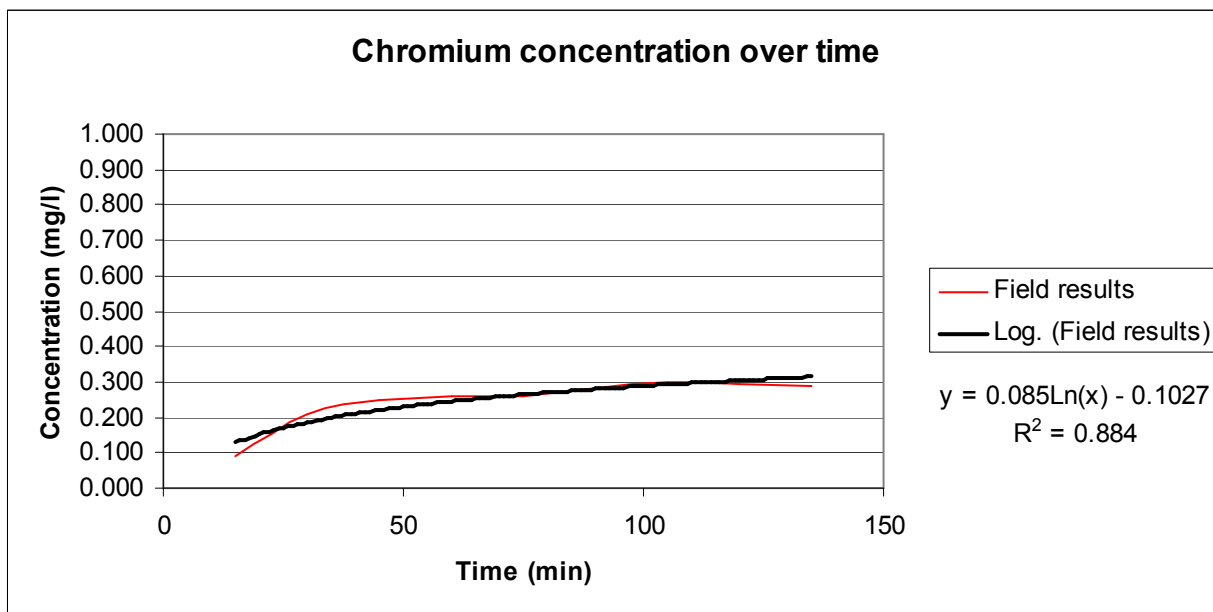


Figure 60: Chromium concentration over time for pumping test done on BH006-D with fitted trend line.

Figure 62 is a graph illustrating the chromium concentration as a function of distance with a fitted trend line. The distances used were from the centre of the chromium source site (the site on the southern boundary of SNP) to BH004-D, BH005-D, BH006-D, and ROSS6 respectively (see Figure 61). The chromium concentrations used for BH004-D, BH005-D, and BH006-D were the averages of the concentrations found during the pumping tests. The equation of the trend line is given by  $y = 2.1364e^{-0.0117x}$  ( $R^2 = 0.9327$ ), where  $y$  is the chromium concentration in mg/l and  $x$  the distance from the source site in meters.

Once again, the limitations of this trend line have to be emphasized. It only describes the concentrations as a function of distance in one direction, there have not been enough samples

collected, and the conditions when collecting the samples were not the same for each borehole, i.e. pumping tests were done in close succession and created cones of depression that influenced each other, and the sample obtained from ROSS6 was taken after the pump had extracted water for only a short period of time.



Figure 61: Map indicating the line used to calculate the chromium concentration as a function of distance from the source.

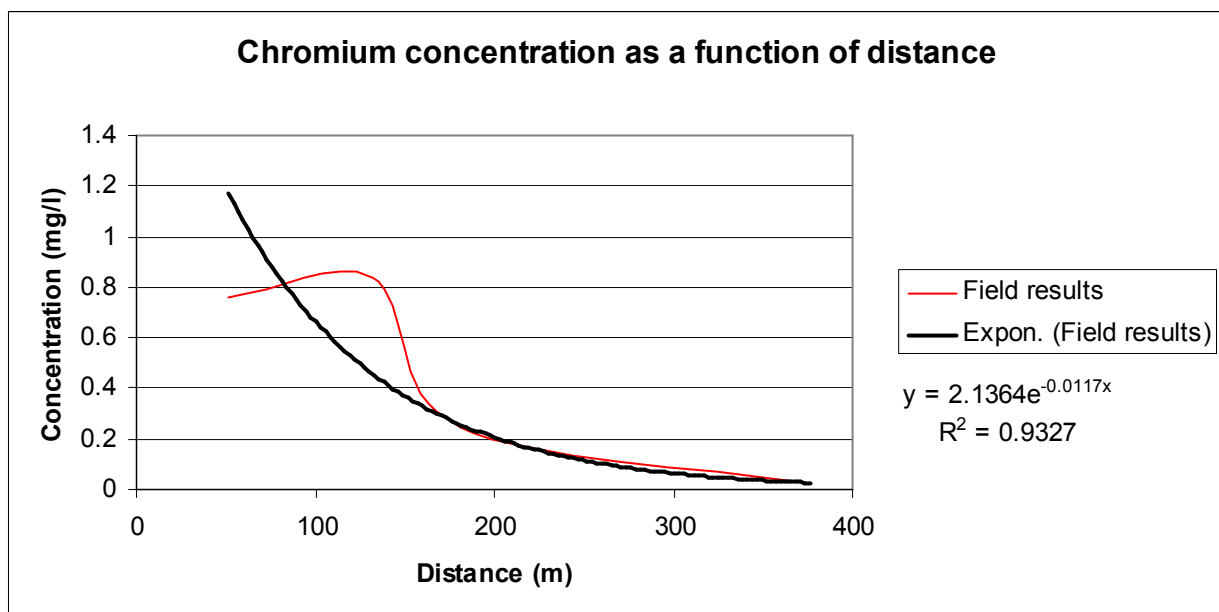


Figure 62: Chromium concentration as a function of distance and fitted trend line (from source to ROSS6).

## Chapter 6: Conceptual model of the SNP site

A conceptual model is a basic visual representation and written description of a complex system. This conceptual model of the SNP site includes the geological and geohydrological characteristics of the subsurface, a discussion of surface elevation, water levels, and hydraulic gradient, and mention of the most predominant contaminants, their location on the site, and the recommended remediation method.

Figure 63 is a three dimensional representation of the site (see file on included CD for three dimensional animation). The top two layers are indicated in two different hues of red, and are ca. 3 and 6m deep respectively. These two layers indicate the main contaminants occurring at these approximate depths respectively. The depth at which a contaminant is predominantly present is dependant on its solubility characteristics. The Hekpoort lava formation is indicated in dark green. The three dimensional animation illustrates the approximate depth of the lava formation in different zones and the location of the main storage and operation points on the SNP site.

Figure 64 - Figure 65 show the conceptual model cross sections of the SNP site's subsurface. Indicated are the approximated thickness of each layer, T-values, and the most predominant contaminants in each layer.

The area is covered with a highly weathered and fractured layer of quartzitic rock, interspersed with perched layers of clayey soil varying in thickness. This layer overlays a Hekpoort lava formation varying in depth from ca. 11m on the eastern side of the SNP site to ca. 22m on the western side. The Hekpoort lava formation acts as an impenetrable barrier for groundwater due to its low transmissivity, causing contaminants to collect and flow on its surface (towards the western and north-western side of the site).

The transmissivity values are generally high, with higher values found on the eastern side of the site. The high resistivity values are due to the highly fractured and weathered quartzitic layer overlying the lava formation.

Water levels on the eastern side of the site are shallower than on the western side (difference of ca. 0.7m). This is caused by the regular irrigation that occurs on the eastern side of the site (for gardening). There is an overall slope of the surface elevation towards the east, with a difference in elevation between the eastern and the western side being approximately 1.5m over 100m, i.e. an gradient of 0.015. This results in the movement of groundwater in a general easterly direction towards Potch Industria, and to a lesser extent the Spitskopspruit, with an effective hydraulic gradient of ca. 0.008 (see Figure 31).

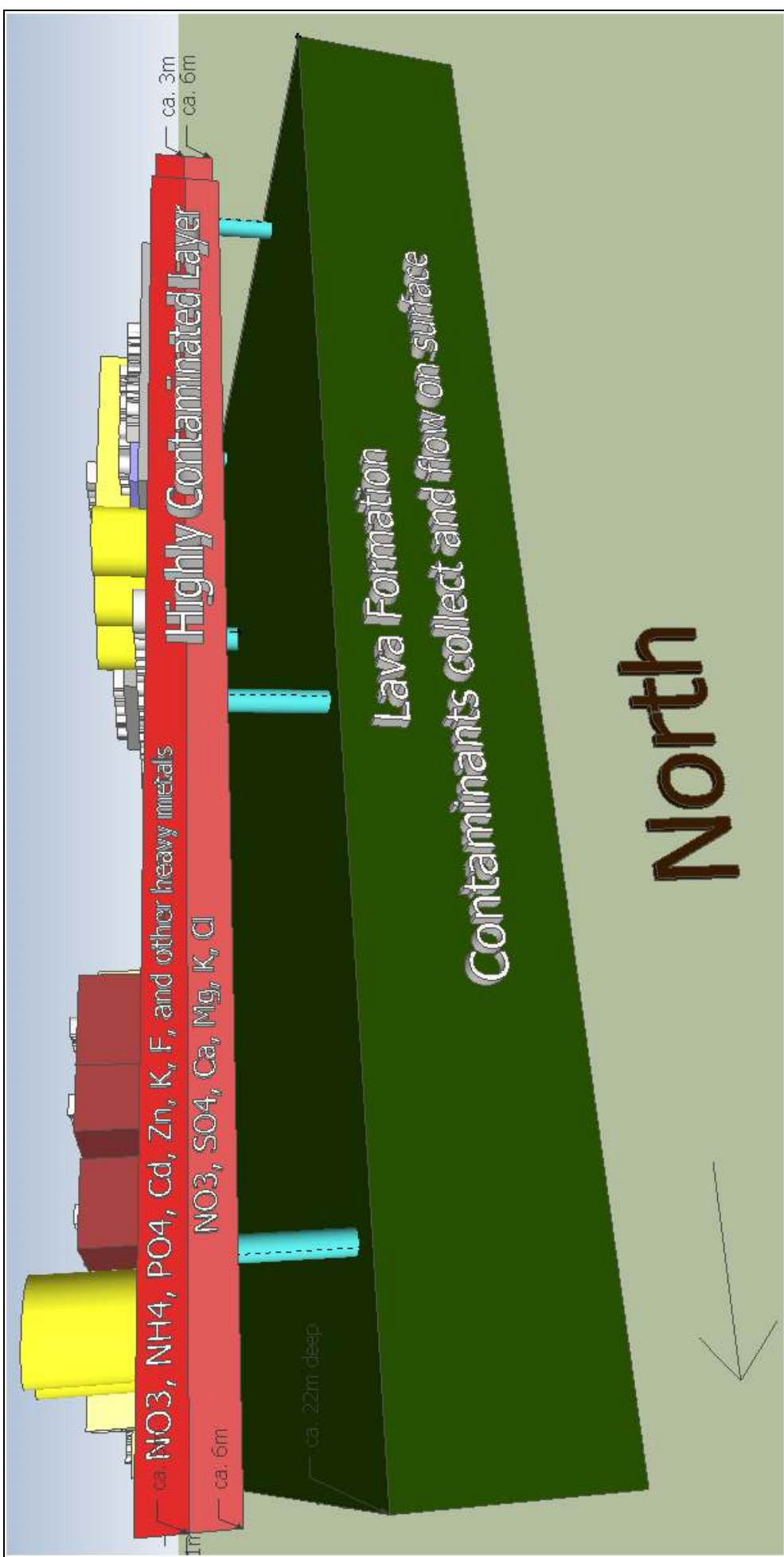


Figure 63: Three dimensional conceptual model of the SNP site (Google Sketchup: see file on included CD for three dimensional animation).



The study conducted by SRK Consulting on KFPP in 2007 showed that the “Gypsum Tailings dam and the Factory [KFPP] both contribute to contamination in the Spitskopspruit” (Skinner, 2007). It is not known what SNP’s contribution is to the contamination of the Spitskopspruit.

The resistivity readings indicated the low transmissivity values of the lava formation at depth on the western side of the site, and the presence of areas of higher conductivity interspersed throughout the site and at various depths. This might indicate the location of clayey layers acting as water (and therefore) contamination traps, or areas of preferential groundwater flow. The resistivity data did not indicate any definite contamination plumes.



Figure 64: Conceptual model: cross sections 1, 2, and 3 indicated on the SNP site.

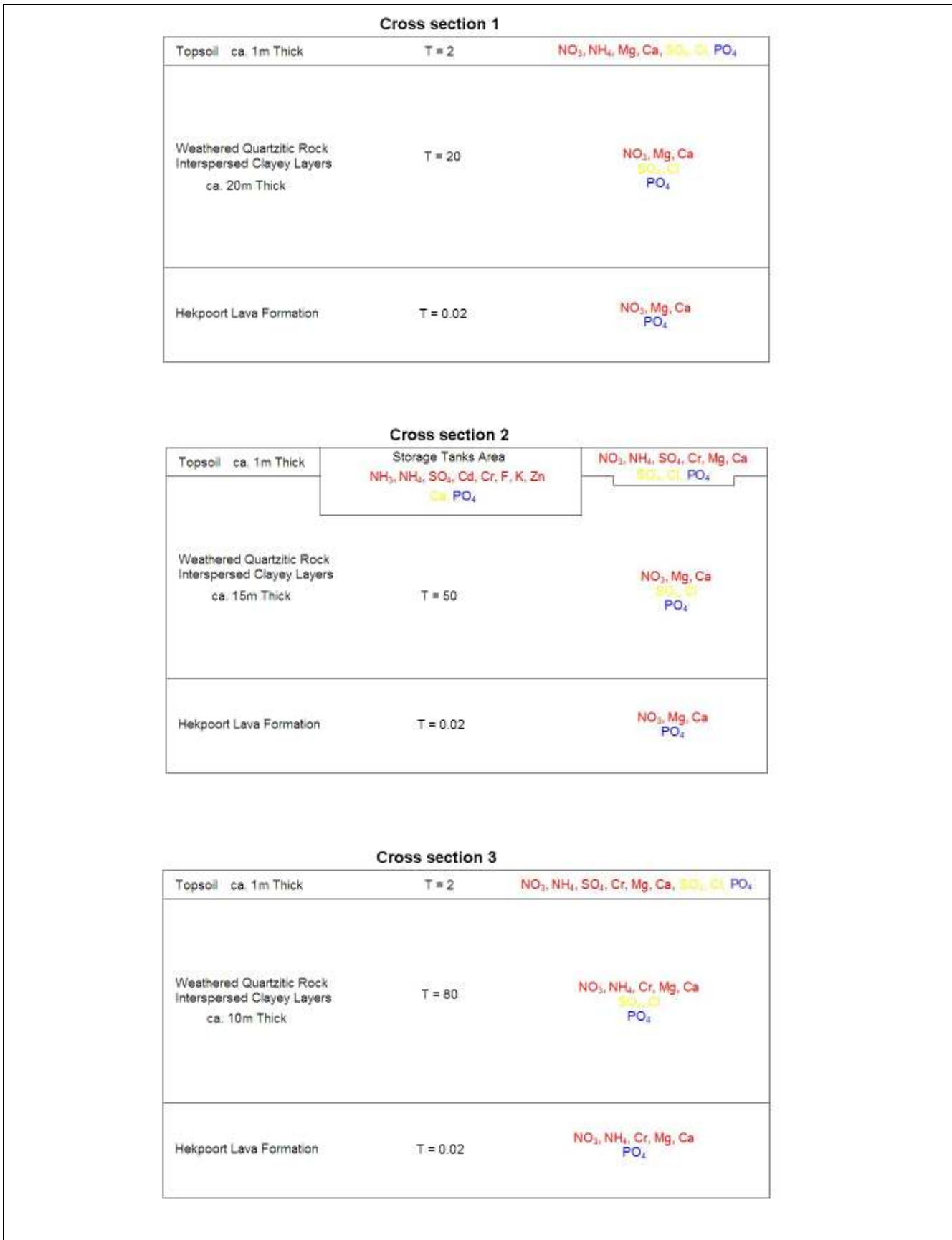


Figure 65: Conceptual model: cross sections of the SNP site's subsurface (T measured in m<sup>2</sup>/d).

In general,  $\text{NO}_3$ , Ca, Mg, Cl, and Mn are found predominantly in solution in the groundwater (i.e., not adsorbed to soil/rock), except where there is loading from the surface within the bounds of SNP, which means that they are present in the unsaturated zone as well and leach down to the saturated zone.

Very high concentrations of  $\text{NO}_3$  are found in both the unsaturated and saturated zone, but almost exclusively in solution in the saturated zone. A higher concentration is found in the saturated- than the unsaturated zone, which may indicate that the nitrate in the unsaturated zone has either mostly leached down, or that the main source is from outside the SNP bounds.

Nitrogen in the subsurface is a complex interaction of the various nitrogen compounds and the respective processes occurring in the saturated- and unsaturated zones. The basic process can be described as follows; the nitrification process occurs in two stages, viz. ammonia is first oxidized to nitrite ( $\text{NO}_2$ ) by autotrophic ammonia-oxidizing bacteria (Nitrosomonas) and then to nitrate by autotrophic nitrite-oxidizing bacteria. Nitrite is quickly reduced or oxidized due to it being a generally unstable form of nitrogen. Nitrate then leaches into the saturated zone and is extremely soluble in water. It is not easily adsorbed by soil, which means that it migrates freely with the groundwater. In the saturated zone, nitrate can undergo denitrification into atmospheric nitrogen by heterotrophic bacteria (Paracoccus and Pseudomonas). Nitrate leaching to the saturated zone from the unsaturated zone have therefore two origins, viz. the nitrate produced by the nitrification of ammonia and nitrite, and nitrate from products stored, mixed, and transferred on the surface (e.g. AN: ammonium nitrate) that enter the unsaturated zone. The ammonium anion is immobilized as a result of adsorption to soil/rock (Joekar-Niasar, 2009).

Cl and Mg are found in significant concentrations in solution in the saturated zone and in very little concentrations in the unsaturated zone. This may indicate that the main source is from outside the SNP site, or that they have mostly leached down from the unsaturated- to the saturated zone.

Relatively high concentrations of Ca are found in the unsaturated zone, but significant concentrations in solution in the saturated zone. This may also indicate that the main source of Ca is from outside the SNP site, or that it has mostly leached down into the saturated zone (which is unlikely, as SNP does not use products containing Ca).

The dolomitic aquifer to the west of the study area may contribute to the high concentrations of Ca and Mg.

Mn is found in relatively the same concentrations in both the saturated and unsaturated zone, but also mainly in solution in the saturated zone.

SO<sub>4</sub> and K were found in little more concentrations in solution than in soil samples (in the saturated zone), but in a lesser contrast than for example; NO<sub>3</sub>, Ca, and Mg. The most predominant concentrations of SO<sub>4</sub> and K are found in the storage area in the middle of the site where KCl and ZnSO<sub>4</sub> is stored.

Zn and F were found predominantly in soil samples, and primarily in the upper layer of soil. Zn is found almost exclusively in the storage area in the middle of the site where ZnSO<sub>4</sub> is stored (Zn may be involved in cation-exchange reactions with Ca and Mg).

PO<sub>4</sub> was almost exclusively found in the upper layer of soil, as well as NH<sub>4</sub>, but to a lesser extent.

NO<sub>2</sub> was found in very little concentrations anywhere on the site. This may be due to NO<sub>2</sub> being a relatively instable form of nitrogen, and hence either undergo oxidation or reduction fairly quickly. This is advantageous, seeing that NO<sub>2</sub> is the most noxious form of nitrogen.

The particular distribution of the contaminants is attributed to their solubility characteristics and/or their tendency to be adsorbed by soil/rock.

Many of the contaminants show a consistent peaking at a depth of ca. 6m. This may be attributed to the fact that pH levels are mildly acidic within the first few meters of soil, after which it increases rapidly to approximately neutral values throughout the depth of the site. This could be due to the Fe-rich quartzites of the Transvaal group (which would lower the pH in the upper regions), the influence of high concentrations of Ca (see section B.1: Ca restricts the mobility of PO<sub>4</sub>, SO<sub>4</sub>, and F), reducing conditions below a depth of ca. 2m, and/or oxidation of contaminants in shallower depths due to higher oxygen concentrations (oxygen enters shallower depths). Contaminants' solubility that are pH dependant (lower pH increases solubility) would hence dissolve and leach through the first layer of soil/rock and precipitate where pH values increase.

The biggest problem area is the storage tank area in the middle of the site, where significant concentrations of nitrate (NO<sub>3</sub>), sulphate (SO<sub>4</sub>), phosphate (PO<sub>4</sub>), ammonium (NH<sub>4</sub>), cadmium (Cd), fluoride (F), potassium (K), chromium (Cr), calcium (Ca), zinc (Zn), aluminium (Al), arsenic (As), copper (Cu), manganese (Mn), and nickel (Ni) are present.

Except for chromium that was found in BH004-D, it is not contaminated by any of the other contaminants found in the other boreholes. This is also the highest point of the lava formation in the subsurface underlying the site, and confirms the notion that contaminants collect and move along the surface of the lava formation.

Chromium (Cr) was found in concentrations between 0.0003 and 0.00045kg/ton in soil samples on two locations on the site, and in all the water samples taken from the boreholes on the eastern side of the site, ranging between 0.4 - 1.925mg/l. A significant concentration (0.023mg/l) of chromium was also found in the water sample taken from ROSS6 which is used on malt products. Mighty Products Company should be advised to cease the use of groundwater for its operations, due to the potential health risks of chromium. The main source of chromium was found to be the site on the southern boundary of the SNP site, which was the location of a leather tannery in the past. Tanneries are known to use large quantities of chromium in their operations. It would be valuable to determine whether the chromium is Cr(III) or Cr(VI) in future, due to Cr(VI) being a significantly more toxic form of chromium than Cr(III).

Due to the evidence of the effectiveness of plants reducing contaminant concentrations in the north-eastern corner of the site, as mentioned in section 5.3.2.2, phytoremediation is recommended as a viable option to rehabilitate the area. It is also the most cost effective option which would continue working as long as the plants are there. In areas where it is not possible to plant plants, a layer of soil would have to be excavated due to the damage contaminants are causing to built structures (see Figure 39).

Contaminants situated deeper and in lesser concentrations would be attenuated by natural processes. The attenuation of contaminants over time would have to be checked with a monitoring plan. This is necessary in order to track the movement of contaminants and draw attention to any worsening of the situation.

(See section 8.6 for a full discussion of the remediation options recommended to SNP).

## Chapter 7: Conclusions

### 7.1 Key findings

- The subsurface on which SNP is situated consists of a highly weathered and fractured quartzitic layer, interspaced with perched clayey layers varying in thickness from ca. 11m on the eastern side of the site to ca. 22m on the western side.
- This weathered and fractured layer overlays a Hekpoort lava formation which acts as an impenetrable barrier on which contaminants collect and flow (towards to western and north-western side of the site). This fact was illustrated with EC measurements and chemical results.
- The geophysical investigation (resistivity) indicated the low conductivity values of the lava formation at depth on the western side of the site and the presence of areas of higher conductivity interspersed throughout the site and at various depths. This might indicate the location of clayey layers acting as water (and hence contamination) traps, or areas of preferential pathways through which groundwater migrate. The resistivity data did not indicate any definite contamination plumes.
- The aquifer on which the SNP site is situated is described as a minor confined fractured rock aquifer comprising of weathered and fractured rock (5 – 15m) and fractured rock deeper than 15m, and has an estimated thickness of 8 – 40m. The weathered and fractured rocks of the minor aquifer are of the Transvaal sedimentary and igneous rocks, which include quartzites, shale, diabase, and andesite (Skinner, 2007).
- The transmissivity values are generally high (ca. 10 - 50m<sup>2</sup>/d), with the highest values being on the eastern side of the site.
- The high transmissivity values are attributed to the overlying heavily fractured and weathered quartzitic layer.
- The Hekpoort lava formation is not intrusive and therefore don't have highly weathered and fractured zones which might serve as preferential pathways for groundwater, and hence will have a very low transmissivity value (it was not possible to measure the transmissivity of the lava formation separately).
- Water levels on the eastern side of the site are shallower than on the western side (difference of approximately 0.7m over 100m). This is caused by the regular irrigation for gardening purposes that occurs on the eastern side of the site.
- Although the water levels are shallower on the eastern side of the site, there is an overall slope of the surface elevation towards the east, with a difference in elevation between the eastern and

the western side being ca. 1.5m, i.e. a gradient of 0.015. This results in the movement of groundwater in a general easterly direction towards Potch Industria, and to a lesser extent the Spitskopspruit, with an effective hydraulic gradient of ca. 0.008.

