From Soil to Groundwater:
Assessing the leaching potential of cadmium across gradients of soil types and land-uses

A thesis

submitted in fulfilment of the requirement for the degree
of

Doctor of Philosophy in Environmental Science

at

The University of Waikato

By

Amir Mohammadi

THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

2022

Abstract

The problem: The productivity of agriculture, the mainstay of New Zealand' economy, relies on millions tons of fertiliser to maintain soil fertility. These fertilisers contain contaminants, including cadmium (Cd) which pose risks to the environment and human health. The assessment of the bioavailability, mobility, and fate of fertiliser-derived contaminants is therefore important in protecting the environment and human health. In order to manage fertiliser inputs accurately, authorities and protection agencies have struggled with tracing the Cd fluxes between fertilised soil, shallow groundwater and the biomass of plants. A number of analytical and experimental challenges hinder the application of conventional methods in these systems.

Proposed research: A realistic assessment of the environmental impact of fertiliser-derived contaminants requires non-perturbing and sensitive sampling techniques for detecting contaminants of interest. Diffusive gradients in thin films (DGT) is an established in-situ technique that can provide information on the concentrations and bioavailability of diverse contaminants in soil, sediment and groundwater. The DGT method has rarely been applied to relatively slowly moving groundwater systems, where the increased length of the diffusive boundary layer (DBL) needs to be taken into account. Three different DGT approaches were tested to overcome the limitations associated with the direct application of DGTs to groundwater systems a static DGT suspension, a DGT shaker, and a pumped flow-cell unit coined the "universal DGT monitoring system" (UDMS). The analysis of stable isotope ratios was used to investigate the Cd cycle in agricultural systems. The isotope data enabled us to trace fertiliser-derived Cd in soil−pasture−groundwater systems across gradients of soil types and land-uses. Additionally, the effects of farm management strategies (urine and farm dairy effluent) on the transport of metals and nutrients from soil to groundwater were determined through testing archived samples from the Lincoln University Dairy Farm (LUDF) lysimeter trial. The hydrogeochemical properties of soils and different treatments may enhance metal leaching and transport. Through a statistical analysis of the data, this study aimed to test the hypotheses that the leaching potential of metals and nutrients in soils varies depending on the type of soil and farm management strategies.

Research outcome: The Universal DGT Monitoring System (UDMS)-a pumped flow-cell setup was developed to overcome stagnant conditions and reducing diffusive boundary layer thicknesses by fourfold. The UDMS method is particularly suitable for monitoring low-level contaminants like Cd and conditions with frequent fluctuations in shallow aquifer concentrations. Coupling UDMS and stable isotope ratio methods demonstrated that Cd isotopes are significantly and systematically fractionated in groundwater, soil, and pasture systems. Fractionation patterns in these systems provide insight into hydrogeochemical processes controlling the mobilisation of contaminants in the subsurface. According to the results of the study, soil types and hydraulic properties of soils are probably more important factors than farm treatments and strategies for the leaching of metals and nutrients. The intrinsic degree of leaching, however, could not be determined without control treatments. To understand the driving factors of high mobilisation events, further study is necessary to determine how amended versus unamended soils differ.

Acknowledgements

The journey to the completion of my PhD would not have been possible without the support of my supervisors, advisors, family members, and friends. I completed my PhD thanks to the efforts of each individual and group.

In many ways, I owe this achievement to my amazing mother, Nazila, as well as to my beloved wife, Vida. I wouldn't have started and finished my degree without their wholehearted support. Thank you for everything!

I would like to express my deepest appreciation to my chief supervisor, Dr Adam Hartland, for accepting me as a PhD student in Waikato Environmental Geochemistry (WEG) research group. I am very grateful to you for your creativity, relentless support, and invaluable insight into this thesis and the published articles. Many thanks for your funding support during the COVID pandemics, which relieved financial stress. I very much appreciate that you have been patient will all my questions. You are a great mentor!

It has been a privilege to work with my co-supervisors, Prof Louis Schipper and Dr Ali Shokri. Thank you for all your insightful feedback and comments, which helped me through designing, testing, and interpreting the results.

I would like to thank Dr Niklas Lehto and Prof Richard McDowell, for providing the lysimeter samples and guidance in data analysis. Special thanks to John Hadfield, Matt Taylor, John Hughey, and Sajeewa Herath at Waikato Regional Council for providing access to the study sites across the Waikato region, as well as installing piezometers in Scott farm. I would like to thank Peter Jarman and Dean Sandwell for their creative ideas in designing and developing the UDMS. Dr Thomas Corbett, it was a great pleasure to work with you and thank you for making the lab works fun! Dr Huma Saeed, thank you for teaching me how to assemble DGTs, and for being my lab supervisor for the few months that Adam was in Europe! Dr Mahdiyeh Salmanzadeh, thank you for your help during the MBIE project. Thanks to Dr Claudine Stirling for the isotope analysis. I appreciate Dairy NZ for providing access to the Scott Farm site and for the research and stipend fund. Thanks to Annie Barker, Amanda French, Renat Radosinsky, Noel Bates, and Jenny Stockdill for constant instrumental and laboratory support. Special thanks to my friends, Mehdi Ghorashi Nezhad for graphical design support, Dr Mostafa Seifan for technical design, and Sajed Golabpars for helping in Arduino programming. Last but not least, thanks to The University of Waikato for the doctoral scholarship and support.

