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Evaluating High-Resolution Site Characterisation Tools and Multiphase Modelling to Predict LNAPL Distribution and Mobility

by Jonás García Rincón

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Dr. Robert G. McLaughlan (UTS) and Mr. John L. Rayner (CSIRO)

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Certificate of original authorship

I, Jonás García Rincón declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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List of publications

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Lenhard, R.J., Rayner, J.L., García-Rincón, J. (2019). Testing an analytical model for predicting subsurface LNAPL distributions from current and historic fluid levels in monitoring wells: A preliminary test considering hysteresis. Water, 11, Article 2404. Impact factor (2018): 2.524.

Gatsios, E., García-Rincón, J., Rayner, J.L., McLaughlan, R.G., Davis, G.B. (2018). LNAPL transmissivity as a remediation metric in complex sites under water table fluctuations. Journal of Environmental Management, 215, 40–48. Impact factor (2017): 4.005.

Martínez-Santos, P., Martín-Loeches, M., García-Castro, N., Solera, D., Díaz-Alcaide, S., Montero, E., García-Rincón, J. (2017). A survey of domestic wells and pit latrines in rural settlements of Mali: implications of on-site sanitation on the quality of water supplies. International Journal of Hygiene and Environmental Health, 220(7), 1179–1189. Impact factor (2017): 4.848.

Technical reports

Bekele, E.B., García-Rincón, J., Rayner, J.L., McLaughlan, R.G., Gatsios, E., Paiva Lago, G. (2019). Groundwater pumping test analyses for a gasoline contaminated site at Donnybrook, Western Australia. Commonwealth Scientific and Industrial Research Organisation.

Conference presentations, papers, and posters

García-Rincón, J., Gatsios, E., Rayner, J.L., McLaughlan, R.G. (2020, March). High-resolution vertical profiling in challenging subsurface settings [Conference session]. High Resolution Characterisation Conference, Sydney, NSW, Australia.

Gatsios, E., García-Rincón, J., Rayner, J.L. (2018, September). LNAPL transmissivity: comparison of theoretical, field and modelling estimations in a multi-layered aquifer in Western Australia [Paper presentation]. 6th International Conference on Industrial and Hazardous Waste Management, Chania, Greece.

García-Rincón, J., Gatsios, E., Rayner, J.L., Lenhard, R.J. (2018, May). Comparison of analytical models to estimate LNAPL distribution and transmissivity in a heterogeneous site [Poster presentation]. New Zealand 5th Contaminated Land Conference, Christchurch, New Zealand.

García-Rincón, J., Johnston, C.D., McLaughlan, R.G. (2015, September). Multiphase modelling of LNAPL remediation options in aquifers with complex geologies [Poster presentation]. CleanUp 2015: 6th International Contaminated Site Remediation Conference, Melbourne, VIC, Australia.

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Nomenclature and acronyms

Symbol	Definition	Units
AHD	Australian Height Datum	n/a
AIC	Akaike information criterion	-
API	American Petroleum Institute	n/a
b_n	In-well NAPL thickness	m
bgl	Below ground level	n/a
B–C	Brooks and Corey	n/a
BTEX	Benzene, toluene, ethylbenzene, xylene	n/a
CP	Cumulative probability	-
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment	n/a
CSIRO	Commonwealth Scientific and Industrial Research Organisation	n/a
CSM	Conceptual site model	n/a
CV	Coefficient of variation	%
CVR	Robust coefficient of variation	%
d	Diameter	mm
d_E	Effective grain size	mm
d_{UU}	d_E from Urumović and Urumović Sr (2017)	mm
d_{VS}	d_E from Vuković and Soro (1992)	mm
D^{max}	Output value when input is set at the maximum	output's
D^{min}	Output value when input is set at the minimum	output's
DGP	Diagnostic gauge plot	n/a
DNAPL	Dense non-aqueous phase liquid	n/a
DPIL	Direct-push injection logging	n/a