- The study conducted by SRK Consulting on KFPP in 2007 showed that the “Gypsum Tailings dam and the Factory [KFPP] both contribute to contamination in the Spitskopspruit” (Skinner, 2007). It is not known what SNP’s contribution is to the contamination of the Spitskopspruit.
- In general,  $\text{NO}_3$ , Ca, Mg, Cl, and Mn are found predominantly in solution in the saturated zone (i.e., not adsorbed to soil/rock), except where there is loading from the surface within the bounds of SNP, which means that they are present in the unsaturated zone and leach down to the saturated zone.
- Very high concentrations of  $\text{NO}_3$  are found in both the unsaturated and saturated zone, but almost exclusively in solution in the saturated zone.
- A higher concentration is found in the saturated- than the unsaturated zone, which may indicate that the nitrate in the unsaturated zone has either mostly leached down, or that the main source is from outside the SNP bounds.
- Nitrogen in the subsurface is a complex interaction of the various nitrogen compounds and the respective processes occurring in the saturated- and unsaturated zones. The basic process can be described as follows; the nitrification process occurs in two stages, viz. ammonia is first oxidized to nitrite ( $\text{NO}_2$ ) by autotrophic ammonia-oxidizing bacteria (Nitrosomonas) and then to nitrate by autotrophic nitrite-oxidizing bacteria. Nitrite is quickly reduced or oxidized due to it being a generally unstable form of nitrogen. Nitrate then leaches into the saturated zone and is extremely soluble in water. It is not easily adsorbed by soil, which means that it migrates freely with the groundwater. In the saturated zone, nitrate can undergo denitrification into atmospheric nitrogen by heterotrophic bacteria (Paracoccus and Pseudomonas) (Joekar-Niasar, 2009).
- Nitrate leaching to the saturated zone from the unsaturated zone have therefore two origins, viz. the nitrate produced by the nitrification of ammonia and nitrite, and nitrate from products stored, mixed, and transferred on the surface (e.g. AN: ammonium nitrate) that end up in the unsaturated zone due to spills and leaks.
- The ammonium anion is immobilized as a result of adsorption to soil/rock (Joekar-Niasar, 2009).
- Cl and Mg are found in significant concentrations in solution in the saturated zone and in very little concentrations in the unsaturated zone. This may indicate that the main source is from outside the SNP site, or that they have mostly leached down from the unsaturated- into the saturated zone.

- Relatively high concentrations of Ca are found in the unsaturated zone, but significant concentrations in solution in the saturated zone. This may also indicate that the main source of Ca is from outside the SNP site, or that it has mostly leached down into the saturated zone (which is unlikely, as SNP does not use products containing Ca).
- The dolomitic aquifer to the west of the study area may contribute to the high concentrations of Ca and Mg.
- Mn is found in relatively the same concentrations in both the saturated and unsaturated zone, but mainly in solution in the saturated zone.
- SO<sub>4</sub> and K were found in little more concentrations in solution than in soil samples (in the saturated zone), but in a lesser contrast than for example NO<sub>3</sub>, Ca, and Mg. The most predominant concentrations of SO<sub>4</sub> and K are found in the storage area in the middle of the site where KCl and ZnSO<sub>4</sub> is stored.
- Zn and F were found predominantly in soil samples, and primarily in the upper layer of soil. Zn is found almost exclusively in the storage area in the middle of the site where ZnSO<sub>4</sub> is stored (Zn may be involved in cation exchange reactions with Ca and Mg).
- PO<sub>4</sub> was exclusively found in the upper layer of soil, as well as NH<sub>4</sub>, but to a lesser extent.
- NO<sub>2</sub> was found in very little concentrations anywhere on the site. This may be due to NO<sub>2</sub> being a relatively instable form of nitrogen, and hence either undergo oxidation or reduction fairly quickly.
- The particular distribution of the contaminants is attributed to their solubility characteristics and/or their tendency to be adsorbed by soil/rock.
- Many of the contaminants show a consistent peaking at a depth of ca. 6m. This is attributed to the fact that pH levels are mildly acidic within the first few meters of soil, after which it increases rapidly to approximately neutral values throughout the depth of the site. This could be due to the Fe-rich quartzites of the Transvaal group (which would lower the pH in the upper regions), the influence of high concentrations of Ca (see section B.1: Ca reduces the mobility of PO<sub>4</sub>, SO<sub>4</sub>, and F), and/or reducing conditions below a depth of ca. 2m. Contaminants' solubility that are pH dependant (lower pH increases solubility) would hence dissolve and leach through the first layer of soil/rock and precipitate where pH values increase.
- Except for chromium that was found in BH004-D, it is not contaminated by any of the other contaminants found in the other boreholes. This is also the highest point of the lava formation in the subsurface underlying the site, and confirms the notion that contaminants collect and move along the surface of the lava formation.



- The biggest problem area is the storage tank area in the middle of the site, where significant concentrations of nitrate (NO<sub>3</sub>), sulphate (SO<sub>4</sub>), phosphate (PO<sub>4</sub>), ammonium (NH<sub>4</sub>), cadmium (Cd), fluoride (F), potassium (K), chromium (Cr), calcium (Ca), zinc (Zn), aluminium (Al), arsenic (As), copper (Cu), manganese (Mn), and nickel (Ni) are present.
- Chromium (Cr) was found in concentrations between 0.0003 and 0.00045kg/ton in soil samples on two locations on the site (A03 and AB2), and in all the water samples taken from the boreholes on the eastern side of the site, ranging between 0.4 - 1.925mg/l.
- A significant concentration (0.023mg/l) of chromium was also found in the water sample taken from ROSS6 which is used on malt products. Mighty Products Company should be advised to cease the use of groundwater for its operations, due to the potential health risks of chromium.
- The source of chromium contamination was found to be the site on the southern boundary of the SNP site, which was the location of a tannery in the past. Tanneries are known to use large quantities of chromium in their operations.
- Due to evidence of the effectiveness of plants reducing contaminant concentrations in the north-eastern corner of the site, as mentioned in section 5.3.2.2, phytoremediation is recommended as a viable option to rehabilitate the area. It is also the most cost effective option which would continue working as long as the plants are there.
- In areas where it is not possible to plant plants, a layer of soil would have to be excavated due to the damage contaminants are causing to built structures (see Figure 39). This is especially noticeable on the northern side of the site where there is significant PO<sub>4</sub> contamination. PO<sub>4</sub> displaces the Ca and Mg in cement, which causes it to become brittle. It also absorbs water causing it to expand and do further damage. The parts of the building affected on the northern side of the site would have to be rebuilt, as the structural integrity might be compromised.
- Contaminants situated deeper and in lesser concentrations would be remediated by natural processes. The attenuation of contaminants over time would have to be monitored with a monitoring plan. This is necessary in order to track the movement of contaminants and draw attention to any worsening of the situation.

## 7.2 Summary of the contaminants in groundwater found in the study area

Table 23 is a summary of the contaminants found in the groundwater in the studied area as a result of fertilizer manufacturing. Listed here are the likely sources of the contaminants, their behaviour in the subsurface, safe concentrations for human consumption, the concentrations found in the studied area, health- and environmental risks associated with excessive concentrations, and the likely remediation methods for each (USGS, EPA, WHO, DWA).

Table 23: Summary of the contaminants in groundwater caused by fertilizer manufacturing. **Green** indicates the recommended operational-, **yellow** the maximum allowable range-, and **red** the not-allowable concentrations for drinking water standards as prescribed by the SANS241:2006 guidelines (USGS(a), USGS(b), USGS(c), EPA, WHO, DWA).

Contaminant	Sources	Behaviour in the subsurface	DWA limits (SANS241:2006) (mg/l)	Concentrations found in study area (mg/l)	Health risks	Environmental risks	Remediation methods
Nitrate (NO <sub>3</sub> )	Ammonia, ammonium nitrate, ammonium sulphate, urea.	Highly soluble, migrates freely with groundwater, consumed by microorganisms.	<10, 10 - 20, >20	>100 - 938	Methemoglobinemia, and nitrate poisoning (livestock).	Eutrophication, increase in BOD.	Non-treatment, ion-exchange, biological denitrification.
Ammonium (NH <sub>4</sub> )	Ammonia, ammonium nitrate, ammonium sulphate, urea. Microorganisms break down organic nitrogen products.	Migrates much slower than nitrate due to chemical and microbial processes.	<1, 1 - 2, >2	0.064 - 1100	Methemoglobinemia, and nitrate poisoning (livestock).	Eutrophication, increase in BOD.	Non-treatment, ion-exchange, biological denitrification.
Phosphorus (PO <sub>4</sub> )	Phosphoric acid, (phosphate rock).	Very limited migration in groundwater. Usually precipitates in first few meters of soil/rock.	No standard	At SNP, mainly found in soil samples; 0 - 5.45kg/ton. KFPF: <10 - 110102.	Kidney damage and osteoporosis.	Eutrophication. Causes damage to built structures; displaces Mg and Ca in cement, and expands with water absorption.	Excavation.

Table 23 (continued): Summary of the contaminants in groundwater caused by fertilizer manufacturing. Green indicates the recommended operational-, yellow the maximum allowable range-, and red the not-allowable concentrations for drinking water standards as prescribed by the SANS241:2006 guidelines (USGS(a), EPA, WHO(a), WHO(c), WHO(e), WHO(f), DWA).

Contaminant	Sources	Behaviour in the subsurface	DWA limits (SANS241:2006) (mg/l)	Concentrations found in study area (mg/l)	Health risks	Environmental risks	Remediation methods
Sulphate (SO <sub>4</sub> )	Sulphuric acid, phosphate rock processing, zinc sulphate, ammonium sulphate.	Highly soluble, but some compounds less soluble than others. Migrates freely with groundwater when dissolved.	<400, 400 - 600, >600	30 - 7600	Mild laxative effect.	SO <sub>x</sub> causes acid rain. Potential negative impact on aquatic systems.	Non - treatment, precipitation, ion-filtration, ion-exchange.
Fluoride (F)	Mainly phosphoric acid manufacturing.	Sodium fluoride is soluble, other compounds less so. Migrates freely with groundwater when dissolved.	<1, 1 - 1.5, >1.5	0.1 - 4100	Mild dental and skeletal fluorosis.	Contamination. Potential negative impact on aquatic systems.	Precipitation, filtration, ion-exchange.
Chloride (Cl)	Potassium chloride.	Highly soluble, migrates freely with groundwater, more persistent than nitrate.	<200, 200 - 600, >600	<300 - 788	Not generally considered a health risk.	Increases corrosivity of water. Contamination of the environment with salt.	Non-treatment, ion-exchange, chemical precipitation.
Cadmium (Cd)	Mainly phosphate rock.	Solubility increases with an increase in acidity.	<5, 5 - 10, >10 (µg/l)	None found in any SNP groundwater samples. No data for KFPF.	Kidney damage. Increased risk of developing Itai-Itai disease.	Contamination. Potential negative impact on aquatic systems.	Precipitation, filtration, ion-exchange.

Table 23 (continued): Summary of the contaminants in groundwater caused by fertilizer manufacturing. **Green** indicates the recommended operational-, **yellow** the maximum allowable range-, and **red** the not-allowable concentrations for drinking water standards as prescribed by the SANS241:2006 guidelines (EPA, WHO(b), WHO(d), WHO(g), DWA).

Contaminant	Sources	Behaviour in the subsurface	DWA limits (SANS241:2006) (mg/l)	Concentrations found in study area (mg/l)	Health risks	Environmental risks	Remediation methods
Potassium (K)	Potassium chloride.	Soluble in water, involved in ion-exchange reactions, especially with Ca, and Mg.	<50, 50 - 100, >100	1.04 - 7.073 (SNP) (More predominant in soil samples).	Only effects individuals in high risk groups, e.g. those with diabetes, heart disease, etc.	Eutrophication. Contamination of the environment with salt.	Precipitation, filtration, ion-exchange.
Zinc (Zn)	Zinc sulphate.	Solubility is a function of pH and total inorganic carbon concentrations.	<5, 5 - 10, >10	0.006 - 0.048 (Concentrations >8kg/ton found in some soil samples) (SNP).	Vomiting, copper deficiency, impairment of immune responses, gastric erosion.	Potential negative impact on aquatic systems.	Precipitation, filtration, ion-exchange.
Chromium (Cr)	Phosphate rock processing.	Forms hydroxides and complexes, adsorbed at relatively high pH values, relatively free migration with groundwater.	<100, 100 - 500, >500 (µg/l)	23 - 1925 (µg/l) (SNP)	Gastrointestinal disorders, haemorrhagic diathesis, convulsions, genotoxic effects, carcinogenic, death.	Potential negative impact on aquatic systems.	Precipitation, filtration, ion-exchange.
Other heavy metals, e.g. Ca, Mg, Al, Fe, Co, Ni, Mn, etc.	Depends on the phosphate rock content.	Varying solubilities, usually pH dependent.	Varies	High concentrations of Ca (>1000) and Mg (>600) found (SNP).	Poses varying health risks.	Poses varying environmental risks. Potential negative impact on aquatic systems.	Precipitation, filtration, ion-exchange.
Radionuclides	Phosphate rock processing	Solubility of different compounds vary, groundwater migration is partly restricted by adsorption.	(<0.1mSv/a (recommended reference dose level (RDL) of committed effective dose) (WHO).	<0.25mSv/a (KFPP). Not tested for at SNP.	Nephritis, increased risk of cancer, kidney toxicity.	Contamination. Potential negative impact on aquatic systems.	Excavation, electrokinetic separation, precipitation, filtration, ion-exchange.

### 7.3 Lessons learnt, shortcomings, and limitations

There are certain limitations and shortcomings to this study, which, when overcome, would result in better quality and quantities of data, and hence a better understanding of the impact of fertilizer manufacturing on groundwater in the study area. These limitations and shortcomings are;

- Budget constraints. The amount of data collection done have to be within the constraints of the available budget. Unlike Western Europe and North America, South Africa in general have relatively low budgets for environmental impact studies. This inevitably reduces the quality and quantity of data. With a bigger budget, more water and soil samples could have been taken, over a wider area, at various depths, and over a longer period of time.
- The confidentiality agreements between industries and environmental consultants make it difficult for third parties to continue with studies in an area. Consultant companies are usually only willing to release limited amounts of data, as was the case with SRK Consulting.
- There is an insufficient amount of data collection and managing done by the relevant government departments. The DWA do not have any data of boreholes in the Potch Industria area, and a hydro-census had to be done by the researcher. The closest boreholes to the study area with data held by the DWA are 30km away.
- There are very few boreholes in the Potch Industria area, which makes it difficult to determine the extent of the migration and concentrations of contaminants in the subsurface.
- Historical data with regards to the soil and groundwater contamination of the SNP site is virtually non-existent.
- The SNP site itself is mostly covered with concrete and built structures (ca. 70%), which means that the location and concentrations of contaminants could not be determined for all areas on site.
- The accessibility of surrounding sites was not easy, which made it difficult to gather sufficient data for the immediate area surrounding SNP and KFPF. Some “data gaps” were filled in by the SRK Consulting report, e.g. whether activities on the SNP and KFPF site impacted water quality in the Spitskopspruit north of the study area.
- It is recommended that all industries operating in the Potch Industria area join a compulsory environmental impact assessment and monitoring program in order to determine their respective contributions to groundwater pollution in the area, and also in doing so to divide rehabilitation costs according to contaminant quantity and quality contribution.

## **Chapter 8: Recommendations**

### **8.1 Introduction**

This focus of this section is on safe practices recommended for the liquid fertilizer industry in order to prevent occupational hazards and environmental pollution (See Appendix C for a discussion of three case studies done on other fertilizer manufacturing facilities around the world). Mention is also made of the remediation options suggested to SNP, and other site specific concerns.

### **8.2 Pollution prevention: Recommended safety measures for hot and cold blend liquid fertilizer plants**

#### **8.2.1 Effluents associated with the liquid fertilizer industry and their control measures**

##### **8.2.1.1 Introduction**

As mentioned in section 3.5, fluid fertilizers are not normally associated with major pollution problems; however, the operations involved can cause significant levels of contamination that necessitate control measures. The handling of solid raw materials may discharge unacceptable levels of particulate matter into the air, and the transference of liquid and gaseous raw materials may leak into the environment through shabby pipe work.

The highest risk of a pollution incident is possibly during the mixing of raw materials. High temperatures resulting from the heat of neutralization of, for example, ammonia and phosphoric acid, may cause boiling and the development of high vapour pressures. This may lead to surges with possible overflows and the emission of fumes and gases at toxic levels. The handling of hot fluids through strainers and other ancillary equipment reduces the risk of pollution, but the probable influence of residual fumes should not be discarded. Over a period of time unwanted contaminants develop on strainers and may need to be treated as a distinct solid waste disposal operation.

Excessive noise is not a major problem in the liquid fertilizer manufacturing industry, but mechanical equipment, e.g. pumps, impellers, fans, and vehicles should be properly maintained to ensure noise levels remain within reasonable limits (Palgrave, 1994).

##### **8.2.1.2 Dust control**

The method of handling solid raw materials significantly affects the potential for dust production. "The use of front-end loaders, which drive into a pile of raw material to fill the bucket prior to tipping it either into an elevator hopper or directly into a mixing vessel, may be expected to create a very dusty atmosphere. Provided that the latter is contained within a building equipped with extractor fans and

dust filters, this may be acceptable. Personnel working inside the building need to be located in a suitably designed enclosure, with a clean, controlled atmosphere. This includes the cab of the front-end loader. It is not practicable or acceptable to rely on the use of personal dust masks” (Palgrave, 1994).

Completely enclosed systems should be used where possible, especially for raw materials with the finest particles. The pneumatic handling of clay is widely practiced, and in many cases clay could be fed directly from the storage to the gelling unit, and in so doing, pre-gel the clay with water (Palgrave, 1994).

### **8.2.1.3 Fume control**

The main emissions likely to occur are ammonia, water vapour, and certain fluorine compounds, which almost all arise during the neutralization stage. The handling of ammonia is particularly important, as it is, in some form or another, often a raw material in fertilizer manufacturing (Palgrave, 1994).

#### **8.2.1.3.1 Ammonia**

However well carried out, the making and breaking of connections between delivery vehicles and storage facilities lead to an almost inevitable but finite gaseous release. Personnel involved should be fully trained and wear full protective equipment to ensure that a product transfer operation does not become a pollution incident. The integrity of the ammonia installation should be monitored and tested frequently. The transfer of aqueous ammonia into the storage tank results in the displacement of air containing ammonia fumes, which should be vented through a scrubber.

“The vapour pressure of ammonia over solutions of ammonium salts in water is a function of concentration, temperature, and pH” (Palgrave, 1994). It is hence important during neutralization to control the feed rates of the reactants in order to keep the temperature and pH down. “Provided that the ratio of acid to ammonia is not allowed to drift, the pH can be kept neutral or slightly acidic. The temperature may be reduced by either physical or thermo-chemical cooling. Physical cooling may be effected by recycling the contents of the mixing vessel through an external cooler or by placing cooling coils in the reaction zone. Thermo-chemical cooling may be employed when supplementary plant nutrients such as potassium chloride or urea are introduced, thereby extracting their heats of solution. Similar considerations apply when nitrogen solutions are being manufactured by the hot-mix technique, from high-temperature ammonium nitrate liquor. The latter, which is often transported in insulated tankers, normally contains free ammonia, and when discharged, can give rise to significant ammonia emissions. These can be minimized by discharging into a urea-water slurry” (Palgrave, 1994).

The geometry of the mixing vessel may influence the control of gaseous ammonia. The possibility for gaseous loss is considerably less when a pipe reactor is used for bringing ammonia and phosphoric acid together to produce either ammonium orthophosphate or polyphosphate, than for when an open-topped vessel is used. It may be a requirement to tip large quantities of solid raw materials into an open-topped vessel, which conflicts with the need to minimize ammonia emissions, but this could be overcome by operating with both in series.

The temperature and pH should constantly be monitored during the neutralization stage, and an alarm system should be installed to provide either a visual or audible warning, or to reduce the raw material feed rate. It would also be desirable to have a system in place to constantly monitor the atmosphere in the vicinity of the neutralizers (Palgrave, 1994).

#### **8.2.1.3.2 Water vapour**

The emission of water vapour itself is not regarded as a significant pollutant, but it may be in admixture with ammonia and fluorine compounds when originating in the processing operations. Sufficient methods to deal with these are likely to remove water vapour as well, but water vapour emerging from secondary cooling towers could pose potential problems for neighbours. The careful siting of such a facility could solve the problem (Palgrave, 1994).

#### **8.2.1.3.3 Fluorine compounds**

The emission of fumes containing hydrofluoric acid, tetrafluoride, and fluorosilicic acid, or possible ammonia derivatives, could accompany the neutralization of wet-process phosphoric acid. Since the concentration process of phosphoric acid is likely to be associated with defluorination, less fluorine is tend to be present when more concentrated phosphoric acid is used. Wet scrubbing should be installed where appropriate, and liquors blended with the finished products (Palgrave, 1994).

#### **8.2.1.4 Liquid control**

The plant design should be such that the only liquids released originate from occasional leaks from valves, flanges, pump and impeller seals, etc. Vessel overflow is an unlikely scenario with qualified staff. Regular inspection and maintenance should be carried out in order to identify corrosion and erosion hot spots which could lead to sources of leakage.

Regulating authorities in most countries regard the containment of leakages as a high priority. Focus normally falls on storage vessels, but all vessels come under scrutiny. The bunding of individual tanks are recommended, although the bunding of whole sites have also been accepted. This involves the construction of a big lagoon in a convenient low lying area into which spillages flow through a system of gullies. The rainwater accumulating in the lagoon can be used for further fluid fertilizer



manufacturing. The emissions from cooling systems and boilers can be dealt with in the same way (Palgrave, 1994).

#### **8.2.1.5 Solid waste**

The fluid fertilizer industry is not associated with excessive solid waste production. Solid waste may become a problem however in plants producing only clear products, but the insolubles produced in these plants contain nutrients which could be incorporated into either solid or suspension grade products. Materials such as solid stones or metallic objects that found their way into bulk solid raw materials are genuine solid waste, and should be disposed of by conventional means.

Materials that develop through cleaning operations should not be disregarded. Vessels used for wet-process phosphoric acid duty contain significant quantities of gypsum that has to be disposed of periodically, and vessels used for storage tend to accumulate large quantities of corrosion products over time for which disposal arrangements have to be made (Palgrave, 1994).

#### **8.2.1.6 Noise**

Noise may not be a chemical pollutant, but it is nevertheless an unwanted part of the environment. As mentioned earlier, fluid fertilizer plants do not normally produce noise levels reaching legal limits, but faulty or unmaintained equipment may be the exception. "Vehicle noise in a confined space, such as a front-end loader in a raw material warehouse, can be severe and it may be necessary to sound-insulate the cab to make it safe for the operator to use. It is not sufficient to supply ear protection for continuous use" (Palgrave, 1994). Installations, e.g. extractor fans, should sometimes be modified or replaced when generating excessive noise. Noise levels should be monitored and recorded on a regular basis (Palgrave, 1994).

### **8.2.2 Containment systems for liquid fertilizer plants**

#### **8.2.2.1 Introduction**

Containment systems for liquid fertilizer plants should be designed in order to keep emissions and effluents inside the facility boundaries, and only the product should ideally leave the site. However, even in a well operated site, it is inevitable to have waste, but this waste should be collected and disposed of in an environmentally friendly manner. Due to the high cost of waste disposal, it is profitable to keep as little waste water as possible, and to reuse it wherever appropriate. Discussed in this section are suggestions for the design of the various parts of an integrated containment system that should prevent the loss of material into the environment. In many instances, various designs will be feasible and construction materials suitable. For this reason, the reader is referred to reputable

environmental engineering firms who have expert knowledge of agrichemical facilities (Mann, Jr., 1994).

“Emphasis should be placed on designing systems that are both safe and convenient for the employees and that allow efficient flow of people, vehicles, and materials in, around, and out of the facility” (Mann, Jr., 1994).

#### **8.2.2.2 Loading and unloading systems**

Loading and unloading systems should all be large enough to contain the entire contents of the tanker in the event that a massive rupture was to occur. The systems however are usually large enough to contain two tankers loading and/or unloading at the same time. The pads should be able to support the entire weight of a fully loaded tanker, and also sloped towards a central sump in order to contain any spillages. The sump should be small and emptied on a regular basis (more than once a day if possible).

In some cases, in order to reduce the loading pad containment volume, some pads are constructed adjacent and connected to a tank farm containment area. The pads should be designed to drain massive ruptures into the tank farm containment area, but so that small spillages drain into the sump.

Ramps onto pads are necessary in order to keep the pad lips from cracking, and to keep most of the dirt and gravel off the pad. The pad should also be bounded by a curb for containment purposes. It is advantageous to have a roof over the pad to keep excessive rainwater out. Piping should be visible, i.e. either overhead or in trenches, in order to identify and repair leakages easily. The electrical system should be well shielded to prevent corrosion, and situated in a place where there is maximum visibility of the loading and unloading operations (Mann, Jr., 1994).

#### **8.2.2.3 Reaction and mixing systems**

The majority of the batch reaction and mixing systems are normally under roof or in a building. The continuous reaction systems, e.g. those producing ammonium polyphosphate fluids are usually located outside. “Both systems should have sufficient containment to retain 100% of the volume of fluid in the largest tank or reaction vessel in the area, plus the submerged volume occupied by the other tanks or equipment in the contained area. An extra 10 to 25% should be added for storm water when the system is outside. Containment in an adjoining tank farm area can be used as part of the volume, when applicable” (Mann, Jr., 1994).

The building walls can be seen as a dike if properly sealed, and when door sills are raised, can provide a continuous wall around the perimeter. Ramps to the doors would provide safe access to and from

the building. Pipes should be visible to expose leakage, but supported to prevent sagging or breakage. Electrical installations should comply with safety standards.

Systems located in the open should have sufficient containment to capture both spillages and storm water. The storm water could be released if uncontaminated, but should be used or disposed of in an environmentally friendly way if contaminated.

Off-gases from the reaction units should be sampled and analyzed on a regular basis. Scrubbers may have to be installed if gases are above legal limits (Mann, Jr., 1994).

#### **8.2.2.4 Raw material and product storage**

The storage tanks should be situated in a secondary containment area which can accommodate the entire volume of the largest tank, including the submerged volume of the other tanks. If storage tanks are outside, the containment volume should be increased to include ca. 150mm of rainfall. A mechanical system should be in place to prevent storage tanks from floating, and leakage detectors should be installed under the pads.