Remembering Mahsa Amini and
176 passengers of flight PS752

Table of Content

List of Abbreviations

A_e	Effective exposure window area
A520E	Polystyrenic Macroporous Strong Base Anion Ion Exchange Resin
ADBL	Apparent Diffusive Boundary Layer
Al	Aluminum
A_p	Physical exposure window area
As	Arsenic
Au	Gold
$Ca(NO_3)_2$	Calcium nitrate
CadBal	Cadmium Mass Balance
Cd	Cadmium
C_{DGT}	Diffusive Gradients in Thin-Films determined concentration
CdS	Cadmium Sulfide
ce	Measured concentration of analyte
CEC	Cation Exchange Capacity
Cl	Chlorine
Co	Cobalt
COOH	Carboxyl
Cr	Chromium
Cu	Copper
CU	Cow Urine
CWG	Cadmium Working Group
DBL	Diffusive Boundary Layer

D_f	Filter membrane diffusion coefficient
D^g	Gel diffusion coefficient
DGT	Diffusive Gradients in Thin Films
dh/dx	Hydraulic Gradient
DI	Deionised
D^{mdl}	Material diffusion layer diffusion coefficient
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
D^w	water diffusion coefficient
EC	Electrical Conductivity
FA	Fulvic Acid
FDE	Farm Dairy Effluent
Fe	Iron
f_e	Elution Factor
f_u	Uptake factor
H_20_2	hydrogen peroxide
$H_2PO_4^-$	Dihydrogen phosphate
H_2SO_4	Sulphuric acid
HA	Humic Acid
$HAsO_4^{2-}$	Hydrogen arsenate
HCl	Hydrochloric acid
$HClO_4$	Perchloric Acid
HF	Hydrofluoric Acid
HNO_3	Nitric acid

ICP-MS	Inductively Coupled Plasma Mass Spectrometer
k	Hydraulic Conductivity
ks	Saturated Hydraulic Conductivity
LUDF	Lincoln University Dairy Farm
M	Mass
MAV	Maximum Acceptable Value
MDL	Material Diffusion Layer
M_e	Mass of analyte in the eluent solution
M_f	Remaining mass of analyte in the solution after the experiment
M_i	Initial mass of analyte
Mn	Manganese
N_2	dinitrogen
N_2O	Nitrous oxide
NH_4	Ammonium
Ni	Nickel
NO	Nitric oxide
NO_2^-	Nitrogen Dioxide
NO_3^-	Nitrate
NZ	New Zealand
O	Oxygen
OH	Hydroxyl
OM	Organic Matter
P	Phosphorus
Pb	Lead

S	Sulphur
Sb	Antimony
SO_4^{2-}	Sulfate
TFMS	Tiered Fertiliser Management System
TWA	Time Weighted Averages
U	Uranium
V^{bl}	Binding layer volume
V_D	Velocity of Water
V_e	Eluent Volume
WHO	World Health Organization
$\overline{Y}$	dataset mean value
Y_i	value of the datapoint
Zn	Zinc
$\delta^{114/111}Cd$	Cd stable isotope ratio
δ^{adbl}	Apparent Diffusive boundary layer thickness
δ^{dbl}	Diffusive boundary layer thickness
δ^{f}	Filter membrane thickness
δ^{g}	Filter membrane and ion-permeable gel membrane thickness
δ^{mdl}	Material diffusion layer thickness

Chapter 1 - Introduction, Thesis Aim and Outline

1.1. Introduction

New Zealand's (NZ) economy is strongly rooted in agriculture. Pastoral farming is the most predominant form of agriculture, producing roughly 25.9 million sheep, 23.1 million lambs, 3.9 million beef, 6.2 million dairy cattle, and roughly 1 million deer and pigs on an annual basis (New Zealand Stats, 2022). To maintain soil fertility for pastoral farming and horticulture, millions of tons of fertiliser are applied annually. Phosphate fertilisers (P-fertilisers) have historically been used to increase soil fertility. There is, however, a wide range of potentially toxic elements (Cd, Ni, U, As, Zn, Cr, and Pb) present in P-fertilisers (Khan et al., 2017; Loganathan et al., 2003; Mortvedt, 1995), which make fertilizer impurities the contaminants of 'greatest concern' in NZ (Abraham, 2020; McDowell & Gray, 2022; Salmanzadeh et al., 2016; Stafford et al., 2018).

Cadmium is a biotoxic heavy metal, which may pose major risks to human health and the environment (Kumar & Sharma, 2019). Ingestion of contaminated soil, edible plants, and livestock are the main pathways for human Cd exposure (Feng et al., 2021; McLaughlin & Singh, 1999). Cd enters the food chain of grazing animals mostly via pasture uptake and soil ingestion (Cadmium Working Group, 2011; Thornton & Abrahams, 1983). Even in trace quantities, over a long period, substantial amounts of Cd bioaccumulate in bodily tissues and offal products, which aside from legitimate health concerns, could also be detrimental to NZ’s primary export market (Fertiliser Matters, 2005).

