

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

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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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Robert J. Lenhard has also provided constant support, advice, and direction since he joined CSIRO. Furthermore, Bob developed one of the multiphase models evaluated in the thesis (LNAPLTRANS). To date, we have co-authored one journal paper (Lenhard et al., 2019) and one conference poster (García-Rincón et al., 2018).

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Evangelos Gatsios participated in practically all the field campaigns in the petrol station site since 2014 and we have extensively collaborated in the analysis of field data. In particular, the interpretation of baildown tests was a central part of his doctoral

dissertation (Gatsios, 2018) and we worked together in the assessment of LNAPL confinement conditions (with my analyses being presented in section 5.2). We have co-authored most of publications associated to our theses.

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Robert Woodbury set up a new soil physics laboratory and assisted in the measurement of LNAPL physical properties. Furthermore, he regularly assisted in the instrumentation, characterisation, and monitoring of the field sites along with other CSIRO Land and Water staff such as Gabriel Paiva Lago, Andrew Furness, Mike Donn, and Geoffrey Puzon. Trevor Bastow and Yasuko Geste assisted in the preparation and chemical analysis of the samples. Other current and former CSIRO staff (Rodrigo Rojas, Mike Trefry, Kaveh Sookhak Lari, Greg Lekmine, John Knight, Jungho Park) have provided valuable input and fruitful discussions.

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# List of publications

## Peer-reviewed journal papers

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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]. 6<sup>th</sup> 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 5<sup>th</sup> 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: 6<sup>th</sup> 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
$\nabla H_n$	Lateral gradient in the LNAPL head	-
$\nabla H_w$	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 <sup>2</sup>
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 <sup>th</sup> 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)
Q <sub>x</sub>	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 <sup>2</sup> /day

$T_w$	Aquifer transmissivity	m <sup>2</sup> /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 <sup>3</sup>
VEQ	Vertical hydrostatic equilibrium	n/a
vG	van Genuchten	n/a
$vG-\alpha$	van Genuchten $\alpha$ parameter	m <sup>-1</sup>
$vG-m$	van Genuchten $m$ parameter	-
$vG-N$	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
$\eta_n$	NAPL viscosity	kg m <sup>-1</sup> s <sup>-1</sup>
$\eta_{rn}$	Relative NAPL viscosity, NAPL viscosity ratio	-
$\Phi$	Porosity	-

$\rho_b$	Bulk density	mg/kg
$\rho_n$	NAPL density	mg/kg
$\rho_{rn}$	Relative NAPL density, NAPL specific gravity	-
$\rho_s$	Particle density	mg/kg
$\theta_g$	Gravimetric water content	-
$\theta_n$	Volumetric NAPL content	-
$\theta_{wr}$	Irreducible water content	-
$\theta_{ws}$	Saturated water content	-
$\sigma_{an}$	NAPL surface tension	mN/m
$\sigma_{aw}$	Water surface tension	mN/m
$\sigma_{nw}$	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.