Tanks exceeding 100 000 gallons (378 542.2l) are too large to be moved easily to install an impervious layer and leak detectors, and hence provide unique challenges for containment. Some companies are able to float the tanks on water or air cushions, or in some instances jack the tank up, in order to install the secondary containment. "Alternative procedures are either to install a second steel bottom separated from the original bottom by a layer of inert porous material or to install a bladder inside the tank on top of the porous layer. The original tank bottom then becomes the secondary containment under the tank and the porous layer becomes a leak detector. Openings are cut into the tank wall below the new bottom or bladder to show when a leak has developed. An impervious surface, either concrete, synthetic sheets, or clay/soil mixtures, is then installed between the tank outer wall and the dike wall" (Mann, Jr., 1994).

The majority of liquid fertilizer plants also use solid raw materials. These should be stored on an impervious surface under roof, or if outside, be covered with rain-resistant covers. Until the area can be tested for contamination, runoff should be prevented from leaving the area where solid raw materials are stored outside (Mann, Jr., 1994).

#### **8.2.2.5 Washing and parking areas**

Many liquid fertilizer plants use the loading and unloading area for washing, while others have separate washing areas installed. "In either instance, the pads should be impervious to the materials

being washed onto them, have curbs or gutters to prevent runoff from leaving the pad, and have a sump to collect the wash water for storage in an adjacent tank or tanks” (Mann, Jr., 1994).

Equipment can be washed in the field if at all possible. It should be kept in mind that wash water should not be applied to the field in excess of the recommended labeled rates for the specific fertilizer and agrichemical used. Washing should also not occur near wells, sink holes, or other areas that would cause the agrichemical or fertilizer to enter directly into the surface and groundwater. If the equipment is washed at the facility, water should be reused for the various operations on site, or can be applied to nearby land.

“Parking areas should be evaluated and constructed from the standpoint of whether the equipment would contain agrichemicals or whether the equipment was empty and clean” (Mann, Jr., 1994). The main risk in any parking area is that a valve or sight gauge could be damaged, either accidentally or through vandalism, which would result in a spillage. Vehicles parked overnight should have their discharge and drain valves locked shut.

Parking areas should be constructed with material impervious to the content contained in the vehicles parked there, and to be able to contain any loss of fluid that may occur. The parking area should be sloped to drain spillages and storm water into a sump where it can either be reused or disposed of in an environmentally friendly way. Curbs and gutters are also recommended to assist in containment. Cleaned and empty vehicles may be parked in areas that do not have containment systems in place (Mann, Jr., 1994).

#### **8.2.2.6 Operational areas**

These are areas that typically include the office, weigh scales (bridge), shop, and any other area not described above. In any area where there is the possibility of a spillage entering surface or groundwater, containment systems should be in place. This includes oils, grease, antifreeze, and other chemicals used around the shop. Waste oil and used batteries should be sent for recycling, and used tires can be handled by tire dealerships (Mann, Jr., 1994).

### **8.3 Current safety procedures in place at SNP**

Table 24 is taken from the official Sasol Nitro “Safe Work Procedure (SWP) (Reference nr: SWP-P-P-07)” document which regulates the safe practice for operations and sets the standard to which the SNP plant should comply. This document was written on the 12th of July 2005 and revised on the 2nd of July 2007.

**Table 24: Sasol Nitro Safe Work Procedure (SWP) (SWP-P-P-07, 2007).**

<i>Safe Work Procedure</i>		
<i>Nr.</i>	<i>Steps (In sequence)</i>	<i>Critical Points (also add PPE) (Items to be emphasized)</i>
1	Batch card is printed for the quantity needed.	Ensure that the correct SAP codes are used while processing a batch card on the computer.
2	Confirm the SG of the raw material: Phosphoric Acid (1.66) and Ammonium Nitrate Solution (1.27) in storage tanks.	Prevent off-spec final product. Ensure you are wearing the necessary PPE: safety gloves, helmet, ear plugs, safety goggles and overall.
3	Ensure to pump water first into the reactor. After circulating the water the next step is to add ANO and Phosphoric Acid.	To ensure that the mixture of raw materials are effective - firstly use 50% (from the batch card quantity) of water and then ANO when the production process starts.
4	Open the ammonia valve slowly until the pH reached is between 5.8 and 6.2.	Opening the Ammonia valve too quickly can result in product splashes that can lead to burning injuries (product temp: 80°C), as well as excessive vibration on the reactor and pressure on pipes. Avoid any contact with raw materials or final product (may cause serious burns or skin irritation). When the pH reaches ca. 4, there will be a high amount of steam in the air - ensure that you are standing outside the steam cloud.
5	When the desired pH has been reached, put the balance of water and ANO into product.	To enhance mixing of the product, check the reactor tank level at all times to prevent overflow.
6	Put the dry raw materials in the process with the screw feeder.	Ensure that the discharge gate of the screw feeder is in the fully open position when discharging product. Ensure that there's no obstruction in the feeder screw. Wear the correct PPE at all times: Safety goggles, gloves, shoes, ear plugs and overall.
7	Add zinc and clay to batch.	Assure accuracy. All raw materials valves are colour coded - ensure that the correct valve is opened when transferring.
8	Circulate the product for ca. 15min.	To ensure the necessary quality, thoroughly mix the product.
9	Final product to be pumped to storage tank or direct into truck.	Two operators are necessary to complete the task. One operator at the reactor and another at the storage tank. Ensure that the correct transferring valves are open.

(See section 8.5 for an evaluation of these safety measures in place at SNP).

## 8.4 Current waste disposal guidelines in place at SNP

### 8.4.1 Introduction

The following section was taken from the official Sasol Nitro "Waste Management" (Reference nr: 10-6) document providing guidelines for the safe handling, storage, transport, and disposal of waste material to which the SNP plant should comply. As quoted from the document; "Waste handling has a three-part objective, namely: cost effectiveness, decrease [of] pollution and health risks during and after disposal, and ensure[ing] conformance to legal requirements. This procedure covers the disposal

of all waste as defined in this procedure and applies to all parties using any of the waste handling or waste disposal facilities described in the procedure”.

The plant manager, SPCs, and lab personnel are responsible for ensuring that this procedure is adhered to. The document was created on the 26<sup>th</sup> of October 2009. The references used for the creation of this document, are; ISO9001:2000, ISO14001:2004, and OHSAS18001:1999.

## 8.4.2 Procedures

### 8.4.2.1 Waste types and disposal area/site

**Table 25: Waste types and disposal area/site (10-6, 2009).**

<i>Waste type</i>	<i>Disposal method</i>	<i>Company</i>
Laboratory waste: Liquid	Recycled into process / Sumps	Sasol
Laboratory waste: Plastic containers, sample	Reclamation yard/ green bins	Sasol
Scrap metals	Reclamation yard	Tender P&SM
Plastic bags, HDPE piping, and old tanks	Reclamation yard / blue bins	Potch Plastics
Personal protective equipment and contaminated rags	Lockable storage bin	Sasol
Paint containers, aerosol cans	Reclamation yard / yellow bins	Sasol
Fluorescent lights	Original packaging	Sasol
Domestic office household and garden refuse	Blue bins marked “Domestic”	Municipality
Crystallized product - from cleaning tanks	Sweeping bay for recycling into process	Sasol
Oil generated from the workshop	Flammable store	Sasol Secunda
Cables and electric motors	Reclamation yard	Sasol Secunda

### 8.4.2.2 Waste handling

#### 8.4.2.2.1 Laboratory waste: Liquids

*Waste to be handled by trained laboratory personnel.*

- Laboratory waste is generated from the following three analytical methods used:
  1. Buchi: Used to measure the nitrogen concentration in the fertilizer samples.
  2. Spectrophotometer: Used to measure the phosphate concentration in the liquid fertilizer samples.
  3. Flame photometer: Used to analyse the potassium concentration in the liquid fertilizer samples.

- Chemical preparations are prepared as per table below (not provided by SNP), batch samples from the operations are then added to the chemical preparation and then analyzed for the % N or % P. This is part of a quality control process.
- Once analysis has been completed, the residual sample and liquid generated/expelled from the analyser/s is collected as a waste sample.
- The waste generated is stored in 5l containers and then disposed of in the sumps, where plant waste water is collected and is recycled back into the production processes.
- Only a maximum quantity of 5l per recycling must be maintained and kept in the laboratory at all times.
  1. The 5l container is to be clearly labelled with the following information:
    - Laboratory waste.
    - Date of first accumulation of waste.
    - Max volume/capacity.
  2. The container must be kept inside the laboratory, locked, labelled, identified and out of reach of an unauthorised personnel.
  3. Access to the hazardous waste materials will be controlled by lab responsible person.
- Ensure that all chemicals in the lab are also clearly identified, and that you adhere to housekeeping standards.

#### **8.4.2.2.2 Laboratory waste: Sample bottles and containers**

- All waste bottles will be stored in the dedicated bin in the reclamation yard.

#### **8.4.2.2.3 Scrap metals: Steel, metal structures, etc.**

- All metal waste generated on this site will be stored in the reclamation yard, where it will be removed by the approved Sasol scrap steel dealer, viz. P&SM.
- All records of the quantity disposed must be filed.

#### **8.4.2.2.4 Plastic bags, HDPE piping, and old tanks**

- All plastic waste generated on this site will be stored in the reclamation yard, where it will be removed by the approved Sasol plastic recycler.
- All old tanks must be cut up into pieces so that it can be safely handled.

- All records of the quantity sent for recycling must be filed.

#### **8.4.2.2.5 Personal Protective Equipment (PPE) including oily contaminated rags**

- All old, used or replaced PPE will be handed to SPC, who will store it in a container and send it to Secunda for further disposal. Information of quantity disposed must be filed.

#### **8.4.2.2.6 Paint containers and aerosol cans**

- All paint tins and aerosol cans will be stored in the dedicated bin in the reclamation yard. Information of quantity disposed must be filed.

#### **8.4.2.2.7 Fluorescent lights**

- All fluorescent lights must be placed back in their cardboard cases. All broken fluorescent tubes must be put into a plastic bag and sealed. Information of quantity disposed must be filed.

#### **8.4.2.2.8 Domestic waste**

- Domestic waste generated from the plant and the offices will be collected and stored on the marked domestic bins or containers.
- When bins are full, they will be disposed at the municipality disposing yard.

#### **8.4.2.2.9 Waste generated at the workshop: Oil**

- Waste oil generated at the workshop will be collected on the marked container and stored at the flammable store.
- When containers are full, registered external disposing companies will be responsible to dispose of the hazardous chemicals.
- Information of quantity disposed of must be filed.

#### **8.4.2.2.10 Crystallized product and sludge from cleaning tanks**

- Waste generated from cleaning storage tanks and sumps will be bagged and stored in the sweeping bay. Ensure that the bags are identified correctly before storing waste product in the bags.
- These products can be sent to the farmers upon signing an agreement to accept the gypsum containing waste. These letters and quantity of sludge must be recorded and filed.



#### **8.4.2.2.11 Surface runoff**

- As mentioned in section 4.5, SNP has seven sumps on site, the location of which is indicated in Figure 13. Any runoff that may occur due to spillages during operations are captured in these sumps and reused in fertilizer products. SNP is also mostly bounded by a concrete wall, and hence runoff from the site does not pose a significant danger to the adjacent sites.

#### **8.4.2.3 Additional information**

- All waste that is removed to Sasol Secunda must be weighted and proof of disposal filed.
- Ensure that all waste generated is stored on site for not more than 90 days.

#### **8.4.2.4 Environmental factors**

- Contamination of water, soil and human exposure.

#### **8.4.2.5 Safety and health factors**

- Personnel, animals, and plants.

#### **8.4.2.6 Quality factors**

- Management and controlling of waste is essential to human health and a clean environment.

### **8.5 Safety measures recommendations for SNP and the liquid fertilizer industry in general**

#### **8.5.1 Introduction**

A thorough investigation of the specific handling, storage, transport, and transference procedures of fertilizers and waste products on the SNP plant is needed. Comments and suggestions are made by using the knowledge of the researcher of the operations occurring on site, and by comparing the suggested safe practice measures with those employed by Sasol Nitro. The findings on the SNP site, in combination with the recommended safety measures discussed in section 8.2, could be used as guidelines for the liquid fertilizer industry in general.

#### **8.5.2 Comments**

Sasol Nitro appears to have comprehensive guidelines in place for the safe handling, storage, transport, and transference of fertilizers and waste materials, as would be expected from such a well renowned and successful company. Their guidelines are well laid out, easy to understand, and covers all areas of operations. There also exists a clear hierarchical system with specified members held responsible for ensuring the adherence to these guidelines.

### 8.5.3 Suggestions

The following suggestions are made with the aim of improving existing SNP safe practice measures. Some of the suggestions will possibly be redundant as they may already be in place.

- When dealing with solid raw materials, e.g. when materials are loaded into front-end loaders, it is recommended to have suitably designed enclosures for personnel, as dust masks are not sufficient.
- A system can be constructed to feed clay directly from storage to the gelling unit in order to further prevent dust pollution.
- The temperature and pH should constantly be monitored during the neutralization stage, and an alarm system should be installed to provide either a visual or audible warning, or to reduce the raw material feed rate automatically.
- It would also be desirable to have a system in place to constantly monitor the atmosphere in the vicinity of the neutralizers.
- Gas scrubbers should be installed over reaction vessels (the researcher is not aware of these being in place).
- Special care should be taken with the ammonia facility. The integrity of ammonia installations should be monitored frequently. Connections between vehicles and storage facilities should also be thoroughly inspected.
- More concentrated phosphoric acid could be used, as it is likely to have a lower fluorine content.
- Pipes, storage vessels, impellers seals, pumps, flanges, valves, and all other equipment used in dealing with fertilizers should be maintained on a continuous basis, in order to prevent the loss of liquid effluents.
- Vehicle noises in confined spaces can be severe (e.g. the front-end loader in a raw material warehouse), and it may be necessary to sound-insulate the cab to make it safe for the operator, as ear protection is not sufficient for continuous use.
- As evidenced from the contaminant concentrations found in soil- and groundwater samples, containment systems will definitely have to be repaired and/or upgraded (as discussed in section 8.2.2). It is recommended that a reputable environmental engineer be contracted to do a thorough investigation.
- Bunding the whole site could be an option. This would prevent contamination migrating further than the bounds of the site, and would involve the construction of a big lagoon in a convenient low lying area into which spillages flow through a system of gullies.

## 8.6 Remediation recommendations for the SNP site

See Appendix B for an introduction to remediation and an in-depth discussion on the recommended remediation procedure and various remediation methods.

Most contaminants (especially those originating from fertilizer mixing and loading operations, i.e. nitrate, phosphate, and ammonium) are situated within the first few meters of the soil/rock layer. Other contaminants (mostly the normally occurring macros) show a consistent peaking at a depth of ca. 6m, and a reduction in concentration with depth (nitrate also show a reduction in concentration with depth).

The contaminants present in the top layer of soil/rock causes severe damage to storage facilities and buildings. This is evident from the damage caused to the building on northern side of the site (see Figure 39). The damage is caused by  $\text{PO}_4$  displacing the Ca and Mg in the cement, making it brittle.  $\text{PO}_4$  also absorbs water which results in it to expanding and causing further damage.

It was not recommended to use a pump and treat method, as there is evidence of chromium contamination beyond the boundaries of the SNP site. A pump and treat method would only draw in chromium from outside, possibly worsening the contamination in the subsurface underlying the SNP site. The source of chromium was found to originate from the site on the southern border of the SNP plant where a tannery was operated in the past. Hence, due to the legacy of the tannery, SNP can not be held responsible for chromium found on the eastern side of its site.

It is recommended that an extensive study be done on the extent of the chromium contamination, as it may pose serious health risks. It would be necessary for the authorities to get involved seeing that the tannery have closed down a very long time ago, and other industries in the area would be not be willing to pay for the study and/or the remediation.

SNP was initially advised to excavate the top layer of soil/rock and implement a monitoring plan to track the migration and concentrations of mobile contaminants in the area. However, as mentioned in section 5.3.2.2, and indicated in Figure 43, the area in the north eastern corner of the site where there is a flourishing garden show significantly less contamination than the rest of the site. The reason for this, and suggesting a promising remediation option, is phytoremediation.

The cost quoted to excavate the entire SNP site area to a depth of 1.2m (no subtraction of void volumes and constructed areas were considered in the estimation) was R 9,584,640.00. The phytoremediation option would hence by far be the cheapest, and possibly most effective. It would also continue to remediate the area as long as the plants exist. Excavation would then be recommended

only for areas where it is not possible to plant plants, and the areas where contaminants have already caused significant damage to built structures, e.g. on the northern side of the site. The affected sections of these buildings would also have to be rebuilt, as it is not possible to remove the contamination from them, and hence the damage would continue to progress.

Plants known to grow deep roots are recommended, in order to reach deeper levels (especially into the aquifer to soak up contaminated groundwater). Where it is not possible to plant these plants and/or trees, due to concerns of damage from roots to built structures, areas needed for operations, etc., Kikoejoe grass could be a viable option, as its roots also penetrate relatively deep into the subsurface. Trees and plants that grow fruit that are edible should be avoided, as contaminants are stored in the tissue of the plants and could pose health risks to anyone eating the fruit.

A monitoring plan is still advised in order to track the decrease in contaminant concentrations and/or flag any worsening of the situation. Monitoring would be required every three months for the first two years in order to build up a database, and thereafter, once every six months. Monitoring the site would include taking groundwater samples at various depths from the boreholes, taking soils samples from various locations and depths, and analyzing these.

### **8.7 Other recommendations**

It is not deemed necessary to test for radionuclides on the SNP site, as SRK Consulting have consistently found concentrations below the recommended limits on the KFPF site, and the main source of radionuclide pollution have been removed. It would however be interesting to investigate.

It is recommended to inform Mighty Products Company of contaminants present in the groundwater they are using on their malt products, as it could pose serious potential health risks.

It is recommended that all industries operating in the Potch Industria area join a compulsory environmental impact assessment and monitoring program in order to determine their respective contributions to groundwater pollution in the area, and also in doing so to divide rehabilitation costs according to contaminant quantity and quality contribution.

A thorough investigation into the contribution of groundwater contamination to surface water bodies is also recommended.

## Chapter 9: References

- Almasri, M.N. (2006). Nitrate Contamination of Groundwater: A Conceptual Management Framework. *Water and Environmental Studies Institute, An-Najah National University, Nablus, Palestine.*
- Ando, J. Chapter 18 and 29 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.
- Aucamp, P.J. (2000). Trace Element Pollution of Soils by Abandoned Gold Mine Tailings Near Potchefstroom, South Africa. *Magister Scientiae, University of Pretoria*. Supervisor, Prof. A. van Schalkwyk.
- Boreal Lazer Inc. (1998). *Citing Internet Resources*. <http://www.boreal-lazer.com/docs/HF%20monitoring%20in%20Phosphates%20manufacture%20-%20Ball%20et%20al.pdf> (accessed 27<sup>th</sup> August 2010).
- Bunus, F.T. Chapter 20 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.
- Ciobanu, T. Chapter 14 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.
- Conference paper. Various authors. (2005). Naturally Occurring Radioactive Materials (NORM IV). In: International Conference, Szczyrk, Poland, May 2004, IEAE-TECDOC-1472. IAEA, Vienna, Austria.
- Cristescu, E. Chapter 7 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.
- Department of Environmental Affairs and Tourism (DEA). (2003). Compilation of South African National Chemicals Profile, Draft Report, *Chapter 2: Chemical Production, Import, Export, and Use*. Project Number: J22044A.
- European Fertilizer Manufacturers Association (EFMA). (2000). *Citing Internet Resources*. <http://www.efma.org/documents/file/bat/BAT%20Production%20of%20Phosphoric%20Acid.pdf> (accessed 27<sup>th</sup> August 2010).

Fertilizer Society of South Africa (FSSA). (2008a). *Citing Internet Resources*. <http://www.fssa.org.za/pebble.asp?relid=64> (accessed 16<sup>th</sup> September 2010).

Fertilizer Society of South Africa (FSSA). (2008b). *Citing Internet Resources*. <http://www.fssa.org.za/medialib/Downloads/Home/Articles/THE%20SA%20FERTILISER%20INDUSTRY%20no%202%20Feb06%20AFA%20Conf%20fin.pdf> (accessed 16<sup>th</sup> September 2010).

Fertilizers Europe (formerly EFMA). (2005). *Citing Internet Resources*. <http://www.efma.org/documents/file/publications/Forecast%20of%20food,%20Farming%20and%20fertilizer%20Use%20in%20the%20European%20Union%202005-2015%20.pdf> (accessed 3<sup>rd</sup> June 2010).

Fertilizers Europe. (2010). *Citing Internet Resources*. <http://www.fertilizerseurope.com/subcontent.asp?id=2&sid=41&ssid=48> (accessed 4<sup>th</sup> June 2010).

Food and Agriculture Organization of the United Nations (FAO). (2008). *Citing Internet Resources*. <ftp://ftp.fao.org/agl/agll/docs/cwfto11.pdf> (accessed 3<sup>rd</sup> June 2010).

Foskor. (2010). *Citing Internet Resources*. <http://www.foskor.co.za/library/FOSKOR%20AR%20EDITORIAL%202010%208.pdf> (accessed 27<sup>th</sup> September 2010).

Geography Department, Potchefstroom University, and North West Department of Agriculture, Conservation, and Environment, Mafikeng. (Date unknown). *Citing Internet Resources*. <http://www.nwpg.gov.za/soer/fullreport/bio-physical.html> (accessed 12<sup>th</sup> October 2010).

Górecki, H.J. Chapter 22 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Minerals and Chemicals Philipp Corporation. (Date Unknown). *Citing Internet Resources*. <http://www.clays.org/journal/archive/volume%2010/10-1-284.pdf> (accessed 30<sup>th</sup> September 2010).

International Atomic Energy Agency (IAEA). (2005). *Citing Internet Resources*. [http://www-pub.iaea.org/MTCD/publications/PDF/te\\_1472\\_web.pdf](http://www-pub.iaea.org/MTCD/publications/PDF/te_1472_web.pdf) (accessed 21<sup>st</sup> January 2010).

Heffer, P. and Prud'homme, M. (IFA). (2008a). Medium Term Outlook for Global Fertilizer Demand, Supply and Trade 2008 - 2012. From: *76<sup>th</sup> A/08/85 Medium-Term Outlook for World Agriculture and Fertilizer Demand 2007/8 - 2012/13 and A/08/73b Global Fertilizers and Raw Materials Supply and Supply/Demand Balances: 2008 - 2012 IFA Annual Conference*, Vienna, May 2008, summary report of two comprehensive reports.

Heffer, P. and Prud'homme, M. (IFA). (2008b). World Agriculture and Fertilizer Demand, Global Fertilizer Supply and Trade 2008 - 2009. From: *34<sup>th</sup> A/08/156 Short Term Prospects for World Agriculture and Fertilizer Demand 2007/8 - 2009/10 and A/08/146b Global Fertilizer Supply and Trade 2008 - 2009 IFA Enlarged Council Meeting*, Ho Chi Minh City, Vietnam, November 2008, summary report of two comprehensive reports.

Heffer, P. and Prud'homme, M. (IFA) (2009). Medium Term Outlook for Global Fertilizer Demand, Supply and Trade 2009 - 2013. From: *77<sup>th</sup> A/09/86 Medium-Term Outlook for World Agriculture and Fertilizer Demand 2008/9 - 2013/14 and A/08/73b Global Fertilizers and Raw Materials Supply and Supply/Demand Balances: 2009 - 2013 IFA Annual Conference*, Shanghai, May 2009, summary report of two comprehensive reports.

Hidetoshi, U. Chapter 10 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Joekar-Niasar, V., Ataie-Ashtiani, B. (2009). Assessment of Nitrate Contamination in Unsaturated Zone of Urban Areas: The Case Study of Tehran, Iran. *Environ Geol* 57:1785 - 1798, DOI 10.1007/s00254-008-1464-0.

Klein, M.O., Reid, K.W., and Goldsmith, E.L. Chapter 24 and 27 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Man, M. Chapter 21 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Mann, Jr., H.C. (1994). Chapter 37 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

NaturalGas. (2008). *Citing Internet Resources*. <http://www.naturalgas.org/overview/resources.asp> (accessed 4<sup>th</sup> June 2010). (From Oil and Gas Journal, December 2008).

Negulescu, L. Chapter 11 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Nitzschmann, R.E. and Reuvers, J.G.A. Chapter 9 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Palgrave, D.A. Chapter 36 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Parish, W.R. Chapter 17 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Reid, K.W., and Klein, M.O. Chapter 25 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Romijn, E. (2002). *Groundwater Quality and Contamination*. In: Zaporozec, A. (2002). *Groundwater Contamination Inventory: A Methodological Guide. Prepared for the International Hydrological Programme with Project 3.1 (IHP-V)*. IHP-VI, Series on Groundwater No. 2. UNESCO.

Rural Industries Research and Development Corporation (RIRDC) (Australia). (1999). *Citing Internet Resources*. <https://rirdc.infoservices.com.au/downloads/99-010> (accessed 27<sup>th</sup> September 2010).

SciFun. (2008). *Citing Internet Resources*. [http://scifun.chem.wisc.edu/chemweek/pdf/phosphoric\\_acid.pdf](http://scifun.chem.wisc.edu/chemweek/pdf/phosphoric_acid.pdf) (accessed 27<sup>th</sup> August 2010).

Sierra, M. Chapter 12 and 13 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.



Sittig, M. (1979). *Fertilizer Industry: Processes, Pollution Control and Energy Conservation*, 1<sup>st</sup> ed. Noyes Data Corporation.