There are four major sources of Cd in agricultural soils globally: (1) Cd naturally occurring in soil, (2) P-fertilisers, (3) atmospheric deposition arising from industry, and (4) sewage application to agricultural land (Kubier et al., 2019; McDowell et al., 2013). Since NZ has relatively less heavy industry and mining than agricultural practices, P-fertilisers are the main source of Cd in soils (Salmanzadeh et al., 2016; Taylor et al., 2007). It is now widely accepted that the historical application of P-fertilisers (since the introduction of European agriculture in the late 1800s) has resulted in an undesirably high concentration of Cd in NZ topsoil (Gray et al., 1999; Kelliher et al., 2017; Salmanzadeh et al., 2017; Schipper et al., 2011).

Due to intensive fertiliser use and phosphate retention by soils, the concentration of Cd has increased in NZ agricultural soils, especially in the Waikato and Canterbury regions, where dairying and sheep farming predominate (Abraham, 2020; Cadmium Working Group, 2011; Taylor et al., 2007). It has been estimated that the concentration of Cd in over 11% of Waikato pasture soil and 17% of horticultural soils has already exceeded 1 mg/kg (Environment Waikato, 2005). Cd enrichment in soil may limit its future land use, since levels above 1.8 mg/kg are considered contaminated sites, and no further accumulation of Cd is permitted until risks and pathways for potential harm are identified (Sneath, 2020). Leachate from fertilisers can percolate into the subsurface and contaminate underlying aquifers. Studies conducted in Waikato and Canterbury have concluded that Cd losses from agricultural soils have accelerated since 2000 (McDowell & Gray, 2022; Salmanzadeh et al., 2017). It is possible that these soils have reached the limit of their Cd carrying capacity. Given the stable Cd concentration in soils as well as the annual application of millions of tons of fertiliser to agricultural soils, it is plausible that the Cd is mobilised more readily from agricultural soils. Uptake by crops or translocation in soils and possible leaching to groundwater are the most probable trajectories for Cd release (Gray & Cavanagh, 2022).

While Cd management strategies and control measures have proven to be effective in slowing the accumulation rate in NZ soil, there is a great deal of uncertainty regarding the potential impacts on NZ agricultural systems. Therefore, further research is needed on the environmental impact of Cd, identifying the sources of Cd in groundwater and pastures, identifying the pathways and transport mechanisms, and assessing the leaching potential across gradients of soil types and land-uses. Thus, the present study is designed to fill the gap in our knowledge regarding the impacts of fertiliser-derived Cd in NZ agricultural soil, pasture, and groundwater systems.

1.2. Thesis Aims and Objectives

This study represents a global first in assessing the impacts of fertiliser-derived Cd on the soil, groundwater, and pasture systems. This research project can be broken down into three components.

Objective 1. Demonstration of the application of DGT for monitoring Cd and other contaminants in groundwater systems

First, a novel set of passive sampling methods were used to better understand the dispersion of Cd in groundwater. Here, the application of diffusive gradients in thin films (DGT) for monitoring Cd in groundwater were tested by deployment in groundwater piezometers. Three different approaches were tested in order to overcome the limitations associated with the direct application of DGTs to groundwater. These results were then compared with those acquired by the standard grab sampling method. In order to cover a wide range of Cd concentrations, DGT units were deployed both in regions exhibiting Cd accumulation and in areas with lower Cd levels. Results were published in the article entitled “Application of diffusive gradients in thin films (DGT) for monitoring groundwater quality”.

Objective 2. Assessing Cd leaching potential across different soil types and farm effluent management strategies

The individual and combined effects of farm dairy effluent (FDE) and cow urine (CU) on the leaching of metals and nutrients in Eyre (excessively-drained) and Templeton (well-drained) soils were assessed. Samples of leachate from sixty lysimeters at Lincoln University Dairy Farm (LUDF) with various treatment combinations were tested. Analytical methods were used to detect high mobilisation events and determine which treatments induced higher degree of leaching. Results will be published in an article entitled “Effects of dairy farm effluent management on cadmium, metal and nutrient leaching: A lysimeter trial on two contrasting soils”.

Objective 3. Isotope based assessment of the extent of fertiliser-derived Cd in soil, groundwater, and pasture

The transfer mechanisms of fertiliser-derived Cd from agricultural soils into groundwater and pastures were studied by coupling stable isotope ratio analysis and diffusive gradients in thin films. This study reports stable isotope ratios of Cd ($\delta^{114/111}$Cd) from two contrasting but uniformly fertilised soils (Te Kowhai and Horotiu) as well as pasture and in-situ groundwater measurements using DGTs. Results will be published in an article entitled “Tracing fertiliser-derived Cd in soil−pasture−groundwater systems: Coupling stable isotope ratio analysis and diffusive gradients in thin films”.

1.3. Thesis Structure and Outline

In Chapter 2 (Literature Review), a focused literature review on Cd in NZ agricultural soils, principles of hydrochemical and biogeochemical processes controlling the transport of Cd and co-contaminants in the sub-surface, dairy farm management strategies, diffusive gradients in thin-films, stable isotope ratio analysis for tracing contaminants in the environment, and the limitations associated with these methods is presented. The purpose of this review is to contextualise the study within a larger body of literature, identify limitations associated with sampling techniques, and provide a theoretical framework for the analysis.

Chapters 3−5 are journal articles presented as independent manuscripts, which consist of an abstract, introduction, methodology, results, and discussion of the conducted research. Throughout each chapter, the above-mentioned objectives (Section 1.2) are discussed in detail.