DTN	Depth to NAPL	m
DTW	Depth to water	m
DvD	Discharge versus drawdown	n/a
e	Residual error	variable's
EC	Electrical conductivity	mS/m
ECDF	Empirical cumulative distribution function	n/a
EEM	Excitation–Emission Matrix	n/a
EPS	Extracellular polymeric substances	n/a
ETBE	Ethyl tert-butyl ether	n/a
f_{oc}	Fraction of organic carbon	-
FID	Flame ionisation detector	n/a
GC	Gas chromatography	n/a
h_{min}	Threshold pressure in the B–C model	cm
∇H_n	Lateral gradient in the LNAPL head	-
∇H_w	Groundwater hydraulic gradient	-
HPT	Hydraulic Profiling Tool®	n/a
HPT P	HPT average pressure	kPa
HPT Q	HPT flow injection rate	mL/min
HRSC	High-resolution site characterisation	n/a
HSA	Hollow stem augering	n/a
IDW	Inverse distance weighting	n/a
IQR	Interquartile range	variable's
ITRC	Interstate Technology and Regulatory Council	n/a
k_{rn}	NAPL relative permeability	-
k_{rw}	Water relative permeability	-
k_{sw}	Water-saturated hydraulic conductivity	m/day

k_n	NAPL hydraulic conductivity	m/day
K	Intrinsic permeability	m^2
LDRM	LNAPL Distribution and Recovery Model®	n/a
LIF	Laser-induced fluorescence	n/a
LNAPL	Light non-aqueous phase liquid	n/a
LNAPLTRANS	Updated version of LNAPLVOL	n/a
LNAPLVOL	Lenhard et al. (2017) model	n/a
LOD	Limit of detection	mg/kg
m_{od}	Mass of oven-dried sample	kg
m_{water}	Mass of water	kg
m_{wet}	Wet mass of sample	kg
M	Median	variable's
M_n	Inherent LNAPL mobility	m/day
MAD	Median absolute deviation	variable's
MAE	Mean absolute error	variable's
MIP	Membrane Interface Probe®	n/a
ML	Silt material or ID code for mult-level wells	n/a
MN	Methylnaphthalene	n/a
MS	Mass spectrometry	n/a
MTBE	Methyl tert-butyl ether	n/a
n	Number of samples	-
NAPL	Non-aqueous phase liquid	n/a
NIQ	Normalised interquartile range	variable's
NSZD	Natural source zone depletion	n/a
OIP	Optical Image Profiler	n/a
pxx	xx^{th} percentile	variable's

P_c-S	Capillary pressure-saturation	n/a
PAH	Polycyclic aromatic hydrocarbon	n/a
PARAFAC	Parallel factor analysis	n/a
PID	Photo-ionisation detector	n/a
PPE	Personal protective equipment	n/a
Q/P	Ratio between HPT P and HPT Q	mL/(kPa·min)
Qx	*x* quartile (first quartile or third quartile)	variable's
R^2	Coefficient of determination	-
RAIS	Risk Assessment Information System	n/a
RE	Reference emitter	n/a
RETC	RETention Curve computer program	n/a
RMSE	Root mean square error	variable's
S_n	NAPL saturation	-
S_{ne}	Entrapped NAPL saturation	-
S_{ne}^{max}	Maximum entrapped NAPL saturation	-
S_{nr}	Residual NAPL saturation	-
S_{nr}^{max}	Maximum residual NAPL saturation	-
S_w	Water saturation	-
S_{wr}	Residual water saturation	-
SD	Standard deviation	variable's
SI	Sensitivity index	-
SM	Silty sand	n/a
SP	Poorly sorted sand	n/a
SW	Well-sorted sand	n/a
t	Time	day
T_n	NAPL transmissivity	m^2/day