Skinner, S.J.W., Duthie, D. (2007). Review of Groundwater Monitoring data for the Kynoch Potchefstroom Fertilizer Production Facility. *SRK Consulting*.

Stanton, J.S, Steele, G.V., Vogel, J.R. (2004). Occurrence of Agricultural Chemicals in Shallow Ground Water and the Unsaturated Zone, Northeast Nebraska Glacial Till, 2002 - 04: *U.S. Geological Survey Scientific Investigations Report 2007 - 5228*, 51 p.

Texas A&M University. (2008). *Citing Internet Resources*. <http://oceanworld.tamu.edu/resources/environment-book/groundwaterremediation.html> (accessed 21<sup>st</sup> June 2010).

ThermPhos International BV. (2005). *Citing Internet Resources*. [http://www.thermphos.com/Documentation/~media/Pdf/public\\_pds/specialty\\_phosphates/TSP%20Pyro%20Fine%20FCC%20G%20VLI%20en.ashx](http://www.thermphos.com/Documentation/~media/Pdf/public_pds/specialty_phosphates/TSP%20Pyro%20Fine%20FCC%20G%20VLI%20en.ashx) (accessed 15<sup>th</sup> September 2010).

Tomlinson, S. (1994). Chapter 38: *Remediation Measures for Existing Plant Facilities and Decommissioned Facilities*. In: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

Tredoux, G., Engelbrecht, P., and Israel, S. (2009). Nitrate in groundwater. Why is it a hazard and how to control it. *Report to the Water Research Commission by CSIR, Natural Resources and the Environment, Stellenbosch*. WRC Report No. TT 410/09.

Turtureanu, M. Chapter 4 in: Hodge, C. A. and Popovici, N. N. (1994). *Pollution Control in Fertilizer Production, Environmental Science and Pollution control Series*, 1<sup>st</sup> ed. CRC Press.

U.S. Census Bureau. (2010). *Citing Internet Resources*. <http://www.census.gov/ipc/www/idb/worldpop.php> (accessed 2<sup>nd</sup> June 2010).

U.S. Geological Survey (USGS(a)). *Citing Internet Resources*. [http://walrus.wr.usgs.gov/infobank/programs/html/factsheets/pdfs/2004\\_3120.pdf](http://walrus.wr.usgs.gov/infobank/programs/html/factsheets/pdfs/2004_3120.pdf) (accessed 24<sup>th</sup> September 2010).

U.S. Geological Survey (USGS(b)). *Citing Internet Resources*. [http://toxics.usgs.gov/highlights/nh4\\_gw/](http://toxics.usgs.gov/highlights/nh4_gw/) (accessed 24<sup>th</sup> September 2010).

U.S. Geological Survey (USGS(c)). *Citing Internet Resources*. [http://toxics.usgs.gov/highlights/phosphorous\\_migration.html](http://toxics.usgs.gov/highlights/phosphorous_migration.html) (accessed 24<sup>th</sup> September 2010).

U.S. Environmental Protection Agency (EPA). *Citing Internet Resources*. <http://water.epa.gov/drink/contaminants/> (accessed 24<sup>th</sup> September 2010).

U.S. Environmental Protection Agency (EPA). (2009). *Citing Internet Resources*. <http://www.epa.gov/region4/waste/npl/nplsc/imcsc.htm> (accessed 12<sup>th</sup> November 2010).

U.S. Environmental Protection Agency (EPA). (2010a). *Citing Internet Resources*. <http://www.epa.gov/reg3hwmd/npl/MDD003061447.html> (Date accessed: 11<sup>th</sup> November 2010).

U.S. Environmental Protection Agency (EPA). (2010b). *Citing Internet Resources*. <http://yosemite.epa.gov/opa/admpress.nsf/0/9F5FF20065598D5985257777005502F8> (accessed 12<sup>th</sup> November 2010).

U.S. Environmental Protection Agency (EPA). (2010c). *Citing Internet Resources*. <http://www.epa.gov/compliance/resources/cases/civil/rcra/cfindustries.html#overview> (accessed 12<sup>th</sup> November 2010).

United Nations Department of Economic and Social Affairs. (2010). *Citing Internet Resources*. [http://esa.un.org/unpd/wpp2008/wall-chart\\_1.htm](http://esa.un.org/unpd/wpp2008/wall-chart_1.htm) (accessed 2<sup>nd</sup> June 2010).

World Health Organization (WHO). (2008). *Guidelines for Drinking Water Quality, Third Edition. Volume 1, Recommendations (Article)*. WHO, Geneva.

World Health Organization (WHO(a)). *Citing Internet Resources*. [http://www.who.int/water\\_sanitation\\_health/dwq/chloride.pdf](http://www.who.int/water_sanitation_health/dwq/chloride.pdf) (accessed 24<sup>th</sup> September 2010).

World Health Organization (WHO(b)). *Citing Internet Resources*. [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/chromium.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/chromium.pdf) (accessed 24<sup>th</sup> September 2010).

World Health Organization (WHO(c)). *Citing Internet Resources*. [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/sulphate.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/sulphate.pdf) (accessed 24<sup>th</sup> September 2010).

World Health Organization (WHO(d)). *Citing Internet Resources*. [http://whqlibdoc.who.int/hq/2009/WHO\\_HSE\\_WSH\\_09.01\\_7\\_eng.pdf](http://whqlibdoc.who.int/hq/2009/WHO_HSE_WSH_09.01_7_eng.pdf) (accessed 24<sup>th</sup> September 2010).

World Health Organization (WHO(e)). *Citing Internet Resources*. [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/fluoride.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/fluoride.pdf) (accessed 24<sup>th</sup> September 2010).

World Health Organization (WHO(f)). *Citing Internet Resources*. [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/cadmium.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/cadmium.pdf) (accessed 24<sup>th</sup> September 2010).

World Health Organization (WHO(g)). *Citing Internet Resources*. [http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/uranium290605.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/uranium290605.pdf) (accessed 24<sup>th</sup> September 2010).

Zaporozec, A. (2002). Groundwater Contamination Inventory: A Methodological Guide. *Prepared for the International Hydrological Programme with Project 3.1 (IHP-V), IHP-VI, Series on Groundwater No. 2, UNESCO.*

## Appendix A: Fertilizer manufacturing

### A.1. Ammonia production

#### A.1.1 Introduction

The principle component in the production of nitrogen fertilizers is ammonia. Fritz Haber and Carl Bosch developed the process by which ammonia is synthesized from elements. This was done on an industrial scale for the first time in Germany in 1913. The nitrogen needed for the process is taken from the air. The hydrogen is obtained from various sources, and this has led to the development of several processes for syngas production. Ammonia plants consume a great deal of energy (Turtureanu, 1994).

#### A.1.2 Raw materials and methods used in ammonia production

The availability and costs of raw materials are key factors taken into account when constructing a new ammonia production facility. Table 26 indicates the principle raw materials in ammonia production.

**Table 26: Raw materials used in ammonia production and their description (Turtureanu, 1994).**

<i>Raw material</i>	<i>Description</i>
<i>Natural gas</i>	<ul style="list-style-type: none"> <li>• Minimum investment and production costs.</li> <li>• Plant is easy to operate.</li> <li>• Minimum environmental problems.</li> <li>• Steam reforming of natural gas is the most widespread process for ammonia production.</li> </ul>
<i>Naphtha</i>	<ul style="list-style-type: none"> <li>• Process used similar to that starting from natural gas.</li> <li>• High cost and use in refineries have limited its use.</li> <li>• Requires feed storage and treatment, which pushes costs up.</li> </ul>
<i>Heavy residual oil</i>	<ul style="list-style-type: none"> <li>• Requires the partial oxidation process for syngas production.</li> <li>• Such a plant has a higher energy consumption than one using steam reforming, due to the required air separating plant and supplementary utility consumption for the gas purification.</li> </ul>
<i>Coke gas</i>	<ul style="list-style-type: none"> <li>• Coke gas contains valuable quantities of H<sub>2</sub>, CH<sub>4</sub>, and CO.</li> <li>• Use not widespread due to the high costs of gas purification and compression.</li> </ul>
<i>Coal</i>	<ul style="list-style-type: none"> <li>• Only used when there is no other source of raw materials.</li> <li>• New facilities are rare, due to higher investment and energy requirements, pollution, and cheap natural gas disposal.</li> </ul>

There are other sources of hydrogen available, but due to their high cost and limited availability they are not considered for industrial-scale production. Some of these include electrolytic hydrogen, a viable source only where very low energy costs are available, and, refinery gas containing light hydrocarbons, a viable source only when it is in excess of the needs of the refinery.

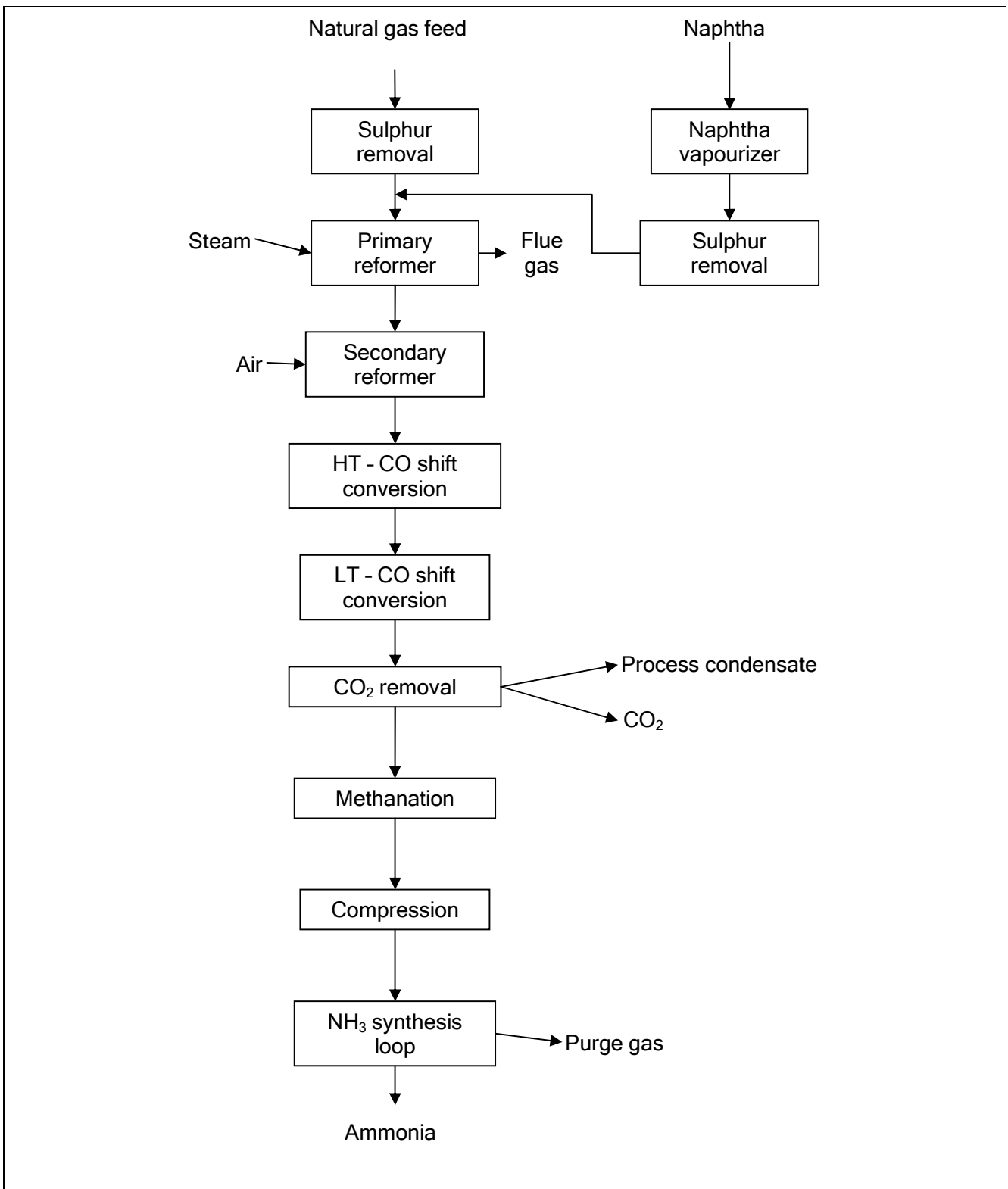


Figure 66: Flow diagram of steam reforming of natural gas and naphtha (HT: High Temperature, LT: Low Temperature (Turtureanu, 1994)).

Flow diagrams of ammonia production as a function of the raw materials used are illustrated in Figure 66 - Figure 68. Three raw materials are selected as representative of the fertilizer industry, viz. natural gas, heavy residual oil, and coal. The main effluents are also indicated after each process step.

Figure 66 is a flow diagram starting with natural gas or naphtha.

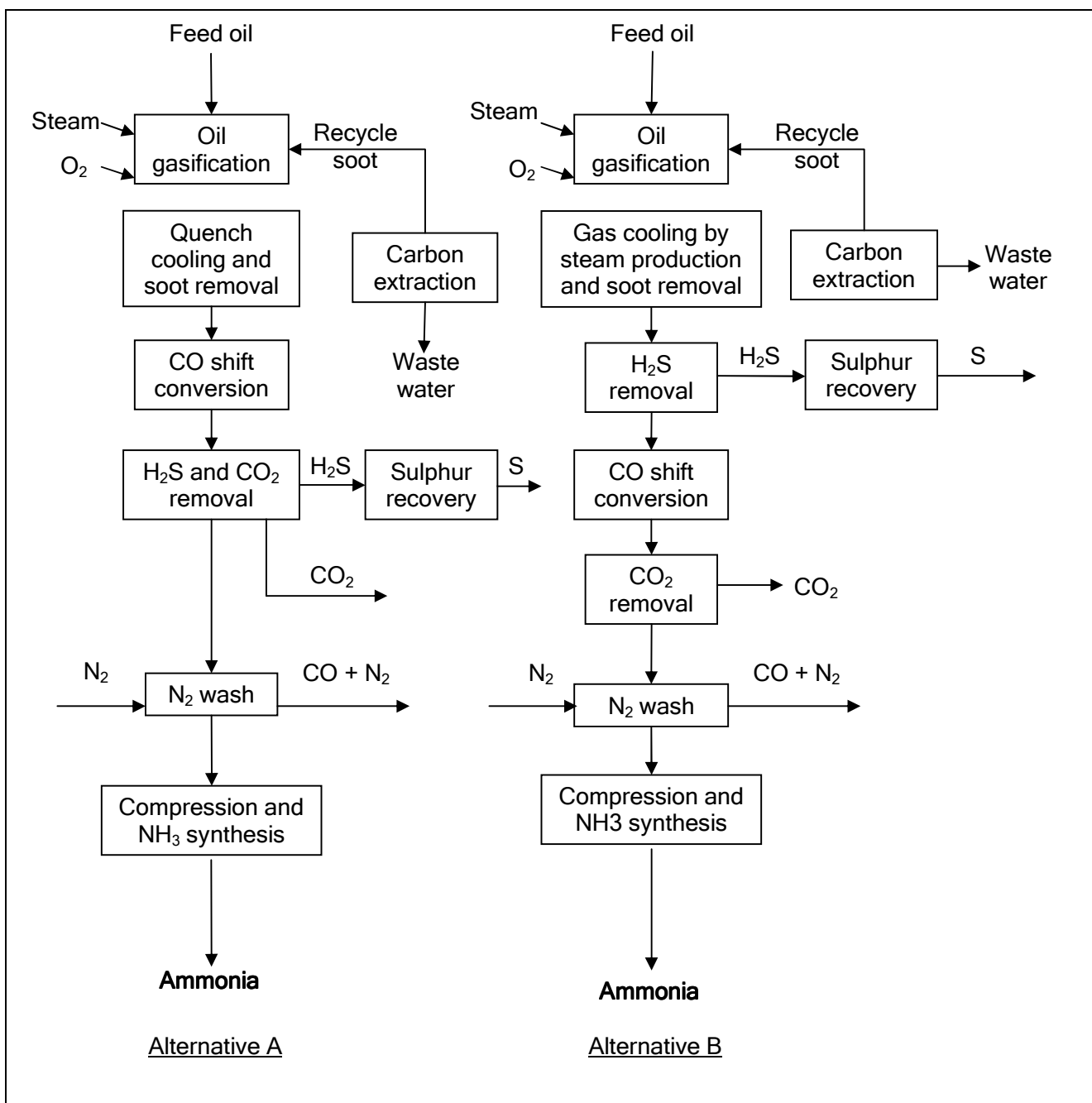


Figure 67: Flow diagram of heavy oil gasification (Turtureanu, 1994).

Figure 67 illustrates a flow diagram of two available options for ammonia synthesis gas production from heavy residual oil as a raw material, developed independently by Texaco Development Corporation and Shell Group. The utilization of heavy oil is based on a non-catalytic partial oxidation process, but the following raw materials can also be used; natural gas, naphtha, fuel oil, vacuum residues, and asphalt. This process is more complex than that of natural gas steam reforming. In this case CO conversion takes place directly after gasification, and a sulphur resistant CO shift catalyst must be used.

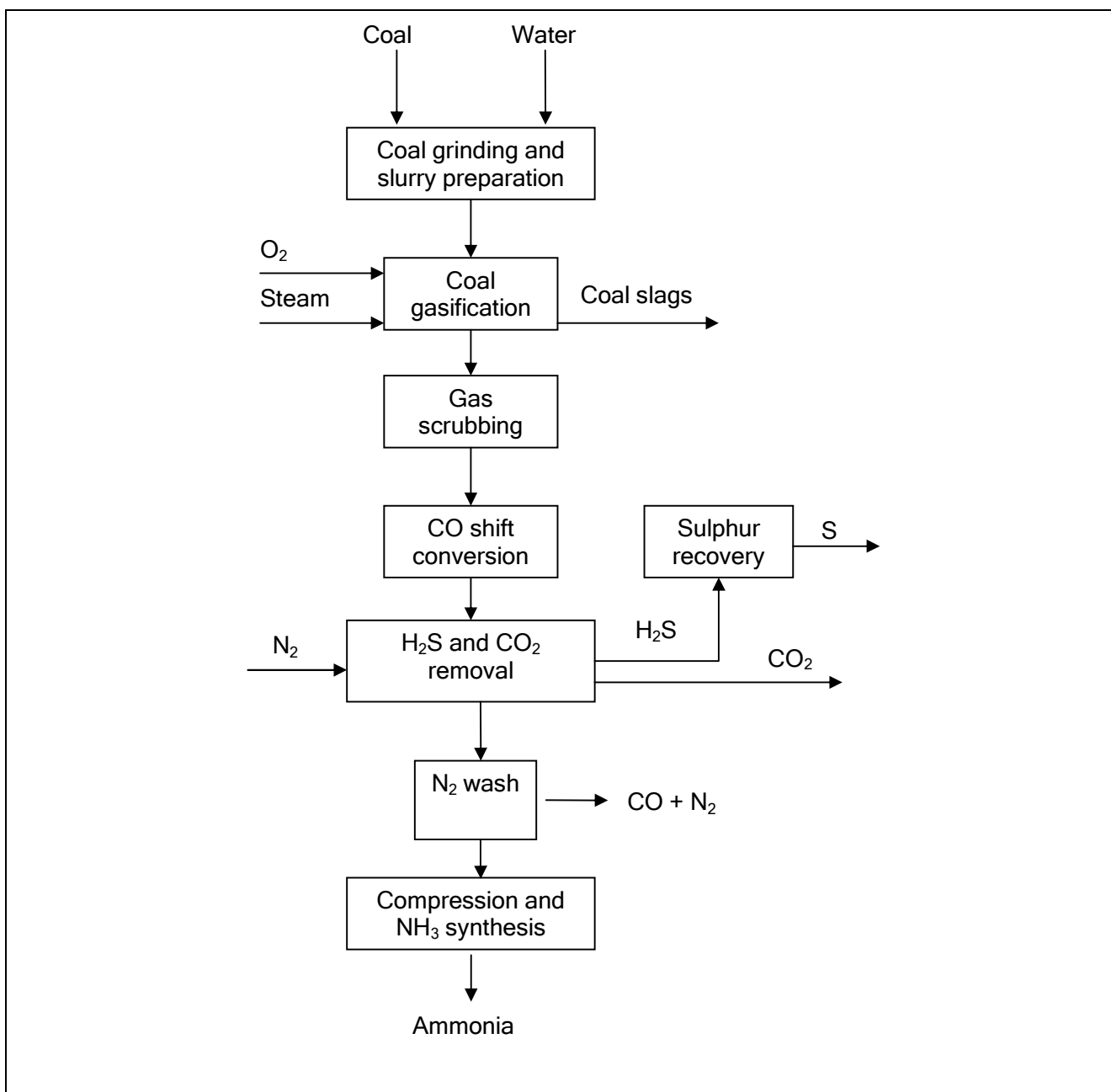


Figure 68: Flow diagram of the pulverized coal gasification process (Turtureanu, 1994).

Figure 68 is a flow diagram for coal-based ammonia production using Texaco's partial oxidation of coal. Coal-based ammonia production was widespread in the period leading up to the second world war, but due to the availability of inexpensive natural gas and the development of the steam reforming process, the construction of new coal-based plants have virtually stopped. The process of ammonia production through the gasification of coal can be categorized into three groups according to the method of gasification used, viz. Fixed-bed gasification (Lurgi process), Fluidized-bed gasification (Winkler process), and Pulverized coal gasification (Koppers Totzek process, Texaco process). The coal-based ammonia production process is very similar to partial oxidation of the heavy residual oil gasification process.

As illustrated in these flow diagrams, the use of natural gas as a feedstock is a simpler process. It also has the least negative impact on the environment with little treatment problems of effluents (Turtureanu, 1994).

The Haber-Bosch process to manufacture ammonia was phased out in South Africa in 2000. Sasol dominates the manufacturing of ammonia in South Africa. This is done at their Secunda and Sasolburg plants as a co-product of coal gasification (the Fisher-Tropsch process), and from the Slurry Phase Distillate process. South Africa is the biggest producer of liquid fuels using the Fisher-Tropsch process in the world (DEA, 2003).

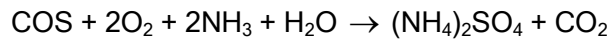
## **A.1.2 Discussion of process steps and their effluents**

### **A.1.2.1 Natural gas desulphurization**

The natural gas in the steam reforming process contains sulphur compounds. The sulphur content in the natural gas used as raw material should be below 0.5ppm, due to it being poisonous for nickel- and copper-based-, reforming-, and low-temperature shift catalysts. SO<sub>2</sub> and flue gases are also released into the atmosphere as a result of sulphur compounds in natural gas being used as fuel release by combustion. Hydrogen sulphide and mercaptans are the main compounds in natural gas. If the natural gas contains noticeable amounts of associated gas, sulphur compounds like disulphides, thiophenes, or carbonyl sulphide may also be present. Various methods are employed to treat these effluents.

Methods of desulphurization depend on the content and nature of sulphur compounds in natural gas. One of these methods is passing the natural gas over metal-impregnated activated carbon. Activated carbon is effective in retaining hydrogen sulphide and light mercaptans if the natural gas content in heavy hydrocarbons is low. Small amounts of ammonia are injected into natural gas when it contains carbonyl sulphide, due to activated carbon not being able to retain it. This is the resulting reaction;





The sulphur compound content of natural gas is usually low, hence in ammonia plants in general, the desulphurization of natural gas feedstock takes place and not that of fuel gas. The entire quantity of natural gas (feedstock and fuel) needs to be desulphurized when the concentration of sulphur compounds is high. The desulphurization of fuel gas has to be considered in connection with the SO<sub>2</sub> content and local emission standards (Turtureanu, 1994).

There are currently international regulations enforcing the desulphurization of flue gas. The World Bank only approved the loan for the build of the new Medupi Power Station in Limpopo when they included plans to desulphurize their flue gas. It is worth mentioning that the desulphurization of flue gas uses vast amounts of water.

#### **A.1.2.2 Steam reforming**

There are two steps in the process of steam reforming of natural gas;

1. *Primary reforming*, where the natural gas feed is converted to H<sub>2</sub> and CO by reaction with steam, and,
2. *Secondary reforming*, where the reaction continues and air is introduced to ensure the required amount of nitrogen for ammonia synthesis.

A reaction temperature (800°C - 900°C) is ensured by burning an amount of natural gas outside the reformer tubes. The flue gases primarily contain carbon dioxide, water vapours, nitrogen, oxygen and small quantities of NO<sub>x</sub> and SO<sub>2</sub>. The temperature of flue gases is lowered to save fuel gas but is kept high enough to prevent water vapour condensation. This is done in one of three ways; either by preheating the combustion air and boiler feed water, by producing low-pressure steam, or by saturation of feed gas with process condensate. "Nitrogen oxides are formed in combustion processes by thermal fixation of atmospheric nitrogen and oxygen from combustion air, resulting in thermal NO<sub>x</sub>, or by conversion of chemically bound nitrogen from the fuel, in fuel NO<sub>x</sub>". Almost the entire amount of NO<sub>x</sub> in reforming furnaces in the ammonia industry that use natural gas as fuel, is thermal NO<sub>x</sub>. CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>2</sub> should be taken into account in environmental considerations. Most countries have regulations enforcing the compulsory treatment of these effluents (Turtureanu, 1994).

#### **A.1.2.3 CO shift conversion and CO<sub>2</sub> removal: Process condensate treatment**

Carbon monoxide conversion is carried out in two steps, viz. high- and low temperature conversion, and there are no effluents from these processes. After leaving the CO shift conversion unit, the gas is

cooled down and CO<sub>2</sub> removed. A potassium carbonate solution with various additives to promote absorption is used for CO<sub>2</sub> removal in most ammonia plants.