Chapter 6 (Summary and Conclusions) summarises the research project, the results and conclusions, discusses how they address the previously identified gaps in our knowledge of Cd mobilisation across soil types and land-management practices, and provides recommendations for future research.

1.4. Ethical Approval

This research does NOT involve human or animal subjects. Therefore, this project was not submitted for ethics approval to the Waikato Management School Ethics Committee.

References

Abraham, E. (2020). Cadmium in New Zealand agricultural soils. New Zealand Journal of Agricultural Research, 63(2), 202–219.

Cadmium Working Group. (2011). Cadmium and New Zealand agriculture and horticulture: A strategy for long term risk management. Ministry of Agriculture and Forestry, Wellington, NZ.

Environment Waikato. (2005). Cadmium Accumulation in Waikato Soils, Waikato Regional Council.

Feng, J., Shen, R. F., & Shao, J. F. (2021). Transport of cadmium from soil to grain in cereal crops: A review. Pedosphere, 31(1), 3–10.

Fertiliser Matters. (2005). Cadmium in New Zealand--an update. Auckland, New Zealand Fertiliser Manufacturer's Research Association. Newsletter, 34.

Gray, C., McLaren, R., Roberts, A., & Condron, L. (1999). Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. European Journal of Soil Science, 50(1), 127–137.

Gray, C. W., & Cavanagh, J.-A. E. (2022). The state of knowledge of cadmium in New Zealand agricultural systems: 2021. New Zealand Journal of Agricultural Research, 1–51.

Kelliher, F. M., Gray, C. W., & Noble, A. D. L. (2017). Superphosphate fertiliser application and cadmium accumulation in a pastoral soil. New Zealand Journal of Agricultural Research, 60(4), 404–422. https://doi.org/10.1080/00288233.2017.1363058

Khan, M. N., Mobin, M., Abbas, Z. K., & Alamri, S. A. (2017). Fertilizers and their contaminants in soils, surface and groundwater. In Encyclopedia of the Anthropocene (Vols. 1–5). Elsevier Inc. https://doi.org/10.1016/B978-0-12-809665-9.09888-8

Kubier, A., Wilkin, R. T., & Pichler, T. (2019). Cadmium in soils and groundwater: A review. Applied Geochemistry, 108(February). https://doi.org/10.1016/j.apgeochem.2019.104388

Kumar, S., & Sharma, A. (2019). Cadmium toxicity: effects on human reproduction and fertility. Reviews on Environmental Health, 34(4), 327–338.

Loganathan, P. A., Hedley, M. J. A., Grace, N. D. B., Lee, J. B., Cronin, S. J. A., & Bolan, N. S. A. (2003). Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine : a review. 501–532.

McDowell, R. W., & Gray, C. W. (2022). Do soil cadmium concentrations decline after phosphate fertiliser application is stopped: A comparison of long-term pasture trials in New Zealand? Science of the Total Environment, 804, 150047. https://doi.org/10.1016/j.scitotenv.2021.150047

McDowell, R. W., Taylor, M. D., & Stevenson, B. A. (2013). Natural background and anthropogenic contributions of cadmium to New Zealand soils. Agriculture, Ecosystems and Environment, 165, 80–87. https://doi.org/10.1016/j.agee.2012.12.011

McLaughlin, M. J., & Singh, B. R. (1999). Cadmium in soils and plants. In Cadmium in soils and plants (pp. 1–9). Springer.

Mortvedt, J. J. (1995). Heavy metal contaminants in inorganic and organic fertilizers. Fertilizer Research, 43(1), 55–61. https://doi.org/10.1007/BF00747683

New Zealand Stats. (2022). Agricultural production statistics. https://www.stats.govt.nz/

Salmanzadeh, M., Balks, M. R., Hartland, A., & Schipper, L. A. (2016). Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history. Geoderma Regional, 7(3), 271–278. https://doi.org/10.1016/j.geodrs.2016.05.001

Salmanzadeh, M., Hartland, A., Stirling, C. H., Balks, M. R., Schipper, L. A., Joshi, C., & George, E. (2017). Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil. https://doi.org/10.1021/acs.est.7b00858

Schipper, L. A., Sparling, G. P., Fisk, L. M., Dodd, M. B., Power, I. L., & Littler, R. A. (2011). Agriculture , Ecosystems and Environment Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer. “Agriculture, Ecosystems and Environment,” 144(1), 95–101. https://doi.org/10.1016/j.agee.2011.08.002

Sneath, G. (2020). Revision of the tiered fertiliser management system for soil cadmium. Nutrient Management in Farmed Landscapes. Occasional Report, 33.

Stafford, A. D., Palmer, A. S., Jeyakumar, P., Hedley, M. J., & Anderson, C. W. N. (2018). Soil cadmium and New Zealand dairy farms: Impact of whole-farm contaminant variability on environmental management. Agriculture, Ecosystems and Environment, 254(August 2017), 282–291. https://doi.org/10.1016/j.agee.2017.11.033

Taylor, M., Gibb, R., Willoughby, J., Hewitt, A., & Arnold, G. (2007). Soil Maps of Cadmium in New Zealand. June.

Thornton, I., & Abrahams, P. (1983). Soil ingestion—a major pathway of heavy metals into livestock grazing contaminated land. Science of the Total Environment, 28(1–3), 287–294.