T_w	Aquifer transmissivity	m^2/day
TMB	Trimethylbenzene	n/a
TPH	Total petroleum hydrocarbon	n/a
UNSODA	Unsaturated Soil hydraulic Database	n/a
USCS	Unified Soil Classification System	n/a
USDA	United States Department of Agriculture	n/a
UVOST®	Ultra-Violet Optical Screening Tool®	n/a
v_n	NAPL velocity	m/day
V_n	NAPL specific volume	m
V_{sample}	Volume of sample	m^3
VEQ	Vertical hydrostatic equilibrium	n/a
vG	van Genuchten	n/a
$vG\text{-}\alpha$	van Genuchten α parameter	m^{-1}
$vG\text{-}m$	van Genuchten m parameter	-
$vG\text{-}N$	van Genuchten N parameter	-
VOC	Volatile organic compound	n/a
z_{an}	Air-NAPL interface elevation	m AHD
z_{an}^{max}	Historical maximum air-NAPL interface elevation	m AHD
z_{an}^{min}	Historical minimum air-NAPL interface elevation	m AHD
z_{aw}	Potentiometric surface elevation	m AHD
z_{nw}	NAPL–water interface elevation	m AHD
z_{nw}^{max}	Historical maximum NAPL–water interface elevation	m AHD
z_{nw}^{min}	Historical minimum NAPL–water interface elevation	m AHD
η_n	NAPL viscosity	kg m^{-1} s^{-1}
η_{rn}	Relative NAPL viscosity, NAPL viscosity ratio	-
Φ	Porosity	-

ρ_b	Bulk density	mg/kg
ρ_n	NAPL density	mg/kg
ρ_{rn}	Relative NAPL density, NAPL specific gravity	-
ρ_s	Particle density	mg/kg
θ_g	Gravimetric water content	-
θ_n	Volumetric NAPL content	-
θ_{wr}	Irreducible water content	-
θ_{ws}	Saturated water content	-
σ_{an}	NAPL surface tension	mN/m
σ_{aw}	Water surface tension	mN/m
σ_{nw}	NAPL–water interfacial tension	mN/m

Abstract

Petroleum hydrocarbons in the form of light non-aqueous phase liquids (LNAPLs) are some of the most common subsurface contaminants in urban and industrial environments. LNAPLs may persist in soil and groundwater systems for decades because of their challenging characterisation and remediation. In this research, high-resolution site characterisation (HRSC) tools such as direct-push injection logging (DPIL) and laser-induced fluorescence (LIF) as well as a recently developed multiphase analytical model (LNAPLTRANS) were evaluated in the assessment of LNAPL distribution and mobility.

Two field sites from Western Australia (a petrol station site showing seasonal LNAPL confinement in a heterogeneous aquifer–aquitard system and an industrial site with multiple types of LNAPL in a sandy aquifer) were investigated. The variability and most likely values of subsurface parameters required by the models were quantified through field methods, laboratory measurements, and the analysis of previous reports. DPIL, LIF, and LNAPLTRANS were compared to other tools such as LNAPL diagnostic gauge plots, hydraulic testing, coring, and the LDRM model.

DPIL allowed rapid collection of comprehensive data sets revealing hydrostratigraphic features overlooked by conventional methods. Predictions of water-saturated hydraulic conductivity were typical of sandy aquifers and not strongly influenced by the presence of LNAPL. The DPIL quantification model could have underestimated the variability of water-saturated hydraulic conductivity according to other field measurements.

LIF logging was used to assess LNAPL mobility. LIF response was correlated with LNAPL transmissivity, unlike LNAPL saturation values from coring. Furthermore, LIF logging facilitated the identification of intervals with long-term entrapped and residual LNAPL because of the multi-wavelength waveforms associated with distinct subsurface characteristics. LIF lifetime data and other LIF metrics could improve the delineation of LNAPL-impacted intervals, although non-unique interpretations of HRSC logs may exist. Therefore, investigators should always consider multiple lines of evidence.

The application of multiphase analytical models represented a practical way to investigate subsurface scenarios partly accounting for the strong variability of

subsurface parameters. LNAPL transmissivity exhibited the largest sensitivity to retention parameters and water-saturated hydraulic conductivity, being also influenced by the relative permeability model. Changes in residual LNAPL saturation affected LNAPLTRANS and LDRM predictions of LNAPL transmissivity in opposite ways. Thus, further research should be conducted on characterisation and modelling of near-immobile LNAPL fractions and retention parameters. Future HRSC approaches should exhibit a more quantitative nature and better integrate scale-appropriate measurements in time and space, eventually resulting in more effective and sustainable management of LNAPL contaminated sites.