The main impurities contained in the process condensate as a result of gas cooling and excess water vapour condensation are, ammonia, methanol, carbon dioxide, and metals from catalysts. In older plants, this process condensate is collected and sent to a stripping column. Here, low pressure steam is fed to the bottom. The stripped condensate is cooled and discharged as effluent outside the ammonia plant battery limit. A mixture of steam and gases desorbed from the process condensate is released into the atmosphere from the top of the stripper. This process is not environmentally friendly and high pressure stripping systems are a significant improvement in treating process condensate.

The process condensate from ammonia plants is usually mixed with wastewater from other fertilizer plants, e.g. ammonia nitrate and urea. The wastewater is then treated for the recovery of pollutants as useful substances. The use of nitric acid as a regenerant for ion-exchange resin makes it possible to obtain 20 to 28% ammonium nitrate solution. Biological treatment can also be used, where ammonia is first removed by oxidizing it to nitrate, and then to nitrogen gas by denitrification.

Syngas, after CO-LT shift conversion has a CO<sub>2</sub> content of ca. 18mol%, depending on the natural gas composition. Trademarks for the main CO<sub>2</sub> removal processes include Activated MDEA, Benfield, Catacarb, Carsol, Giammarco-Ventrococoke, Rectisol, Selexol, etc. Most of these processes are based on CO<sub>2</sub> absorption under pressure in various absorbents, followed by desorption through a pressure decrease and temperature increase. The CO<sub>2</sub> is cooled after desorption and used in the manufacturing of urea and dry ice, or for other purposes. Special care should be taken in the Giammarco-Ventrococoke process, where K<sub>2</sub>CO<sub>3</sub> solution activated with As<sub>2</sub>O<sub>3</sub> is used as an absorbent, which could pose serious potential health and environmental risks.

In most cases, CO<sub>2</sub> is only partially utilized in urea and dry ice fabrication. This means that a significant amount is continuously discharged into the atmosphere, which contributes to the worsening of the greenhouse effect and acid rain (Turtureanu, 1994).

#### **A.1.2.4 Methanation, compression, and NH<sub>3</sub> synthesis: Purge gas treatment**

After leaving the CO<sub>2</sub> absorption unit, the gas goes on to the methanation section. Here it is compressed and fed to the ammonia synthesis loop, which includes the refrigeration process. A centrifugal compressor driven by a steam turbine is normally used to compress the syngas. Pressure oil is used for shaft sealing. The syngas dissolves in oil at high inner pressure and is released when the oil pressure decreases. The gases released contain mainly H<sub>2</sub> and N<sub>2</sub>, and are normally released

into the atmosphere. They could however be used as fuel for the primary reformer. The main effluent resulting from the synthesis loop is the purge gas.

In order to maintain a constant level of inert gas concentration in the synthesis loop, a quantity of recycled gas is discharged from the system continuously. The concentration and composition of the purge gas vary, depending on the operating characteristics of the ammonia synthesis loop. The ranges of the composition of purge gas are as follows: H<sub>2</sub>, 55 to 65%; N<sub>2</sub>, 18 to 23%; Ar, 3 to 5%; CH<sub>4</sub>, 8 to 18%; NH<sub>3</sub>, 1 to 4%. Other rare gases in the purge gas are; krypton, xenon, neon, and helium.

The purge gas is used as a supplementary fuel for the primary reformer in older ammonia plants. Newer plants retain the purge gas components, resulting in improved natural gas feedstock utilization. The separation processes for purge gas are also varied. These processes primarily include partial condensation at low temperature, cryogenic distillation, adsorption, and permeation, or a combination of all of them. An example where these processes are combined is where a purge gas passage across a separation membrane yields a high purity hydrogen flow. The membrane non-permeated gas is rich in N<sub>2</sub>, CH<sub>4</sub>, and Ar, and can be separated further by cryogenic distillation. This leads to the reduction of energy consumption and plant volume, due to the decrease in processed gas quantity (Turtureanu, 1994).

## A.2 Radioactive components

Uranium, thorium and potassium are the only known radioactive elements found in nature. Their half-lives have permitted them to survive through the geologic ages. Uranium is the main component of the occurrence of radioactivity in natural phosphates, and by far the most radioactive. The uranium content in natural phosphates of sedimentary origin ranges between 0.005 - 0.02% U and is attended primarily by its decaying products. Thorium is virtually absent in sedimentary phosphates and prevalent over uranium in igneous apatites. Studies have suggested that uranium substitutes for calcium in the apatite structure. Table 27 indicates examples of uranium and P<sub>2</sub>O<sub>5</sub> content found in phosphates in different regions in the world.

**Table 27: Examples of Uranium and P<sub>2</sub>O<sub>5</sub> content found in phosphates of different regions (%) (Bunus, 1994).**

<i>Region</i>	<i>Uranium</i>	<i>P<sub>2</sub>O<sub>5</sub></i>
<i>Florida central Bone Valley formation</i>	0.014	30 - 36
<i>Phosforia formation (Rocky Mountains)</i>	0.009	30
<i>Moroccan phosphate deposits</i>	0.014	34%
<i>Israeli phosphates (Zefa deposits)</i>	0.012 - 0.018	20 - 30
<i>Jordanian (Ruseifa, Al Hasa, and Shadya deposits)</i>	0.0014 - 0.0156	5 - 34
<i>Central African phosphates</i>	0.166 - 0.56	8.75 - 33.6
<i>Russian volcanic deposits (Kola Peninsula)</i>	0.001 - 0.002	-

Uranium as an element has two isotopes ( $^{234}\text{U}$  ignored);  $^{238}\text{U}$  and  $^{235}\text{U}$  with 99.28% and 0.72% abundance respectively. Due to the half-lives involved, uranium isotopes emit  $\alpha$  and  $\gamma$  rays.

The  $^{238}\text{U}$  is transformed in successive decays to radium ( $^{226}\text{Ra}$ ), and continues until stable  $^{206}\text{Pb}$  is formed.  $^{235}\text{U}$  undergoes a similar series of decay steps. The main contaminant of phosphate fertilizers is  $^{226}\text{Ra}$ . A ton of phosphate with 0.02% U has 70pCi/g Ra (0.07mg Ra).  $^{226}\text{Ra}$  is carried in gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) due to the chemical rebalance of Ca and Ra. The radioactivity of gypsum from sedimentary rocks is 25 - 45pCi/g. Gypsum stacks are therefore a source of radioactive pollution, due to dust spread by the wind and  $^{222}\text{Rn}$  gas that continuously evolve.

$^{226}\text{Ra}$  decays by energetic  $\alpha$  particles on excited levels of  $^{222}\text{Rn}$ . The process is attended by strong  $\gamma$  emission. When  $^{226}\text{Ra}$  is inhaled, it decays at a high rate to a solid  $\alpha$  and  $\gamma$  emitter that is retained in the lung tissue.  $\alpha$  particles are known to release all the energy in the tissue (3 - 5MeV).  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  are therefore the most hazardous nuclides.

“Uranium in phosphate rock, predominantly in the tetravalent state, is best solubilized concomitantly with an oxidation process. However, in a phosphoric acid medium, uranium behavior depends on the redox potential of the couple Fe(II)Fe(III). When  $\text{H}_2\text{PO}_4$  is absent, Fe(III) oxidizes U(IV) because standard redox potentials are Fe(II)Fe(III) 0.77V and U(IV)U(VI) 0.33V. In the presence of  $\text{H}_2\text{PO}_4$ , oxidation by Fe(III) is slowed down, and at concentrations higher than 2M  $\text{H}_3\text{PO}_4$ , reverse reaction is possible. This behavior is due to strong complexation of Fe(III) by  $\text{H}_2\text{PO}_4$ .” (Bunus, 1994).

**Table 28: Uranium content in technical phosphoric acid (Bunus, 1994).**

<i>Sample</i>	<i>Phosphate origin</i>	<i>Uranium (g/L)</i>
1	Jordan	0.07012
2	Morocco	0.12016
3	Israel	0.07014
4	Tunis	0.02006
5	Florida	0.08017
6	Togo	0.10012
7	Egypt	0.08011
8	Kola	0.01002

Phosphoric acid is predominantly produced in the chemical reaction of rock dissolution by the dihydrate process. The acid obtained in this way is denoted as WPA. More than 90% of uranium from phosphate rock is dissolved in WPA with ca. 95% being in the hexavalant state. Table 28 indicates results of chemical analysis of clarified (aged) WPA of 26 - 28%  $\text{P}_2\text{O}_5$  obtained from various phosphates determined for several years. WPA is considered to contain a small amount of

radioactivity. WPA has to be concentrated (to 47 - 54%) for use in fertilizer manufacturing, which results in uranium also following an increasing concentration trend.

Most fertilizers resulting from sulphuric attack of phosphate rock are obtained from phosphoric acid, with the exception of single superphosphate. Uranium is the only radioactive component of WPA. TSP fertilizer for example, prepared from concentrated WPA, will contain 0.01 - 0.018% U. There is however extra radioactivity present due to uranium and radium in the rock used in the reaction. In general, TSP has a radioactivity of 15 - 40pCi/g <sup>226</sup>Ra and 30 - 80pCi/g <sup>238</sup>U, and DAP fertilizer a radioactivity of 0.5 - 2pCi/g <sup>226</sup>Ra and 25 - 30pCi/g <sup>238</sup>U. Table 29 indicates the radioactivity of natural phosphates and gypsum from different areas in the world.

The recovery of uranium from fertilizer processes for nuclear use is not economically viable at present, but the practice may develop in future (Bunus, 1994)

**Table 29: Radioactivity of natural phosphates and gypsum (Bunus, 1994).**

<i>Phosphate origin</i>	<i><sup>226</sup>Ra(pCi/g)</i>
<i>Morocco</i>	43
<i>Jordan</i>	32
<i>Florida (central)</i>	46
<i>Israel</i>	25
<i>Kola (volcanic)</i>	5
<i>Morocco gypsum</i>	30
<i>Jordan gypsum</i>	20
<i>Kola gypsum</i>	3
<i>Concrete, bricks</i>	0.7617

Table 30 indicates the activity concentrations of the phosphate rock and tailings found in the Phalaborwa Igneous Complex (IAEA, 2005).

**Table 30: The activity concentrations of phosphate rock mined at Phalaborwa, South Africa (IAEA, 2005).**

<i>Radionuclide</i>	<i>Activity concentration (Bq/g)</i>	
	<i>Phosphate rock</i>	<i>Tailings</i>
<sup>238</sup> U	0.14	0.26
<sup>226</sup> Ra	0.14	0.27
<sup>210</sup> Pb	0.12	-
<sup>232</sup> Th	0.47	0.31
<sup>228</sup> Ra	0.55	0.33
<sup>228</sup> Th	0.55	0.35

## Appendix B: Remediation

### B.1 Introduction

Due to the significant increase in awareness of the dangers related to fertilizer production, and use and pressure from environmental groups in recent years, there has been a significant development and implementation of legislation designed for the fertilizer industry, especially in developed countries. In developing countries, awareness has been low and the industry has been largely allowed to operate without regulation. It has been and will continue to be a challenge to universalize regulations for safe practice. Although fertilizer consumption in developed countries has seen a decline due to the abovementioned reasons, the decline was also a result of the increasing scientific and efficient methods of application which prevented a decrease in soil productivity.

In the manufacturing and use of fertilizers, many chemicals are generated, which, when released into the environment, can have detrimental affects over large areas. Fauna, flora, air, and water can be adversely affected. When considering pollution, one has to consider the immediate impact, long term effects, and the indirect influence of pollutants.

Different pollutants affect the environment in different ways and to different extents.  $\text{NO}_x$  and  $\text{SO}_x$  released into the atmosphere by fertilizer plants are added to those released into the atmosphere by industries like; electric power, steel, and non-ferrous metallurgy industries, as well as emissions from internal combustion vehicles ( $\text{NO}_x$ ). Large quantities of these emissions are the cause of “acid rain” and are severely detrimental to the environment. Fluorine released into the atmosphere by plants producing phosphates adds to other volatile fluorine compounds used at present, and is responsible for the reduction of the ozone layer.

Pollutants containing nitrogen compounds and heavy metals, especially cadmium, are the most noxious for waters. Nitrogen compounds are soluble in water, especially nitrates which is also responsible for methemoglobinemia, or “blue baby syndrome”. Links have been made between nitrate intake and gastric cancer, but conclusive evidence has yet to be produced.

Phosphate processing in wastewaters produces pollutants like  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and F-ions. These pollutants are slightly less harmful, except for fluorine, and they have a low solubility when coming into contact with  $\text{Ca}^{2+}$ -ions. This is advantageous because it restricts their flow in groundwater.  $\text{Ca}^{2+}$  is used in a controlled neutralizing process and is found in many types of soils. Figure 69 demonstrates this neutralizing capacity on the  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and F-ions in a residual water sample from a fertilizer unit.

Natural factors can attenuate the effects of pollutants, but at present this is not possible. Industries dumping their waste into waterways, the ocean, somewhere on land, or releasing pollutants into the atmosphere untreated were tolerated in the past, but today the quantity of waste generated is too significant to rely on natural factors to attenuate pollutants to acceptable safe levels, and authorities have been increasingly coming down on these practices. They are nowadays not tolerated since the technology exists to deal with waste products (Popovici, 1994).

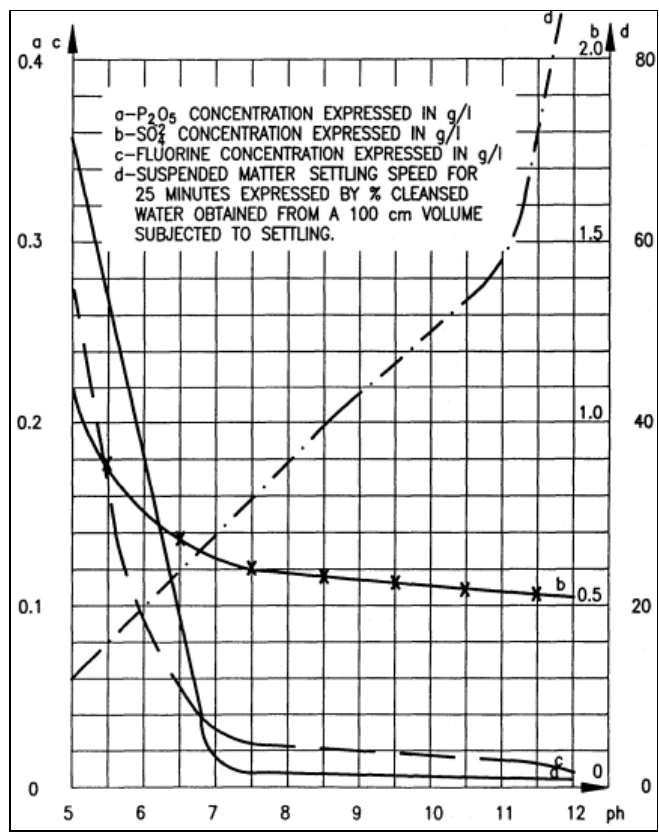


Figure 69: Parameter variation during pH neutralization (Popovici, 1994).

The process of restoring contaminated soil and water can be a complex, lengthy, and costly undertaking. Many months can go by going through all the regulatory steps before remediation work can actually begin. It is important to assess a site carefully in order to develop and implement the appropriate remediation plan effectively. With the increasing environmental concern over the past few decades, more and more sites are being remediated with the result that procedures have become systematic, more effective, and commercialized. Any site where hazardous substances are released during manufacture, storage, or transport may be earmarked for a potential remediation investigation (Tomlinson, 1994).

Once a site has been identified to be a potential environmental risk and needs to be remediated, this may be the possible sequence of events;

1. *Preliminary Assessment (PE)*: The priorities are set for the site inspection. Existing information, a description of the hazardous substances released and treatment, the source and nature of release, and possible routes of exposure are reviewed,
2. *Site Inspection (SI)*: A site inspection is conducted to determine the potential need for removal action, to collect or develop additional data, to develop field sampling and analysis and quality assurance plans, and also to conduct field sampling. A report is compiled after the site inspection, indicating the nature of contamination and threats to people and the environment, and includes recommendations.
3. *Remedial Investigation/Feasibility Study (RI/FS)*: Appropriate remedies that protect human health and the environment, that can be maintained over time, and minimize the risk of untreated waste is considered during this phase of the process. This phase should also include a more comprehensive characterization of the site and a definition of the extent of contamination that is present.
4. *Design and Construction of the Remedial Project*. The last phase, cleanup, may result in a great deal of extra money and time spent in addition to the previous stages of the process. If hazardous pollutants remain after the cleanup process, a reassessment of the site has to be done, with the possible help of other experts (Tomlinson, 1994).

## B.2 Remediation methods

### B.2.1 Introduction

There are many different methods that can be used to remediate contaminated groundwater. This section lists a few of these methods (B.2.1), and discusses a selected few in more detail (B.2.2 - B.2.9). The method of remediation depends on several factors, viz. hydrogeological setting, contaminant characteristics, physical properties (sink or float), chemical properties (solubility and sorption), surface access, land use, toxicity risk, and cost (Stewart, 2008).

List of some of the remediation methods;

1. *Air sprarging or stripping*: Volatile contaminants are evaporated from soil or water by passing a flow of air through the substrate.
1. *Anaerobic pyrolysis*: This involves the decomposition of waste materials with little or no oxygen present at high temperatures.
2. *Biodegradation*: Microorganisms are used to break down noxious chemicals.
3. *Bioremediation*: Controlled use of microorganisms at hazardous waste sites; can be aerobic or anaerobic degradation.



4. *Crystallization*: Involves the formation of crystalline substances from solutions or melts.
5. *Fractional crystallization*: Involves the separation of a cooling magma into mineral components as the minerals cool and congeal at different temperatures.
6. *Fractionation*: Involves the separation of a mixture in successive stages (see also *Fractional crystallization*).
7. *Incineration*: High temperature combustion of wastes so only ash remains.
8. *In situ vitrification*: Involves the process of entrapping contaminants in a glass produced by electrically melting soils containing waste.
9. *Liquid extraction*: See *Solvent extraction*.
10. *Soil washing*: A process that uses solvent surfactant combinations to remove contaminants.
11. *Solidification/stabilization*: The process of mixing the contaminated material, like soil, with a binder or solidification agent to entrap the contaminants.
12. *Solvent extraction*: Contaminants are dissolved in a solvent or solvent mixture and then separated from the solute. Different chemical types and solubilities of materials are separated by preferential extractive action.
13. *Steam stripping*: Similar to air stripping except that steam is used instead of air.
14. *Supercritical fluid extraction*: This method is basically a solvent extraction method using materials such as carbon dioxide or light hydrocarbons at temperatures and pressures above their critical points.
15. *Supercritical water oxidation*: This is a wet air oxidation process using water above its critical point.
16. *Thermal desorption*: Volatile and semi-volatile contaminants are evaporated from soil at moderate temperatures.
17. *Vapour extraction*: A vacuum is drawn through soil to vaporise and extract volatile contaminants. This process is also sometimes referred to as soil venting (Tomlinson, 1994).

Non-treatment options, viz. digging out and removing contaminated soil and transferring it to authorized landfills, were tolerated in the past, but regulations have progressively moved towards the treatment and hence permanent remediation of contaminated material. There exists inconsistency in remediation goals and describing the results of remediation processes, viz. many remediation procedures are called treatment, but only prevent mobility or reduce the volume of contaminants without reducing toxicity.

Sometimes it is necessary to control or isolate contamination before treatment can begin, and subsurface barriers are used in such cases. Examples of commonly used barriers, are; slurry trench

walls, grout curtains, vibrating beam walls, bottom sealing, block displacement, and liners (Tomlinson, 1994).

### B.2.2 Pump and Treat

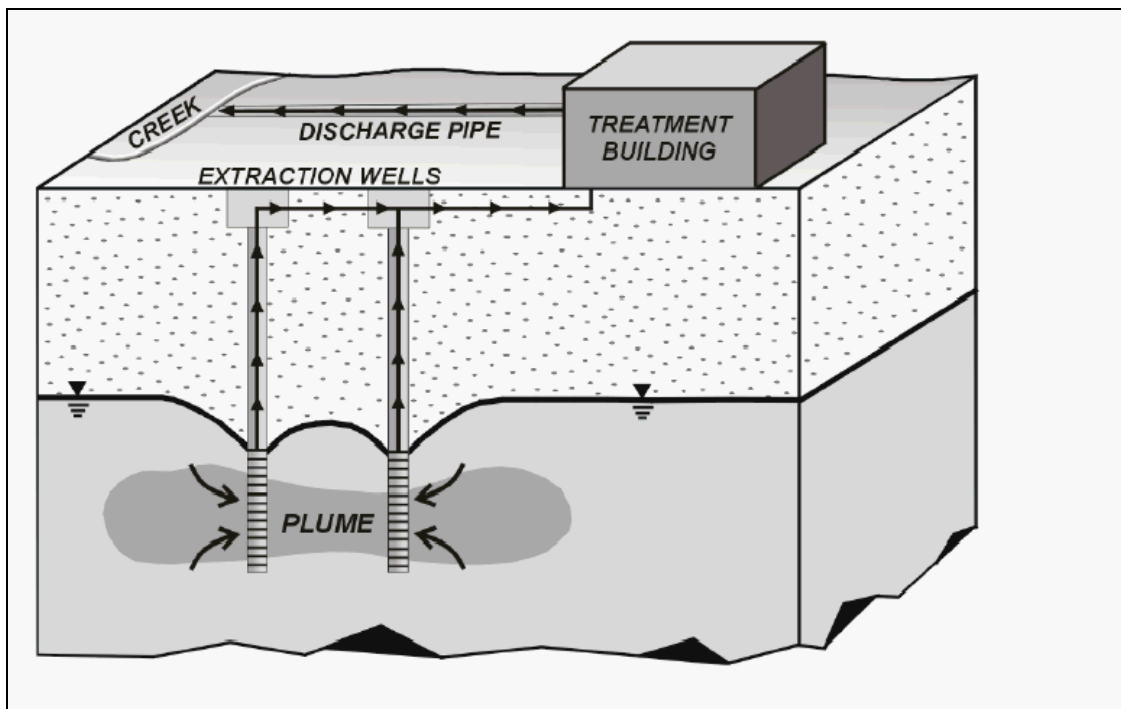


Figure 70: The pump and treat method (EPA, cited by Stewart 2008)

With the pump and treat method water is extracted from the aquifer via strategically placed wells, and contaminants are removed mechanically, chemically, or biologically on the surface. The treated water can be discharged onto the surface, into the subsurface, or into the municipal sewage system.

The disadvantages of this method are, that the effectiveness depends on the geology of the aquifer and the contaminants, it is a very slow process and can take decades or centuries to remove all the contaminated groundwater, it is very costly, and it doesn't always work, because some contaminants stick to the soil and rock (adsorption), e.g. NAPLs (Stewart, 2008).

### B.2.3 Hydraulic Containment

Water can be pumped from strategically placed wells to change the flow of groundwater in an aquifer, in order to prevent contaminants reaching wells used for human and agricultural purposes.

This method can mostly be used where the flow of groundwater in the aquifer is relatively simple. It has the added disadvantage of finding an appropriated site for disposal of the extracted water. In some

cases this method can be combined with the pump and treat method, and then it has the same disadvantages as mentioned in B.2.2.

### B.2.4 Air sparging/soil vapour extraction

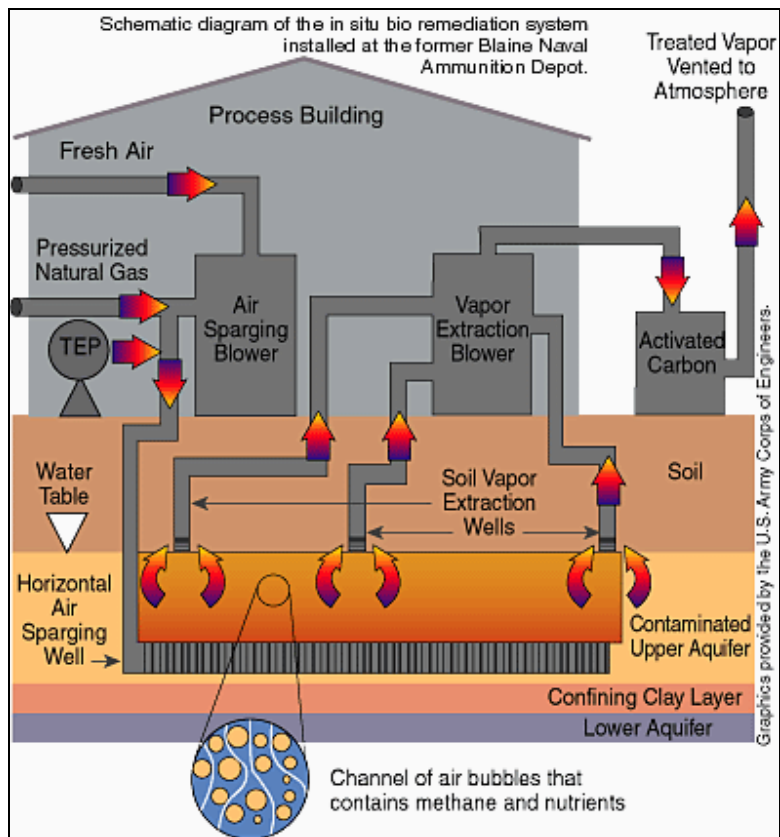


Figure 71: An example of air sparging (North Carolina Division of Pollution Prevention and Environmental Assistance, cited by Stewart, 2008)

Air sparging involves injecting a flow of air, sometimes containing specific chemicals, through the substrate to release volatile contaminants in order for it to evaporate straight into the atmosphere, or first into a treatment facility and then into the atmosphere.