Chapter 2 - Literature Review

2.1. Cadmium in New Zealand Soil−Pasture−Groundwater Systems

It is now widely accepted that the historical application of P-fertilisers has resulted in undesirably high concentrations of Cd in NZ agricultural soils (McDowell, 2012; Salmanzadeh et al., 2017; Schipper et al., 2011). In P-fertilisers, Cd originates from the phosphate source rock, and depends on the source rock and the ratio of acid to rock used in manufacturing (Syers et al., 1986). Before 1997, Nauru Island phosphorites (mean concentration of 450 mg Cd/kg P in fertiliser) were the main source of P-fertilisers in NZ. To reduce the pressure on New Zealand's natural resources, the fertiliser industry decided to produce P-fertilisers with a lower Cd concentration from 1997 onwards. Thus, the main source of phosphate rocks was changed to produce fertilisers with < 280 mg Cd/kg P, which for context is slightly lower than Australia (300 mg Cd/kg P) and about 2−5 times higher than Scandinavian countries (50−150 mg Cd/kg P) (Loganathan et al., 2003). Currently, there appears to be no economically viable way to remove Cd from P-fertiliser during manufacturing (Cadmium Working Group, 2011). Accordingly, sourcing low Cd phosphate rocks is the path adopted by the NZ fertiliser industry in order to produce P-fertilisers with lower Cd concentrations.

In 1990, the average accumulation rate of Cd for NZ pastoral and horticultural soils was 11.8 µg/kg soil/year (Environment Waikato, 2005). Since the change in phosphate rock source in 1997, the Cd accumulation rate in agricultural soil in some areas has decreased to two-thirds of the previous rate (Cadmium Working Group, 2011). Between 2005 and 2010, the national average accumulation rate was approximately 5.0 µg/kg soil/year. Between 2002 and 2003, it is estimated that the average accumulation rate in horticultural soils and pastoral soils over the Waikato region was 8.1 and 9.0 µg/kg soil/year, respectively (Environment Waikato, 2005). In New Zealand soils, the naturally-occurring Cd concentration is estimated at 0.16 mg/kg (range 0−0.77 mg/kg), and the national average Cd concentration in all agricultural soils is estimated at 0.35 mg/kg (Figure 2.1, range of 0−2.52 mg/kg) (Cadmium Working Group, 2011; Taylor et al., 2007). Hence, agricultural topsoils have approximately 2x the natural background level of Cd.

The presence of Cd in agricultural soils raises the issue of potential Cd leaching to groundwater. Water that percolates through soil and leaches metals from the unsaturated zone, can eventually translocate Cd to the saturated zone, conceivably leading to Cd accumulation in groundwater. Excessively-drained soils and those with low CEC can accelerate contaminant leaching compared to soils with higher CEC and/or poor drainage (Environment Waikato, 2005).

NZ relies primarily on groundwater for drinking water. Consequently, groundwater monitoring by NZ regional councils aim to ensure the high quality of drinking water sources. Additionally, groundwater is widely used for irrigation and can therefore contribute to Cd leaching from soil (Salmanzadeh, Schipper, et al., 2017).

Gray and Cavanagh (2020) found that Cd concentrations in groundwater samples from irrigation-consented wells in Canterbury, Marlborough, and Wellington, and 81% of the samples from Waikato were below the instrumental detection limit (0.05 µg/L). In the Waikato region, 15 samples were above 0.1 µg/L, with a maximum value of 0.8 µg/L. Taylor et al. (2017) found detectable Cd in only 16% of groundwater monitoring sites in 2017, with the highest Cd concentration at 50% of the maximum acceptable value (MAV) for Cd in drinking water (4 µg/L). In a study of six regional council's groundwater quality datasets between 1995 and 2008 (1283 samples), Nokes and Weaver (2014) reported that Cd levels in 87% of the samples were below detection limits. Also, no Cd concentrations exceeded the MAV for Cd in drinking water. According to a related study by Daughney and Randall (2009), the general groundwater quality was either constant or slowly degrading (2−5% annually) at about two-thirds of the monitoring sites. The other one-third, however, was rapidly degrading (> 5% deterioration annually) as a result of human activity. While these studies concluded that there was no immediate public health risk associated with Cd in groundwater, soil should not necessarily be considered a permanent sink for Cd, but rather a temporary storage for Cd, which can increase groundwater concentrations overtime.

Plant uptake also contributes to soil losses of Cd if the plant biomass is removed (through cropping or grazing) (Wiggenhauser et al., 2016). Cd contamination of soil leads to considerable accumulation in edible parts of crops (Uraguchi et al., 2009). Plant tissues can absorb Cd from the soil, which is then ingested by animals or humans that consume the plants. Generally, the order of Cd accumulation in plants is roots > straw > shoots (Cadmium Working Group, 2011). Cd is mainly absorbed by plants through root adsorption (Zanders, 1998). Genetic differences in plant species affect the amount and rate of Cd accumulation (Hamon et al., 1997). To prevent negative effects on human health, it is necessary to reduce the translocation of Cd to the edible parts of the crops.