Figure 71 illustrates the system used to remove trichloroethylene from the soil and an aquifer below the Blaine Naval Ammunition Depot, east of Hastings, Nebraska. This 50 000 acre facility produced vast amounts of munitions; 40% of all the munitions during the Second World War at one time. Later in the remediation, air containing natural gas and triethyl phosphate was pumped into the groundwater to improve the bioremediation of the soil bacteria.

The disadvantages of this system are, that it is difficult to flush contaminants from aquifers with a low permeability, operating becomes difficult below 9m, and it is difficult extracting multi-component phases.

With the bioremediation of nitrate pollution in groundwater, air sparging can be used to remove the excess nitrogen accumulating in the soil and the aquifer (Stewart, 2008).

### B.2.5 In-situ redox manipulation

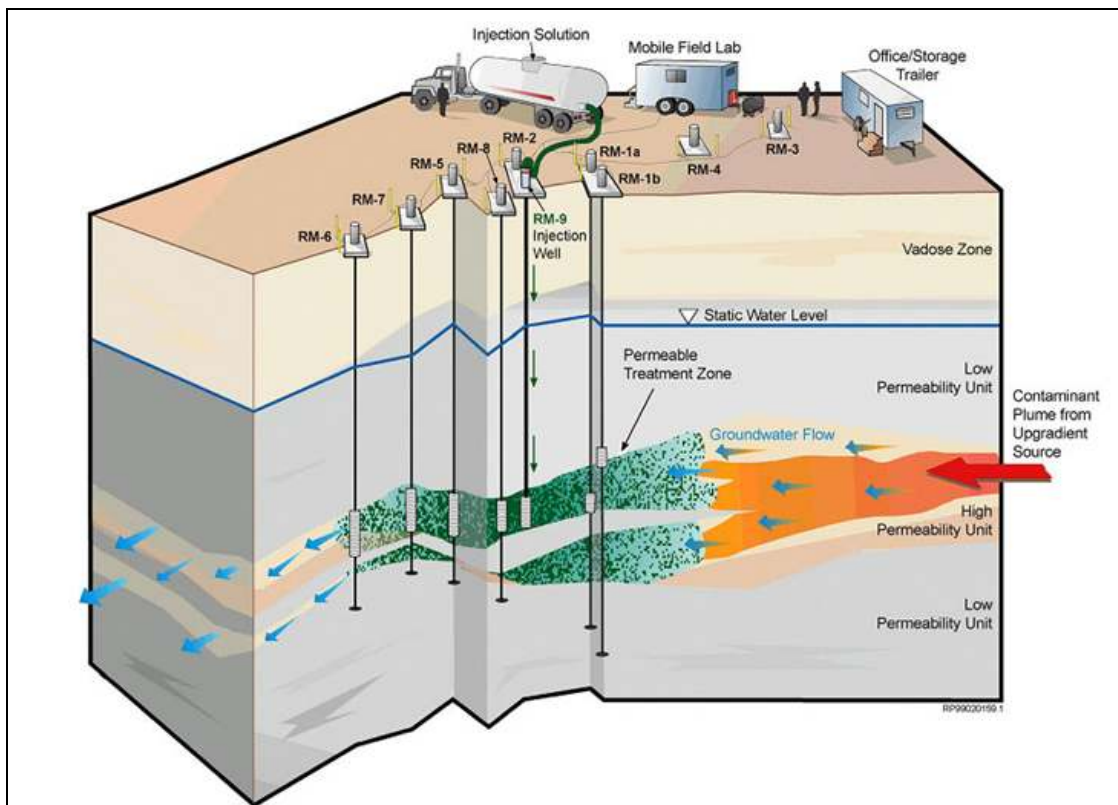


Figure 72: An example of in-situ redox manipulation (Field Hydrology and Chemistry Group of the Pacific Northwest National Laboratory of the US Department of Energy, cited by Stewart, 2008)

With in-situ redox manipulation (oxidation), an oxidant such as hydrogen peroxide is injected into the contaminated aquifer. The contaminant is oxidized and produces primarily carbon dioxide and water.

The disadvantage of this system is that unwanted by-products can be created which clogs the aquifer or further contaminates it. These by-products inevitably also have to be removed and the process of complete remediation usually involves several successive stages.

### B.2.6 Permeable reactive barriers

This method involves contaminants in the groundwater passing through a strategically placed trench, backfilled with material such as iron filings, activated carbon, or peat which absorb or transform the contaminants.

The disadvantage of this method is that it works only for relatively shallow aquifers.

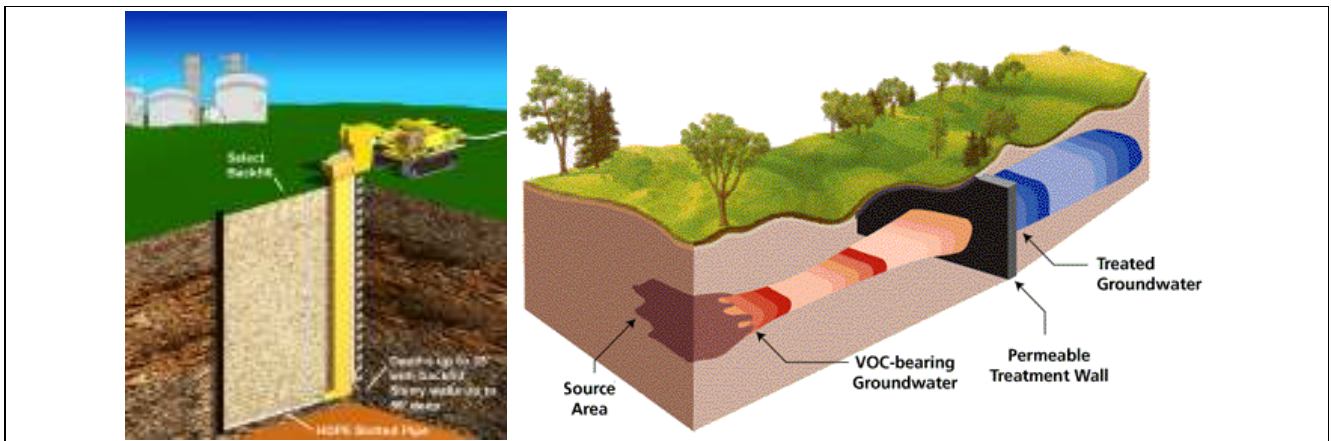


Figure 73: Examples of permeable reactive barriers (Right: Dewind one pass trenching. Left: from EPA Research Highlights, cited by Stewart, 2008)

### B.2.7 Phytoremediation

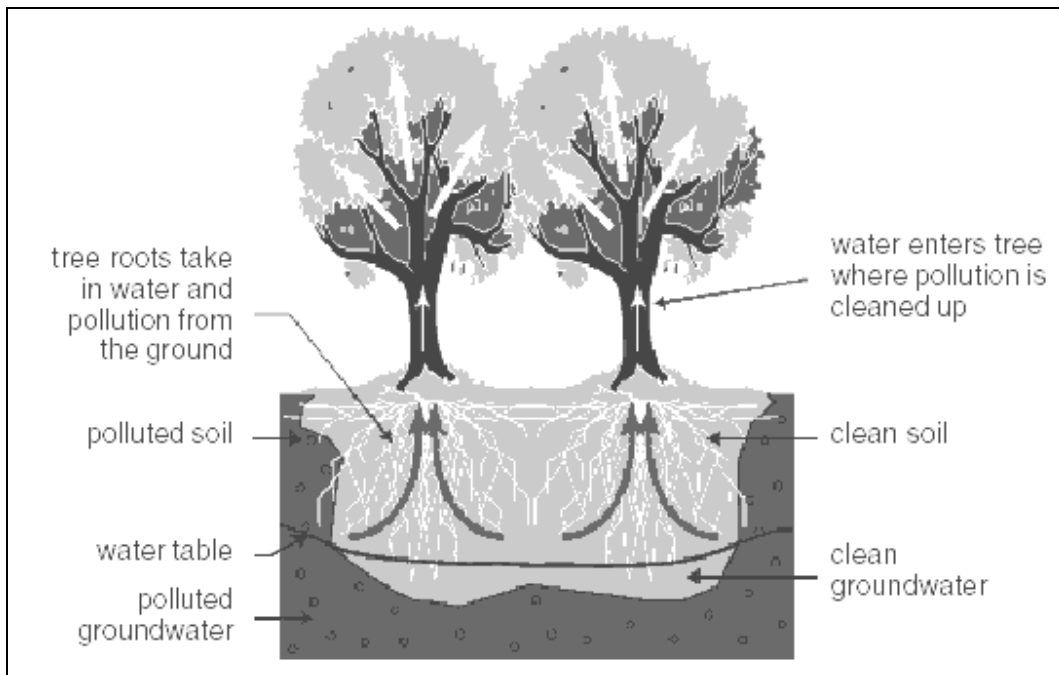


Figure 74: Phytoremediation (EPA, cited by Stewart, 2008)

With this method, selected plants are used to accumulate heavy metals and metal-like elements, viz. arsenic, lead, uranium, selenium, cadmium, and other toxins, viz. nutrients, hydrocarbons, and chlorinated hydrocarbons. Examples of such plants and the contaminants they are known to efficiently accumulate are; the Chinese ladder fern (*Pteris Vittata*) which accumulates arsenic very well, genetically altered cotton wood trees which accumulate mercury very well (in Danbury, Connecticut), and transgenic Indian mustard plants which accumulates dangerously high selenium deposits (in California).

Remediation of the groundwater involves growing these plants so that their roots reach into the aquifer and soak up the groundwater. The plants are then harvested and disposed of.

The disadvantage of this method is that only groundwater close enough to the surface for the roots to reach can be “treated”. It is also not sufficient in cases where immediate remediation of the groundwater is required, because the roots take time to fully penetrate the aquifer (Stewart, 2008).

### **B.2.8 Natural attenuation**

In some cases no human intervention is needed, and natural processes remove contaminants. The attenuation may involve dilution, radioactive decay, sorption, volatilization, or natural chemical reactions that stabilize, destroy, or transform contaminants (Stewart, 2008).

### **B.2.9 Intrinsic and enhanced bioremediation**

Hydrocarbons and other contaminants can be metabolized by bacteria and archaea, converting them to less toxic products. Enhanced bioremediation involves injecting nutrients and/or carbon compounds into the subsurface in order for bacteria and archaea to become more prolific. Depending on the contaminant, specific organisms are injected into the groundwater. Some organisms require additional nutrients which are injected along with the microbes.

Natural bioremediation occurs when there are bacteria and archaea already present in the subsurface breaking down harmful contaminants into less toxic compounds. Natural bioremediation works best when there are plentiful naturally occurring microbes and low contaminant concentrations (Stewart, 2008).

## Appendix C: Case Studies

### C.1 CF Industries

CF Industries (CFI), a subsidiary of CF Industries Holdings, Inc. in Deerfield, Illinois, is one of the largest manufacturers and distributors of nitrogen and phosphate fertilizers in North America. Their phosphoric acid and ammoniated fertilizer manufacturing facility in Plant City, Florida was investigated by inspectors of the EPA and the Florida Department of Environmental Protection between December 2004 and January 2005. An agreement between the said parties was reached on the 6<sup>th</sup> of August 2010, where CFI agreed to spend ca. \$12 million to reduce and properly manage hazardous wastes. In addition, CFI had to pay a civil penalty of more than \$700 000 and provide \$163.5 million in financial assurances to guarantee the appropriate closure and long term care of the closed facility. This agreement resolved their Resource Conservation and Recovery Act (RCRA) violations, and is the first case concluded under the EPA's National Enforcement Initiative for Mining and Mineral Processing (EPA, 2010b).

A summary of the violations by CFI identified by the EPA under the Resource Conservation and Recovery Act (RCRA);

- “Failure to make hazardous waste determinations for scrubber effluents and cleaning wastes,
- Treatment, storage and disposal of hazardous wastes without a permit or interim status,
- Failure to perform land disposal determinations and to meet land disposal restrictions for hazardous wastes,
- Failure to develop cost estimates and to provide financial assurance for closure, long-term care, and third-party liability for the phosphogypsum stack system, and,
- Failure to comply with recordkeeping requirements” (EPA, 2010c).

In accordance with the injunction imposed by the EPA, CFI have taken the following actions;

- “CFI has eliminated the release of hazardous wastewaters from fertilizer production through a novel reconfiguration of current operations. CFI's three fertilizer production trains produce ammoniated fertilizers. The three secondary scrubbers on these production trains will no longer pump corrosive wastewater back to the Phosphogypsum Stack System as CFI has reconfigured these scrubbers to use phosphoric acid as the scrubbing media. Since the effluent acid is recycled back into the process, there is no media-shifting.
- CFI will capture all ammonia prior to release to the environment. Ammonia will now be captured in the closed loop recirculation of phosphoric acid in the secondary scrubbers.

- CFI will build an elementary neutralization unit to treat all hazardous wastes from fertilizer operations.
- CFI will implement a Best Management Plan to address leaks and spills of phosphoric acid from phosphoric acid plant operations and a Sulphuric Acid Waste Management Plan to address leaks and spills of sulphuric acid from its nearby sulphuric acid plant.
- Assessment of current contamination is complete. All necessary remedial actions have been taken.
- CFI has agreed to comprehensive financial assurance provisions to guarantee \$163.5 million for closure and long-term care, minimizing financial risk to the U.S. and to the Florida Department of Environmental Protection” (EPA, 2010c).

As a result of the actions taken by CFI, pollutants are reduced in the following quantities (values are in tons per year (tpy));

- “4.9 million tpy of hazardous waste reductions (for heavy metals and corrosivity).
- 4,500 tpy net reduction of ammonia effluent to the phosphogypsum stack system.
- 5.8 million pounds of hazardous wastes treated. CFI will design and operate an elementary neutralization unit to treat wastes generated from cleaning pipes and tanks in the phosphoric acid and ammoniated fertilizer processes.
- 4,922 cubic yards of contaminated soil removed. The decree requires CFI to remove contaminated soil from outside the sulphuric acid plant” (EPA, 2010c).

The actions taken mean that there is a reduced risk of the release of billions of gallons of wastewaters into the environment. It is worth mentioning that the EPA has especially focused on the compliance in the phosphoric acid industry because of the high risk of releases of acidic wastewaters at these facilities. These acidic wastewaters results in the contamination of the groundwater and can cause fish kills in local rivers and lakes (EPA, 2010c).

## **C.2 Central Chemical**

Central Chemical is located in Hagerstown, Maryland in Washington County on 19 acres of land. The chemical plant operated as a blender of agricultural pesticides and fertilizers from the early 1930s to the mid 1980s. The old buildings were demolished in the summer of 2005. The raw materials used in products were manufactured at other locations, and were blended with inert materials using air and hammer mills and wetting agents to produce commercial grade products. All waste materials generated on site were disposed of in an on-site depression. The main contaminants found in the soil and groundwater, and also in fish caught downstream from the site, are; arsenic, lead, benzene, aldrin, chlordane, DDD, DDE, DDT, dieldrin, and methoxichlor (EPA, 2010a).



EPA issued a “Record of Decision” (ROD) in September 2009 which outlines the cleanup methods for contaminated soils and waste on the site. This included the on-site solidification/stabilization of the waste lagoon, excavation, consolidation, and capping of contaminated soils, and the installation of a groundwater extraction and treatment system. Groundwater was confirmed to extend beyond the boundaries of the Central Chemical plant, and would therefore require further delineation in order to determine the extent of the groundwater contamination (EPA, 2010a).

The cleanup history of the site can be listed as follows;

- “In early 1997, it was discovered that elevated levels of site contaminants extended several feet beyond the old fence line along the northern end of the property. Land use north of the property is residential.
- In the spring of 1997, EPA entered into an agreement with the site owner under which the owner erected a new fence as an interim measure that now prevents people from coming into contact with these contaminants.
- EPA entered into an agreement with seven potentially responsible parties, including Allied Signal, FMC, Novartis, Olin, Shell Oil, Union Carbide, and Wilmington Securities, to conduct a remedial investigation and feasibility study (RI/FS) at the site. These cooperating companies have notified EPA that an additional seven companies including the site owner, Central Chemical, have joined the group.
- In February 2003, the Remedial Investigation/Feasibility Study (RI/FS) work plan was completed.
- In 2004, the majority of the environmental sampling at the site was completed.
- Samples were collected of site soil, groundwater, and storm water. In addition, samples were collected from surface water and sediment from the nearby Marsh Run and Antietam Creek.
- Sampling confirmed that pesticides and metals are present at elevated levels in surface soil across the site, and high concentrations of pesticides and metals have been buried in a disposal area in the north end of the property. To a lesser degree, pesticides were also detected in storm water leaving the site and in surface water and sediment samples from Marsh Run and Antietam Creek.
- Groundwater contamination has moved beyond the property boundaries and additional wells [were] being installed and sampled in 2006/2007 to determine the extent of off-site groundwater contamination.
- During the Spring and Summer of 2005, all former pesticide and fertilizer manufacturing buildings were decontaminated, demolished and disposed of in an appropriate manner.
- In December 2006, the Potentially Responsible Parties (PRP) provided EPA with the final Remedial Investigation (RI) for the site. The final RI for on-site soil and waste is complete.

- Groundwater contamination has been confirmed to extend beyond the boundaries of the Central Chemical property. Therefore, further delineation of groundwater contamination will be performed.
- In 2006, the PRP provided EPA with early portions of the Feasibility Study (FS), which evaluates the best cleanup options for the site.
- In 2007, the first draft of the feasibility study was completed and provided to EPA.
- In 2009, a Proposed Plan, describing EPA's preferred cleanup alternative for the site soils and wastes, was issued.
- In September 2009, EPA issued a Record of Decision (ROD) for contaminated soils and waste at the site. The ROD includes on-site solidification/stabilization of a former waste lagoon; excavation, consolidation, and capping of contaminated soils; and the installation of a ground water extraction and treatment system” (EPA, 2010a).

### **C.3 International Mineral and Chemical Corp (IMC)**

The International Mineral and Chemical Corp (IMC) is located in the Arkwright neighbourhood just south of Spartanburg, South Carolina and is ca. 41 acres. The surrounding properties include residential, industrial, and undeveloped areas. An abandoned dump borders the site, and there is an active chemical manufacturing facility to the south and “Mt Vernon Mills” to the west of the site. IMC manufactured NPK fertilizers from c.1910 to 1987. The primary operations included sulphuric acid production (from 1947 to 1970), superphosphate production, and fertilizer mixing operations.

There were two primary lagoons before the 1970s, one for scrubber water and the other for sewage. The sewage lagoon was later divided expanded and divided in two, one for scrubber water and the other for storm water.

The only structures remaining on site include the security fence, some asphalt paving, the concrete floors to the main fertilizer building, the office and garage areas, the former above ground bulk fuel storage area, the concrete potash storage area, and a concrete pad north of the former trestle.

The site is located within a 500 acre area forming part of a revitalization effort known as the “ReGenesis Project”. “This project is led by the community organization, ReGenesis, Inc., and supported by numerous Federal, State, and local partners, including EPA, South Carolina Department of Health and Environmental Control (SCDHEC), and the City and County of Spartanburg”.

An in-depth site investigation was conducted between 2004 and 2007, and indicated that ca. 6000 cubic yards of process residuals and 700 cubic yards of soil required cleanup. The primary

contaminants were; arsenic, polychlorinated biphenyls (PCBs), lead, fluoride, 2,4-dinitrotoluene (DNT), and 2,6-DNT. There is a risk for individuals being exposed to site contaminants located in surface and subsurface soil through skin contact or accidental ingestion (EPA, 2009).

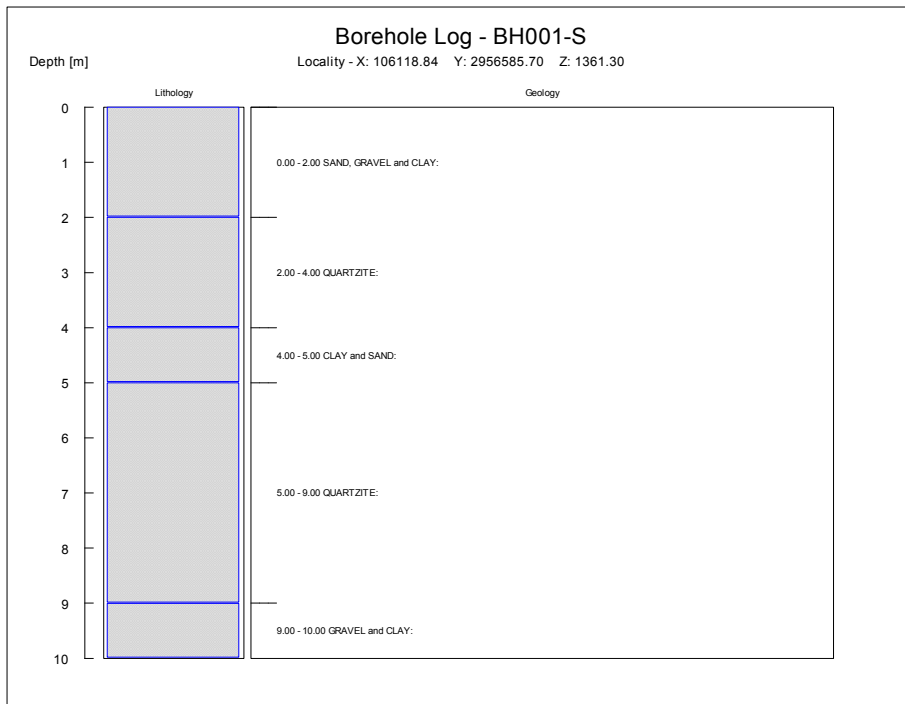
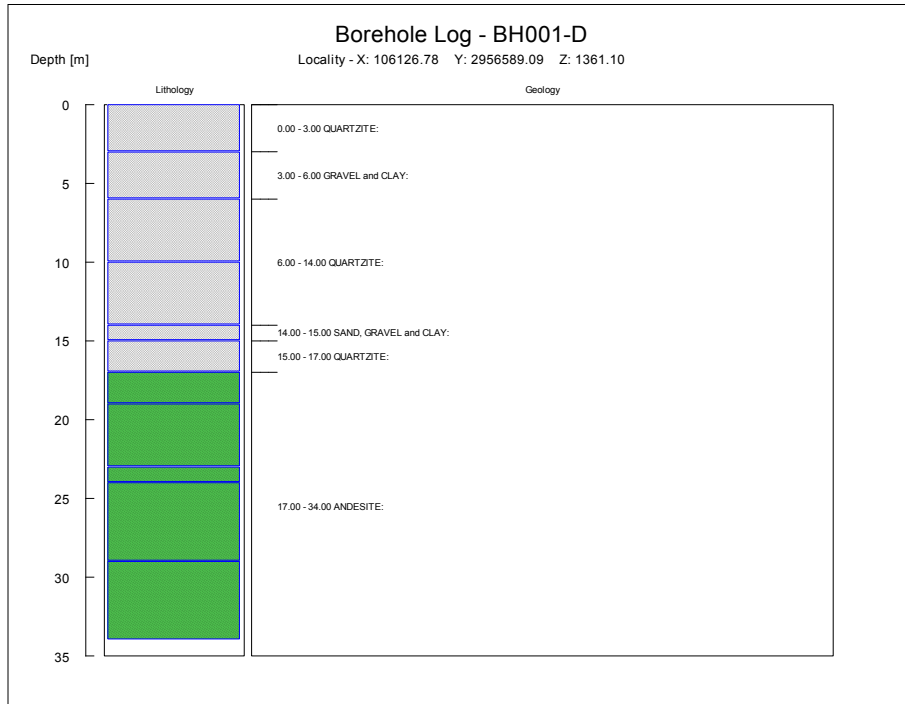
A Remedial Investigation/Feasibility Study (RI/FS) was initiated in 2004. After evaluation, the site will now undergo a “Non-Time-Critical Removal Action” (NTCRA) in order to address additional contaminated soil and fertilizer residuals. The major components of the proposed action plan included;

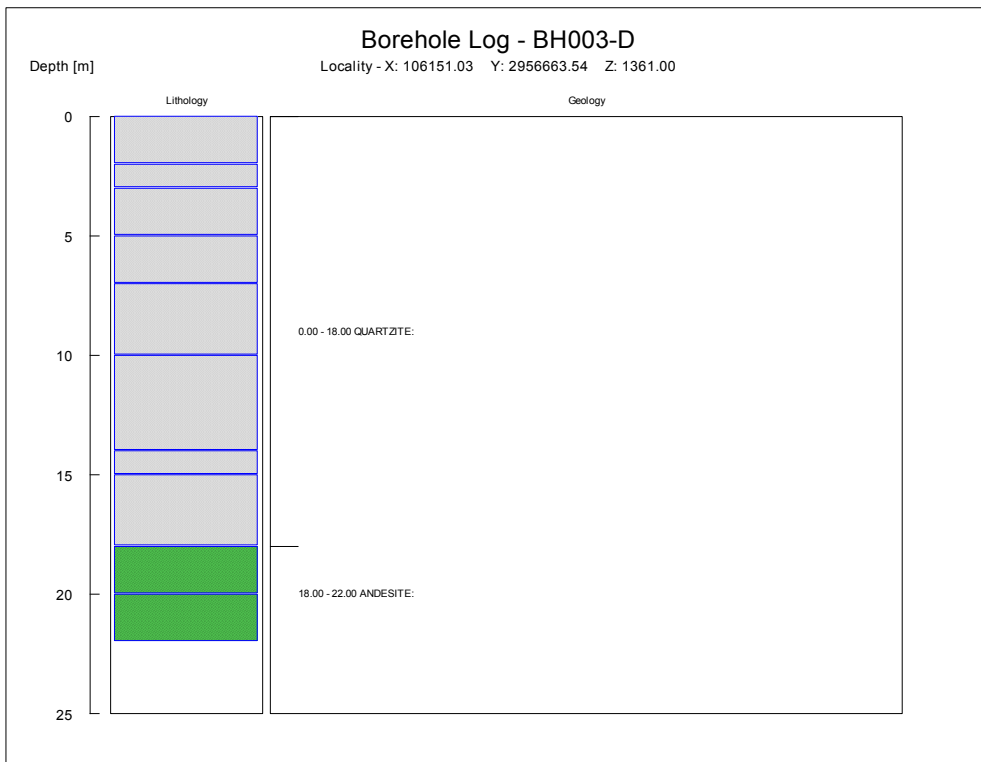
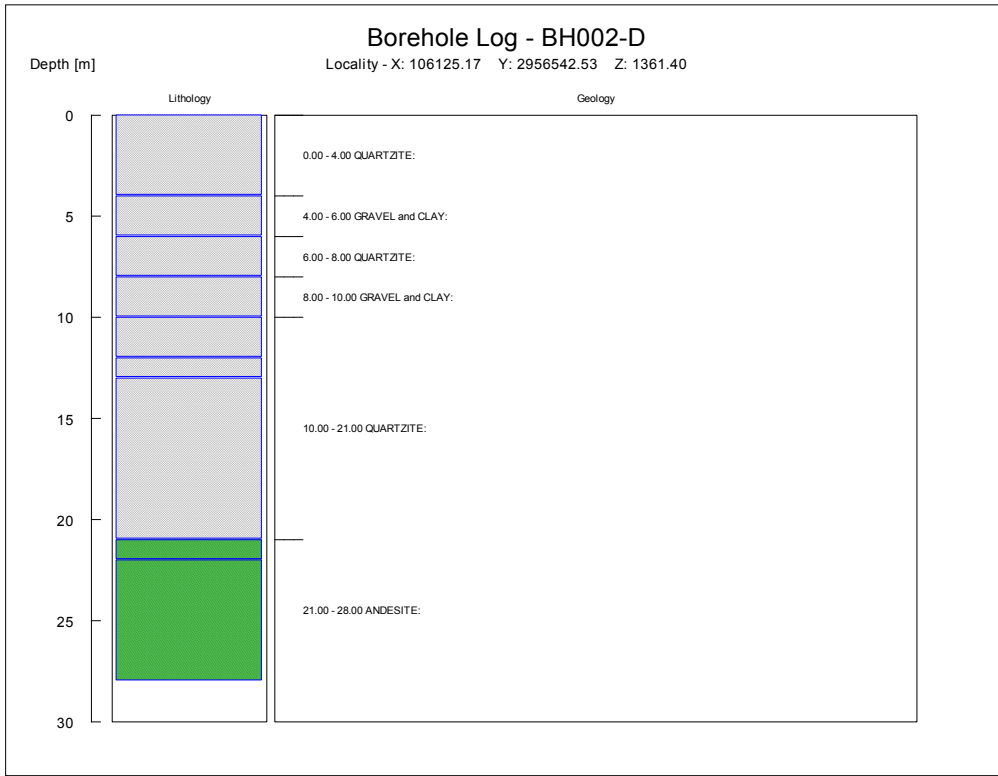
- “The excavation of affected soil and process residuals.
- Placement of a buffering/neutralizing chemical at the base of the excavations, backfill, and grade for positive drainage.
- On-site consolidation of the excavated materials under a cover system that also covers potential source areas in the former sulphuric acid plant area.
- Inspection and removal of the on-site explosives bunker under the supervision and direction of an explosives expert.
- Implementation of a ground water monitoring program” (EPA, 2009).