Ryegrass and clover mixtures are the traditional pastures of New Zealand. However, in recent years, there has been a substantial change in the types of forage species used in livestock grazing systems in New Zealand, with chicory and plantain becoming more popular (Gray & Cavanagh, 2022). Both of these forage species have consistently shown higher Cd concentrations (0.23−4.50 mg Cd/kg dry weight) than traditional pasture species and most other forage species (0.02−0.30 mg Cd/kg dry weight) (Cavanagh et al., 2015; Stafford, 2017). Plant uptake of Cd is also affected by soil properties. As an example, soil moisture cycles, water retention capacity, and waterlogging have been demonstrated to control Cd uptake in rice and plantains (Liu et al., 2017; Stafford et al., 2018). Results indicate that Cd solubility is affected by increases in soil moisture following periods of drainage, but not by short periods of soil saturation (Stafford et al., 2018).

2.1.1. Cadmium in offal products and drinking water

The MAV in offal products for human consumption is 1.25 and 2.25 mg Cd/kg fresh weight for kidney and liver, respectively (Fertiliser Matters, 2005). Cd concentrations exceeding the MAV set by authorities were found in offal products in the early 1990s. 20% of livestock had Cd concentrations higher than the MAV in their livers and kidneys (Loganathan et al., 2003). Consequently, Cd accumulation in NZ agricultural soils was identified as a long-term management concern.

The MAV for Cd in drinking water set by the World Health Organization (WHO) is 5 µg/L (World Health Organization, 2011) and the tolerable Cd intake for human adults is 1 µg Cd/kg body weight per day. Surveys of NZ residents' dietary Cd intake have shown that the monthly Cd intake is well below the provisional tolerable monthly intake of 25 µg/kg Body weight per month set by the WHO (Ministry for Primary Industries, 2019); however, Cd intake from supplies is likely underestimated because of difficulties in monitoring Cd levels in groundwater.

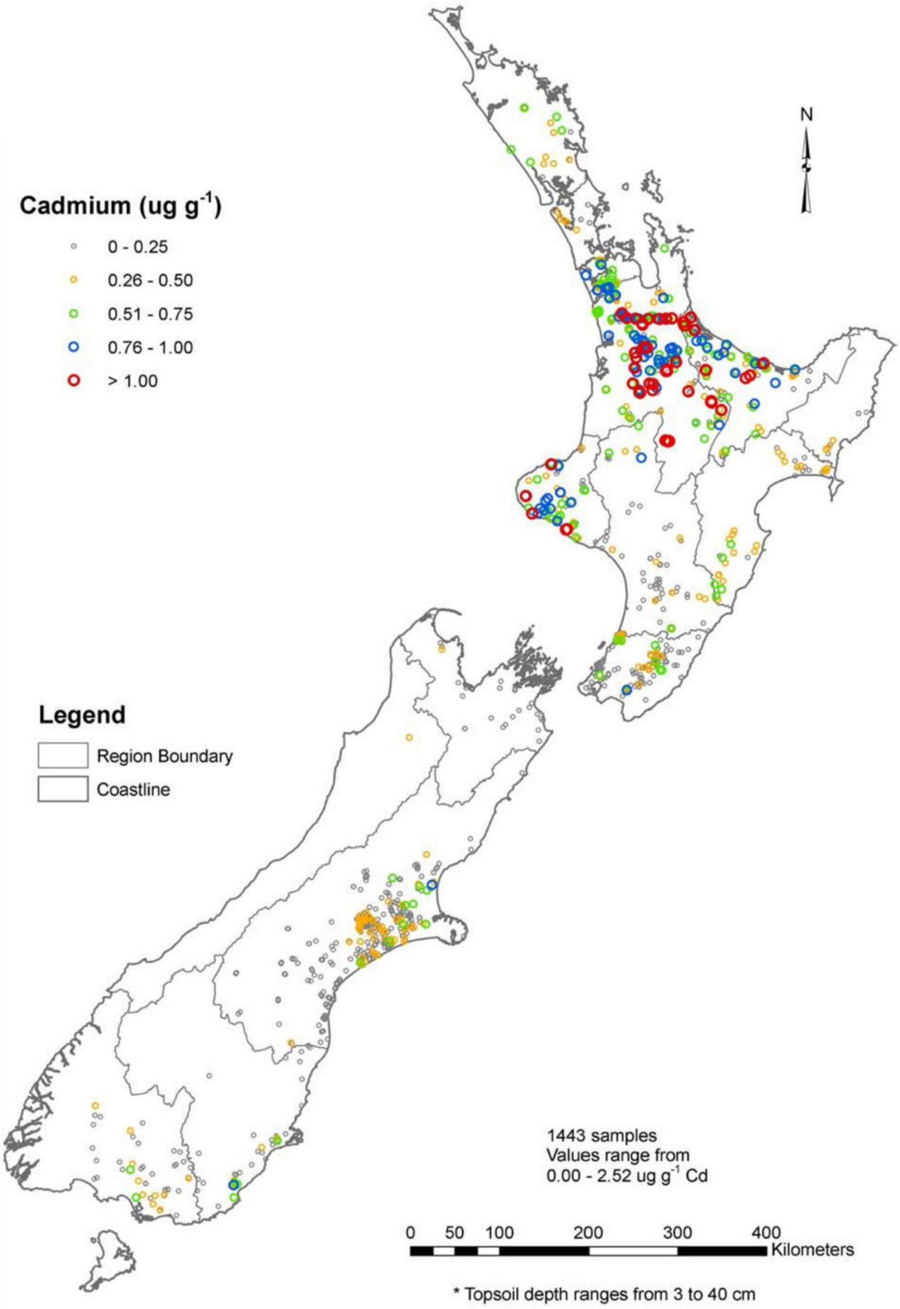


Figure 2.1: Regional map of topsoil cadmium levels, 1649 samples (Taylor et al., 2007)