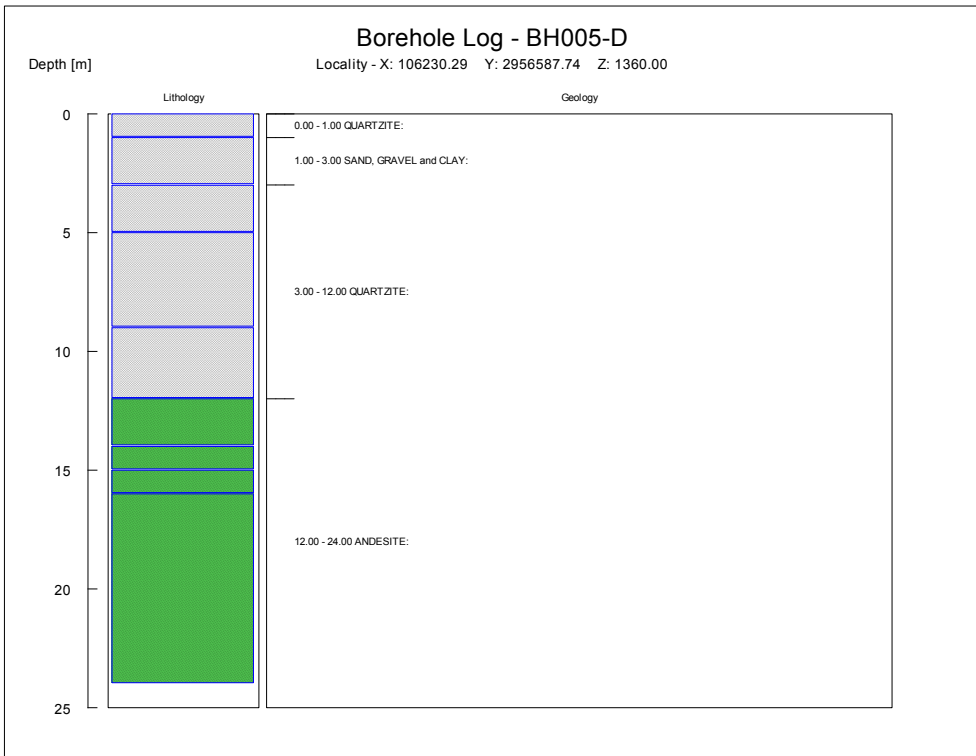
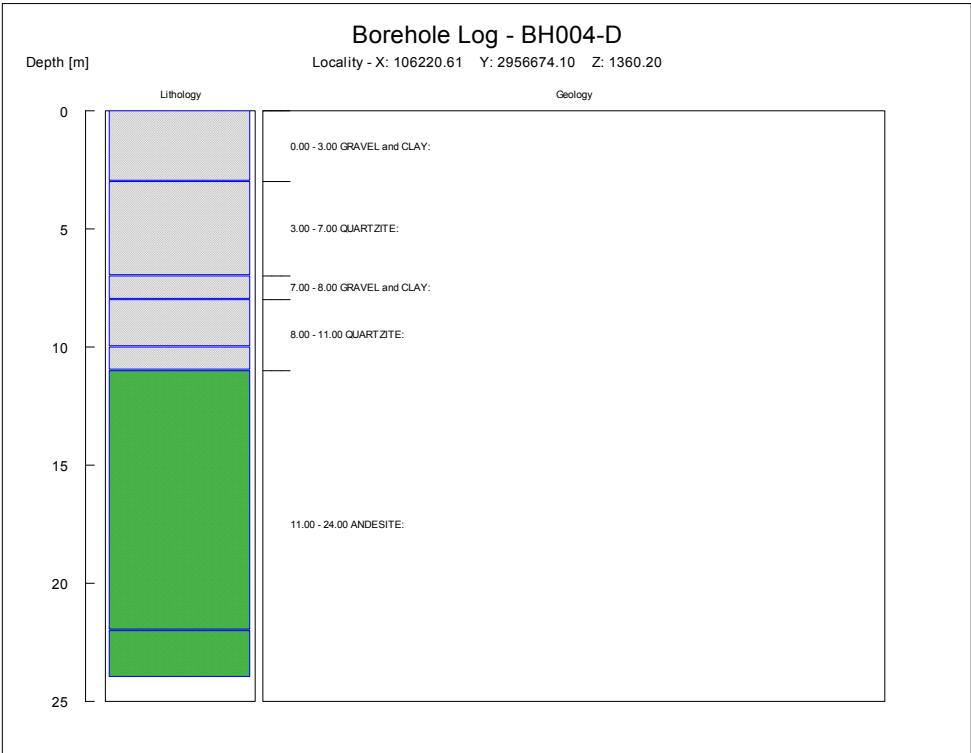
Progress in cleanup operations;

- “In 1987 when the plant closed, the lagoons were dredged and cleaned. Monitoring wells were also installed.
- In 1999, Vigindustries, a subsidiary of IMC Global, deconstructed the remaining facility buildings.
- A removal action was conducted by Vigindustries in 2002. Soil in the former pond area was removed, along with fertilizer residuals and existing stockpiles. Approximately 15,500 tons of soil were removed and sent off-site for disposal.
- Site cleanup activities are being led primarily by potentially responsible parties with oversight by EPA” (EPA, 2009).

## Appendix D: Borehole logs and profiles







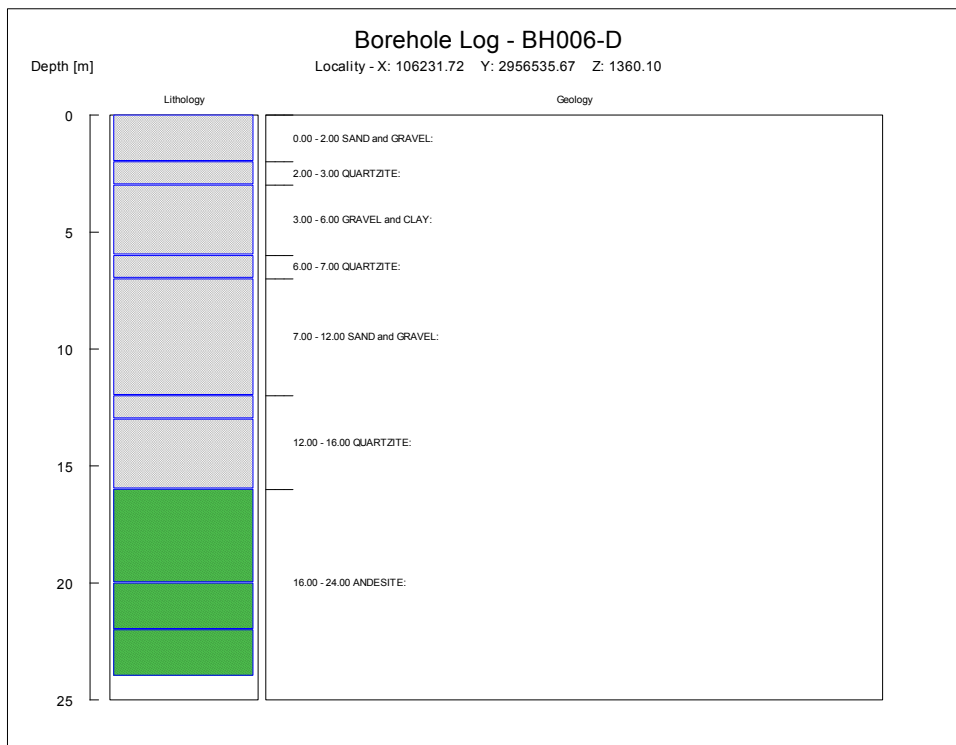
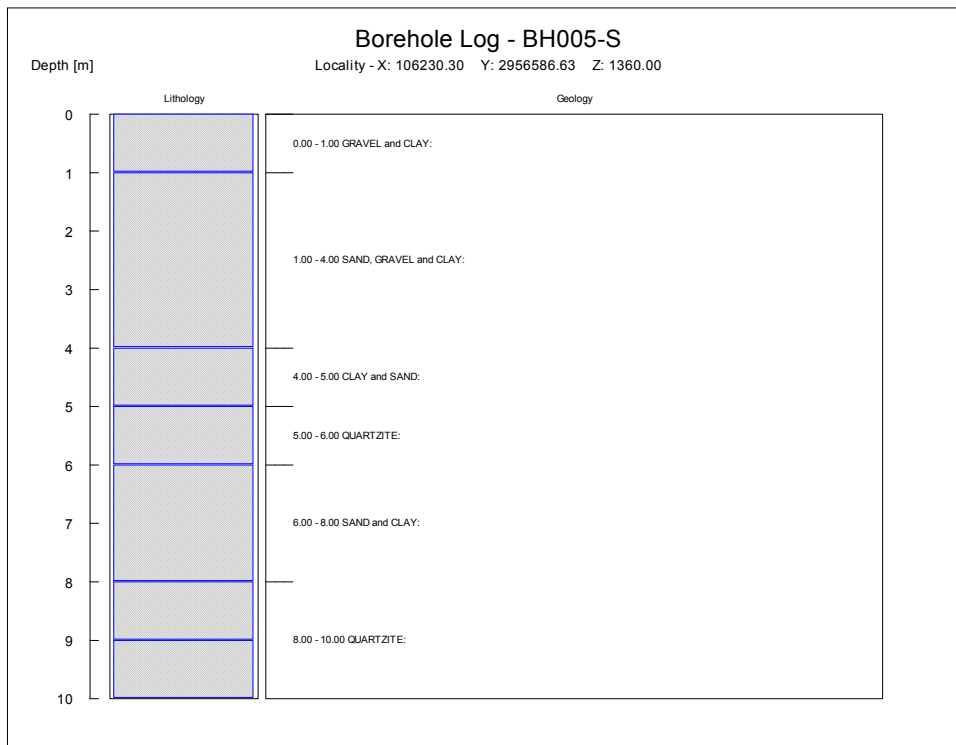
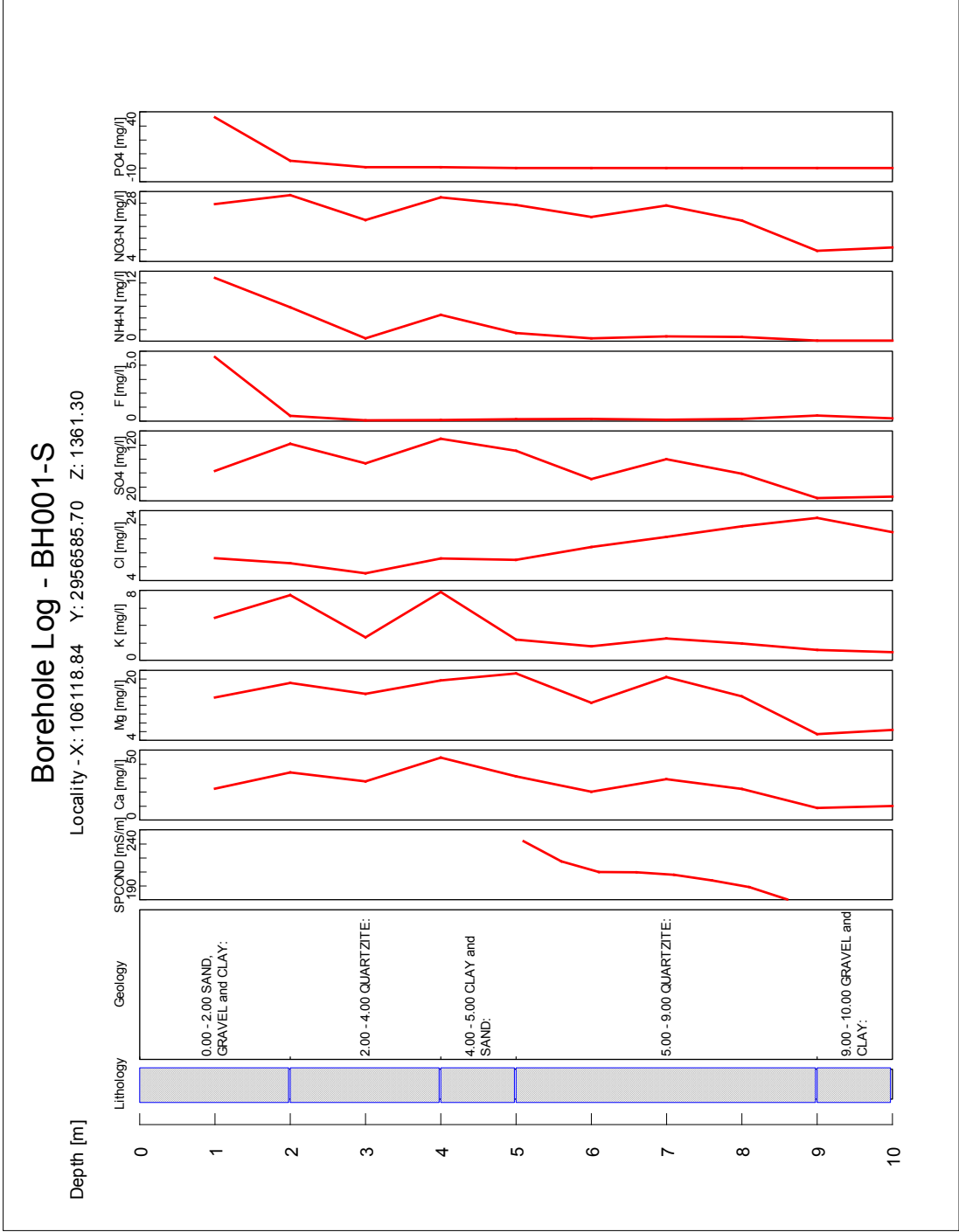
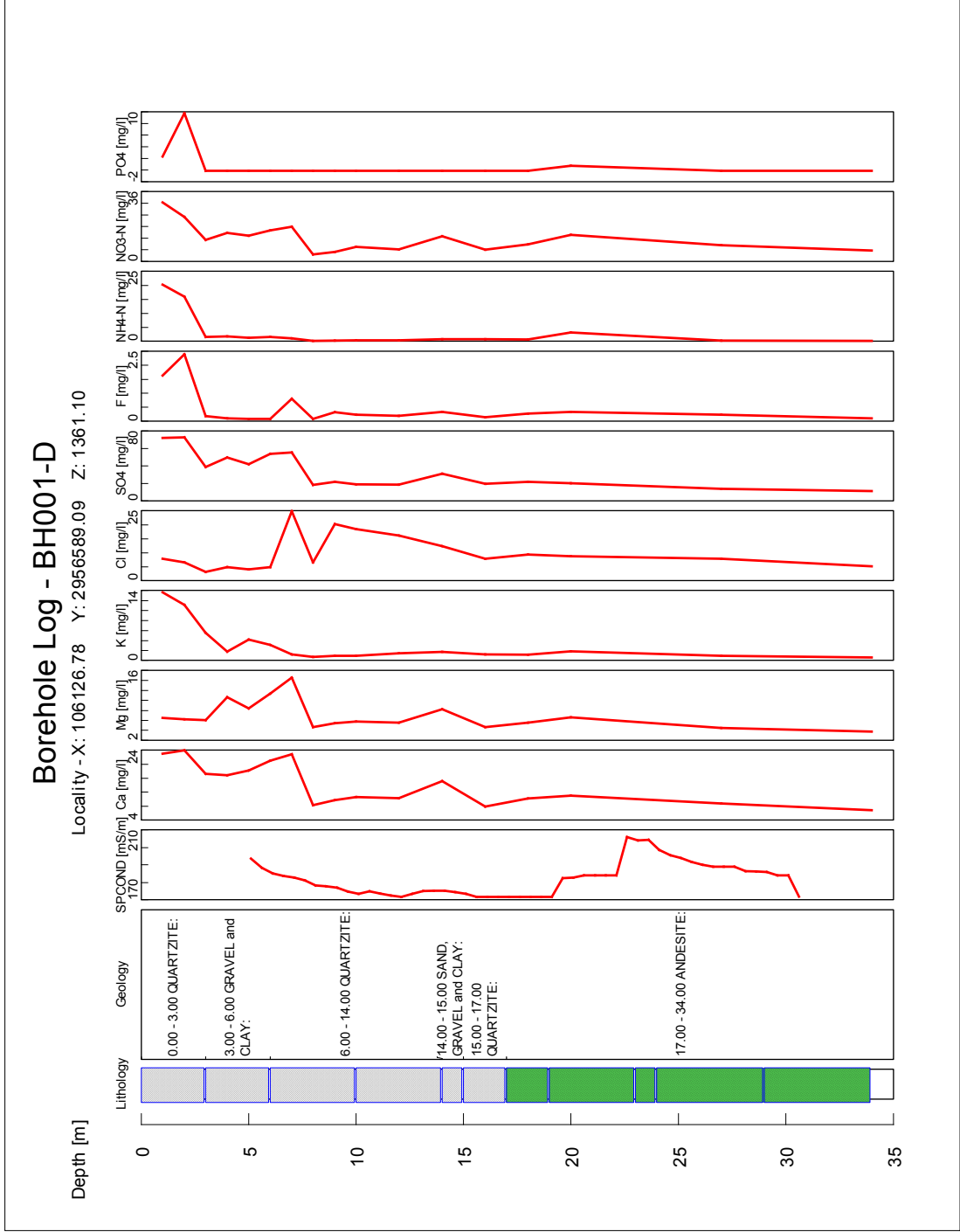
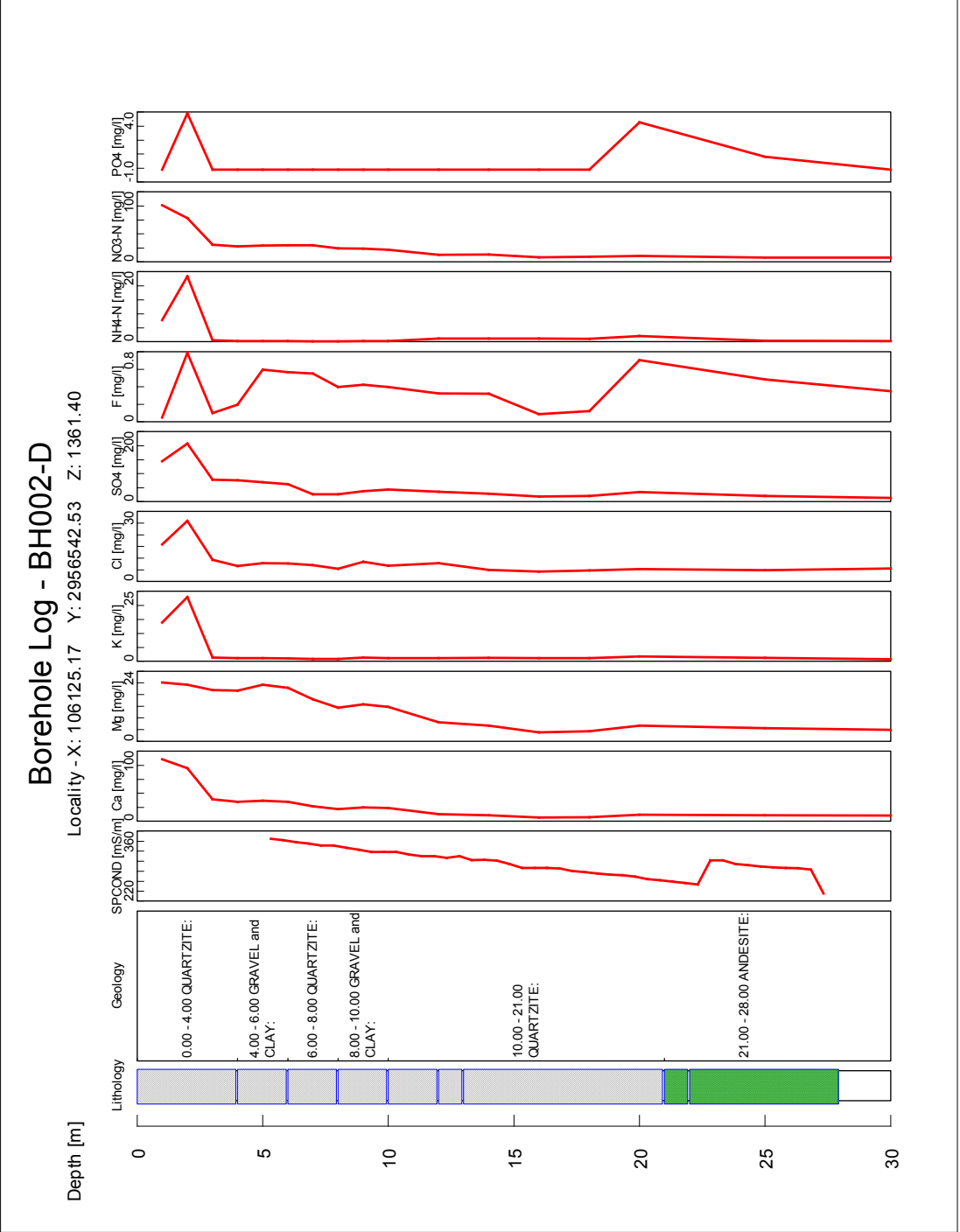


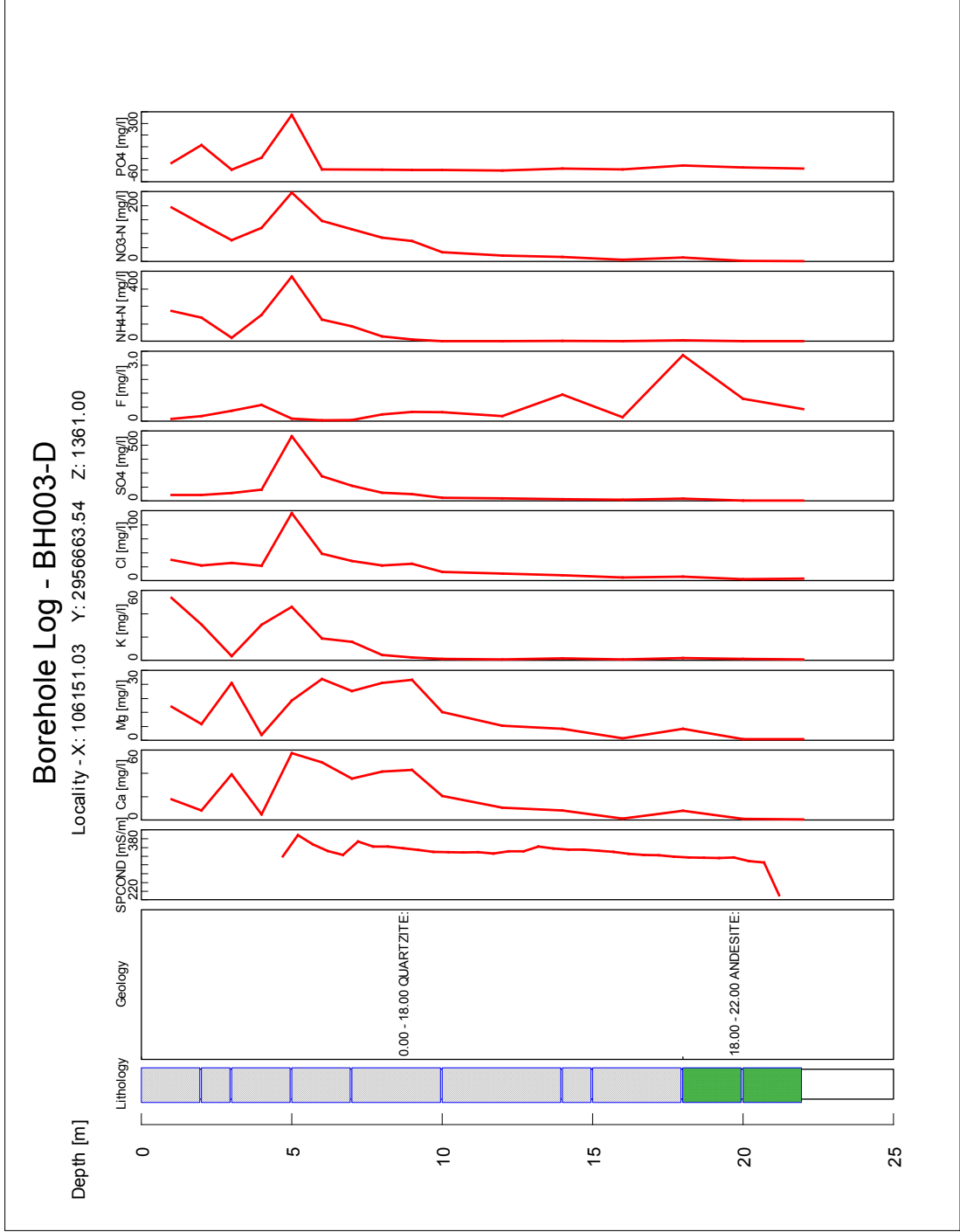
Figure 75: Borehole logs of the eight boreholes on the SNP site.