2.2. Cadmium Concentrations Across Gradients of Soil Types and Land-uses

A national survey was conducted in the early 1990s to identify the effect of soil types and land-uses on Cd concentration in NZ agricultural topsoil (Longhurst et al., 2004). While the results showed no enrichment of Zn, As, Cu, and Pb of fertilised soil compared to the background soils, a two-fold enrichment of Cd was observed at farmed sites (0.44 mg/kg) over non-farmed sites (0.20 mg/kg). In 1994, Roberts et al. reported that Cd concentrations ranging from 0.04 to 1.53 mg Cd/kg (mean = 0.44) in pastoral topsoil (A horizon), which was two times higher than non-agricultural topsoil which ranging from 0.02 to 0.77 mg/kg (mean = 0.20). Among the soil groups, Yellow Brown Pumice (0.75 mg Cd/kg), Yellow Brown Loam (0.70 mg Cd/kg) and Peat (0.69 mg Cd/kg) showed the highest Cd concentrations.

Based on 1649 soil samples collected between 1989−1995 and 2000−2006, soil Cd concentrations ranging from 0 to 2.52 mg/kg (Table 2.1) (Taylor et al., 2007). For background soils (reserves, tussocks, bush, indigenous forests, and plantation forestry sites), the mean Cd concentration was 0.16 mg/kg, while the national mean soil Cd concentration for P-fertilised soils was 0.35 mg/kg. In this report, soil Cd concentrations varied between land-uses, with dairying having the highest Cd levels (0.73 mg Cd/kg), followed by kiwifruit (0.71 mg/kg). They also reported that the average value for drystock farming (0.40 mg/kg) was close to the national average.

Table 2.1: Soil Cd concentration in New Zealand by land-use (Taylor et al., 2007)

Category	**Land-use**	**Number of samples**	**Average Cd (mg/kg)**	**Range (mg/kg)**
Background	Native	69	0.10	<0.00–0.39
	Forestry	42	0.14	0.02–0.65
	Parks	36	0.11	0.06–0.20
	Tussock	4	0.08	0.07–0.09
	Unfertilised	221	0.19	0.02–0.77
	Total	372	0.16	**<0.00–0.77**
Cropping	Barley	6	0.15	0.10–0.25
	Maize	11	0.25	0.10–0.40
	Peas	3	0.15	0.11–0.17
	Tobacco	5	0.34	0.20–0.70
	Wheat	8	0.11	0.09–0.16
	Total	301	0.24	**<0.00–0.99**
Pasture	Dairy	144	0.73	0.00–2.52
	Deer	12	0.68	0.40–1.20
	Beef	48	0.42	0.04–1.40
	Horses	4	0.53	0.40–0.60
	Sheep	34	0.33	0.03–1.20
	Total Drystock	111	0.40	**<0.00–1.40**
	Total Pasture	825	0.43	**<0.00–2.52**
Horticulture	Berries	50	0.68	0.20–1.20
	Kiwifruit	37	0.71	0.30–1.20
	Vineyard	12	0.38	0.20–0.70
	Market Gardening	142	0.46	<0.00–2.00
	Orchard	49	0.66	0.10–1.50
	Total	296	0.50	**<0.00–2.00**

Consistent trends in soil Cd concentrations across land-uses were reported by Cavanagh (2014), with dairying (0.59 mg Cd/kg) and orchards (0.55 mg Cd/kg) having the highest levels. In this investigation which was conducted on 3900 samples from 2007 to 2013, it was shown that fertilised soils, particularly in farms with intensive P-fertiliser application (dairy and orchard), have elevated Cd concentrations ranging between 0 to 2.14 mg Cd/kg (mean = 0.44 mg Cd/kg). The Taranaki (0.70 mg Cd/kg), Waikato (0.74 mg

Cd/kg) and Bay of Plenty (0.58 mg Cd/kg) regions were also found to be the most contaminated (Cavanagh, 2014).

According to a study conducted by the Ministry for the Environment (2011), the mean and upper 99th percentile concentrations of Cd in topsoil in the country were 0.15 mg/kg and 0.65 mg/kg, respectively. In general, the Cd concentrations in NZ agricultural soil (<0.00−2.52 mg/kg) were within the lower end of the worldwide range (0.01−10 mg/kg) (Mann et al., 2002; Shi et al., 2019; Tóth et al., 2016). As a comparison, the Cd concentration in North America and Europe range up to 4.3 and 8.9 mg/kg, respectively (Kabata-Pendias, 2000).

In a national groundwater survey between 1995−2008, Daughney and Randall (2009) found no relationship between land-use and groundwater quality. However, at one-third of the sites (out of 973 sites), they reported that general groundwater quality was rapidly degrading, with patterns of change that appeared to be influenced by human activity. They suggested that the absence of correlation was caused by the groundwater not entering the aquifer in the area where land-use observations were made. Unfortunately, we do not have a complete understanding of the subsurface distribution of Cd, nor its origin and trajectory. This makes monitoring and regulating groundwater quality difficult.