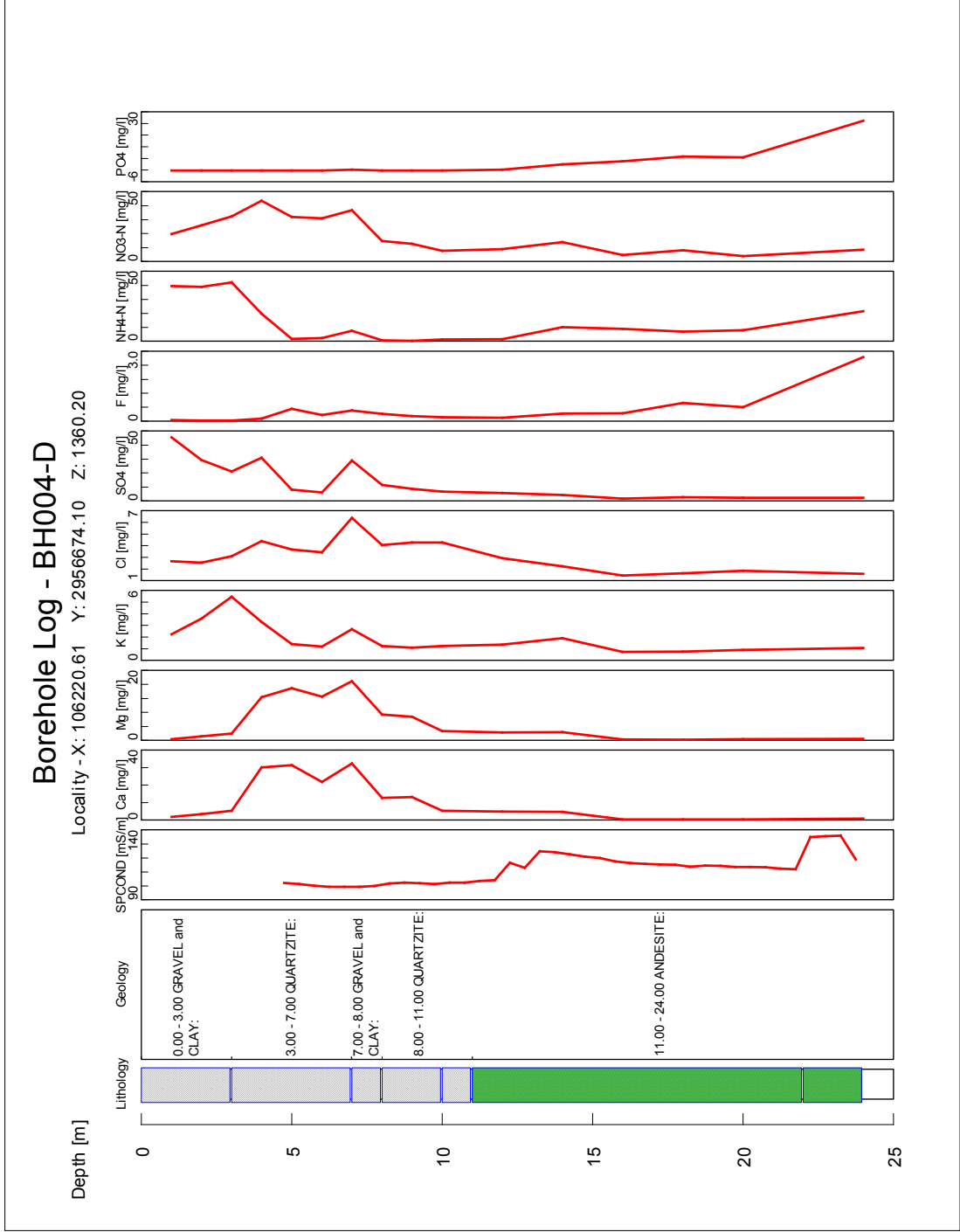


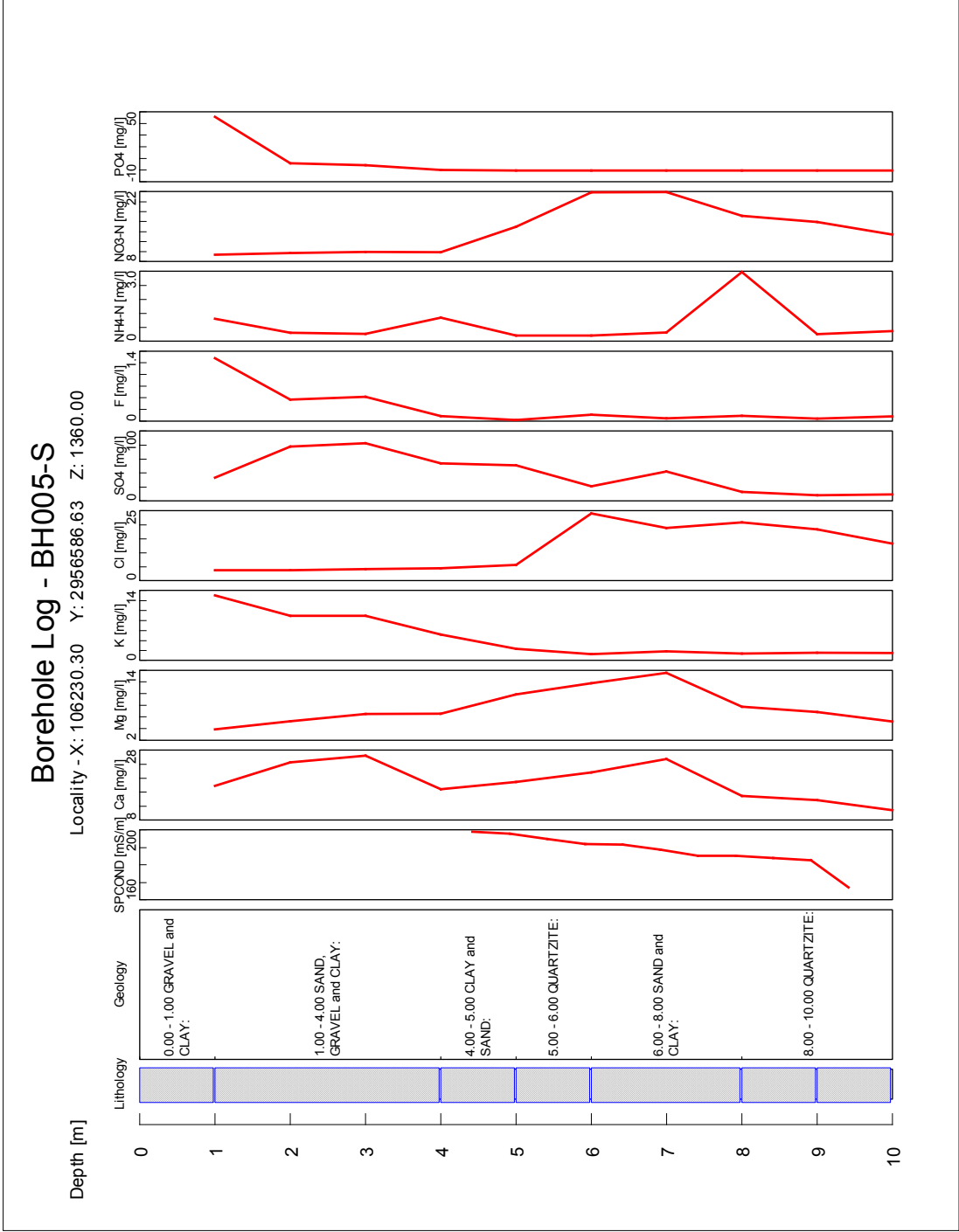


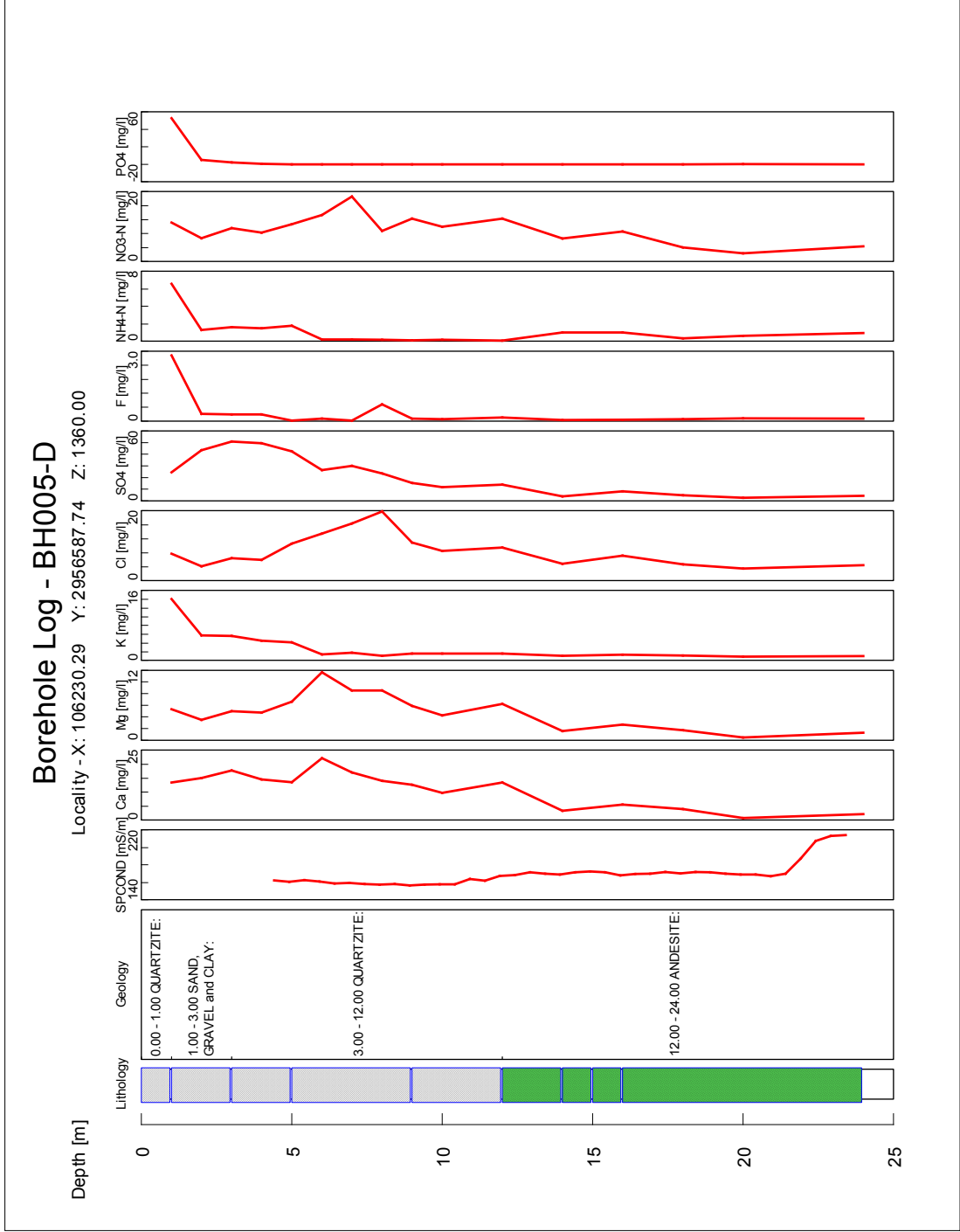












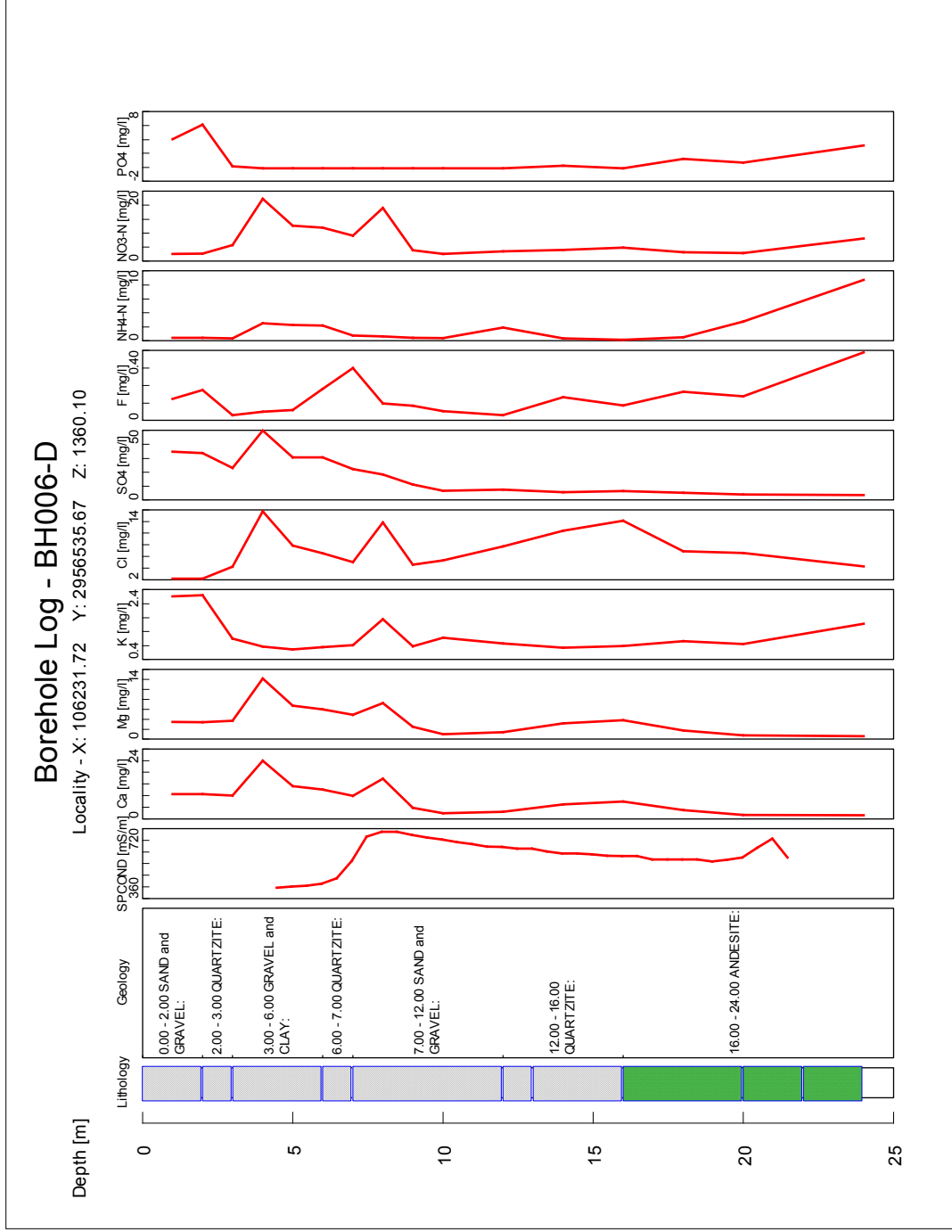


Figure 76: Borehole geology, EC profile (groundwater), and chemical results profiles (for soil samples) of all eight boreholes.

# The Impacts of Fertilizer Manufacturing on Groundwater in South Africa

## Abstract

As a result of the fertilizer industry's rapid growth, and the increasing global awareness concerning environmental issues, fertilizer production facilities have come under growing pressure to comply with ever more stringent environmental regulations.

There are numerous contaminants associated with the fertilizer industry. These may be released into the environment through dusts, fumes, air emissions, liquid pollutants, or solid wastes. Some of these contaminants pose serious potential health and environmental risks.

Groundwater is one of the aspects of the environment heavily effected by the fertilizer industry, and the aim of this study is to provide more clarity on the extent of the pollution caused by the fertilizer industry on the quality of groundwater.

The site investigated is located in the industrial area of Potchefstroom, South Africa, and includes Sasol Nitro Potchefstroom (SNP), the Kynoch Fertilizer Production Facility (KFPPF), and the surrounding area. SNP is a hot and cold blend liquid fertilizer plant, and KFPPF manufactured fertilizers on a full scale from 1967 until mid 2006. An in-depth investigation was conducted on the SNP site by the researcher, and data from the KFPPF site were provided by SRK Consulting who carried out a study there in 2007.

The predominant contaminants associated with the fertilizer industry, also found in significant concentrations the investigated area, are; nitrate ( $\text{NO}_3$ ), ammonium ( $\text{NH}_4$ ), phosphate ( $\text{PO}_4$ ), sulphate ( $\text{SO}_4$ ), fluoride compounds (F), chloride (Cl), cadmium (Cd), and zinc (Zn). Various other heavy metals and radionuclides posing potential health and environmental risks may be released into the environment during the processing of phosphate rock; the types and quantities of which depend on the content of the phosphate rock.

In general,  $\text{NO}_3$  (the most predominant contaminant found throughout the site), Ca, Mg, Cl, and Mn are found predominantly in solution in the groundwater (i.e., not adsorbed to soil/rock) in the saturated zone, except where there is loading from the surface within the bounds of SNP, which means that they are present in the unsaturated zone as well and leach down to the saturated zone.  $\text{SO}_4$  and K were found in little more concentrations in solution than in soil samples (in the saturated zone), but in a lesser contrast than for example,  $\text{NO}_3$  and Ca. Zn and F were found predominantly in soil samples, and primarily in the upper layer of soil.  $\text{PO}_4$  was almost exclusively found in the upper layer of soil, as well as  $\text{NH}_4$ , but to a lesser extent.



The general distribution of contaminants on site is attributed to their respective solubility characteristics and their tendency to be adsorbed by soil/rock.

Many of the contaminants show a consistent peaking at a depth of ca. 6m. This may be attributed to the fact that pH levels are mildly acidic within the first few meters of soil, after which it increases rapidly to approximately neutral values throughout the depth of the site. Contaminants' solubility that are pH dependant (lower pH increases solubility) would hence dissolve and leach through the first layer of soil/rock and precipitate where pH values increase.

Significant chromium (Cr) concentrations were found in all the water samples taken from the boreholes on the eastern side of the site, ranging between 0.4 - 1.925mg/l. The main source of chromium was found to be the site on the southern boundary of the SNP plant, which was the location of a tannery in the past.

Due to the evidence of the effectiveness of plants reducing contaminant concentrations in the north-eastern corner of the site, phytoremediation is recommended as a viable option to rehabilitate the area.

### **Keywords**

Fertilizer manufacturing, impacts, groundwater, nitrate, phosphate, safe practices, prevention, remediation.

## Opsomming

As gevolg van die vinnige groei in die kunsmis bedryf, en die internasionale bewuswording van omgewings kwessies, het die kunsmis bedryf onder groeiende druk gekom om aan al hoe meer omgewings regulerende voorvereistes te voldoen.

Daar is 'n menigde aantal besoedelingsstowwe wat geassosieër word met die kunsmis bedryf. Hierdie kan vrygestel word in die omgewing d.m.v. stof, dampe, lug emissies, vloeistof besoedeling, en vastestof afval. Sommige van hierdie besoedelingsstowwe hou ernstige potensieële gevare in vir menslike gesondheid en die omgewing.

Grondwater is een van die aspekte van die omgewing wat swaar beïnvloed word deur die kunsmis bedryf, en die doel van hierdie studie is om vas te stel wat die impak van die kunsmis bedryf op die kwaliteit van grondwater is.

Die studie area is geleë in die industrieële gebied van Potchefstroom, Suid Afrika, en sluit die "Sasol Nitro Potchefstroom" fabriek (SNP), die "Kynoch Fertilizer Production Facility" (KFPF), en omgewing in. SNP is 'n warm en koue meng vloeistof kunsmis fabriek, en KFPF het kunsmis volskaal vervaardig vanaf 1967 tot middel 2006. 'n In-diepte studie is gedoen deur die navorser op die SNP fabriek, en data van die KFPF fabriek was verskaf deur SRK Consulting wat 'n studie daar gedoen het in 2007.

Die mees algemene besoedelingsstowwe wat geassosieër word met die kunsmis bedryf, en wat ook gevind is in groot konsentrasies in die studie area, is; nitraat ( $\text{NO}_3$ ), ammonium ( $\text{NH}_4$ ), fosfaat ( $\text{PO}_4$ ), sulfaat ( $\text{SO}_4$ ), verskillende forms van fluoried (F), chloried (Cl), kadmium (Cd), and sink (Zn). Verskeie ander swaar metale en radionukliedes wat 'n potensieële bedreiging vir gesondheid en die omgewing inhou mag ook vrygestel word deur die prosessering van fosfaat klip. Die tipes en hoeveelhede hang af van die inhoud van die fosfaat klip.

In die algemeen word  $\text{NO}_3$  (die mees algemene besoedelingsstof gekry in die studie gebied), Ca, Mg, Cl, en Mn hoofsaaklik in oplossing in die grondwater gevind (d.w.s. nie geadsorbeer deur die grond/klip nie) in die versadigde zone, behalwe waar daar lading op die oppervlakte is, wat beteken dat daar besoedelingsstowwe ook teenwoordig is in die oversadigde zone wat dan loog na die versadigde zone.  $\text{SO}_4$  en K word in bietjie meer konsentrasies in oplossing gevind as in grondmonsters (in die versadigde zone), maar met 'n kleiner kontras as bv.  $\text{NO}_3$  en Ca. Zn en F word hoofsaaklik gevind in grondmonsters en oor die algemeen slegs in die boonste laag grond.  $\text{PO}_4$  word hoofsaaklik net gevind in die boonste laag grond, so ook  $\text{NH}_4$ , maar tot 'n mindere mate.

Die algemene distribusie van besoedelingsstowwe word toegeskryf aan hul onderskeidelike oplosbaarheids-karakteristieke en hoe maklik hulle deur grond/klip geabsorbeer word.

Baie van die besoedelingsstowwe wys 'n konstante piek in konsentrasies op 'n diepte van ongeveer 6m. Dit kan toegeskryf word aan die feit dat pH waardes in die eerste paar meter grond relatief suur is, waarna dit vinnig toeneem tot ongeveer neutrale waardes vir die res van die diepte van die area. Besoedelingsstowwe wat se oplosbaarheid dus afhang van pH (sommige besoedelingsstowwe los beter op in omgewings met laer pH waardes), sal loog deur die eerste paar meter grond en dan presipiteer waar pH waardes weer toeneem.

Beduidende konsentrasies chroom (Cr) (0.4 - 1.925mg/l) is gevind is al die boorgate aan die ooste kant van die SNP fabriek. Dit was vasgestel dat die oorsprong van hierdie chroom die gronde aan die suide kant van SNP is waar daar 'n leerlooierij in die verlede was.

A.g.v. die bewyse van die effektiwiteit van die plante in die noord-oostelike hoek van die fabriek wat die konsentrasies van besoedelingsstowwe verlaag, word Phito-remediasie voorgestel as 'n goeie opsie om die area te rehabiliteer.