2.3. Tiered Fertiliser Management System

The Cadmium Working Group (CWG) was established and supported by the Ministry of Agriculture and Forestry to assess the potential risks of Cd to agriculture and food systems. The CWG objective is "*To ensure that cadmium in rural production poses minimal risks to health, trade, land use flexibility and the environment over the next 100 years*" (Cadmium Working Group, 2011). In response to growing concerns about the accumulation of Cd in NZ agricultural soil, this group developed a Cd management plan called "Tiered Fertiliser Management System" (TFMS), which imposes stringent fertiliser management practices to control the concentration of Cd in NZ soils. The principles behind this program are based on a tiered system separated by 'trigger values' to ensure that Cd concentrations enriched by fertiliser inputs will not exceed unsafe concentrations over a given period. This program includes five tiers with recommended fertiliser application rate as a management tool for each tier (Cadmium Working Group, 2011; Ministry of Agriculture & Forestry, 2011; Sneath, 2020).

- Tier 0: Cd concentration < 0.6 mg/kg, if during a five-yearly screening soil test, Cd concentration remains within the range, no restriction on the application of P-fertiliser is considered.

- Tier 1: 0.6 ≤ Cd concentration < 1.0 mg/kg, fertiliser application is restricted to a set of products and application rates to minimise Cd accumulation. A five-yearly Cd test using an approved program is required. In addition, restrictions are introduced on the choice and rate of phosphate fertiliser.

- Tier 2: 1.0 ≤ Cd concentration < 1.4 mg/kg, a Cd balance program is required to ensure that Cd concentrations will not exceed the acceptable threshold (tier 4) in the next 100 years. The choice and rate of phosphate fertiliser are more restricted.

- Tier 3: 1.4 ≤ Cd concentration < 1.8 mg/kg, a Cd balance program is required to ensure that Cd concentrations will not exceed the acceptable threshold (tier 4) in the next

100 years. The choice and rate of P-fertiliser application are further restricted (to an absolute minimum amount) during the interim seven-year period. The choice and rate of phosphate fertiliser are further restricted.

- Tier 4: Cd concentration ≥ 1.8 mg/kg, no further accumulation of Cd is allowed unless a detailed site-specific investigation is done to identify risks.

Under this strategy, if the Cd concentrations are within tier 2 to 4, a restricted P fertiliser application rate plus a Cd balance program should be implemented. To estimate soil Cd accumulation due to fertilisers, the Cadmium mass balance (CadBal) model was developed in New Zealand (Roberts & Longhurst, 2005). It consists of an inventory of all the sources (inputs) and sinks (outputs) for Cd. Hence, CadBal provides an estimation of the magnitude of Cd leaching from soil to groundwater. The TFMS also lists a number of recommended managing practices, including (1) measuring Cd concentrations on a five-year basis, (2) applying fertilisers with a lower Cd content, (3) maintaining soil pH and organic matter at the recommended level, and (4) growing crops with lower Cd uptake risks. The TFMS is designed to ensure that Cd concentration remains below the Tier 4 trigger value of 1.8 mg Cd/kg over the next 100 years. Therefore, the TFMS takes a conservative approach assuming that all fertilisers applied to land over this period contain greater than the maximum agreed value of Cd concentration in fertiliser (280 mg Cd/kg P) (Sneath, 2020). In a national investigation (from 2007 to 2013, ~3900 samples, ranging from 0 to 2.14 mg/kg, mean = 0.44 mg/kg), it was shown that fertilised soils, particularly in farms with intensive P-fertiliser application (dairy and orchard) have elevated Cd concentrations within tier 1. However, a few isolated cases fall within tiers 2, 3 and 4 (Cavanagh, 2014).

2.4. Principles of Cd mobility in Soil−Pasture−Groundwater Systems

There is evidence that Cd is actively leaching from NZ agricultural soil to groundwater (Section 2.1), but the impact is not immediately evident due to analytical challenges (i.e., contamination maybe on the cusp of detection, but falls below LODs). Hence, protecting soil, groundwater, and plants from fertiliser-derived contaminants, especially Cd and monitoring these systems is of interest. Once pollutants enter soils, hydrogeochemical processes, especially sorption and desorption, and groundwater flow control their mobility (Figure 2.2). Therefore, understanding Cd binding processes in the subsurface is the key step in studying the fate of fertiliser-derived Cd in the subsurface.

Field trial investigations conducted on a Pallic Soil in NZ over 10 years in which 4 types of fertiliser were applied have shown that 93% of the Cd introduced to the soil remained within the A & B Horizons (Loganathan & Hedley, 1997). While this research shows that Cd leaching to the subsurface is probably minimal, recent studies have shown that Cd loss from agricultural soil in the Waikato and Canterbury regions could have accelerated since 2000 (McDowell & Gray, 2022; Salmanzadeh et al., 2016; Salmanzadeh, Schipper, et al., 2017). Based on the stable concentration of Cd in soils and the annual introduction of millions tons of fertiliser to soil, there is a compelling case for the enhanced mobility of Cd from agricultural soil. Uptake of Cd by crops or translocation through soil and possible leaching to groundwater are the most probable pathways for Cd release.

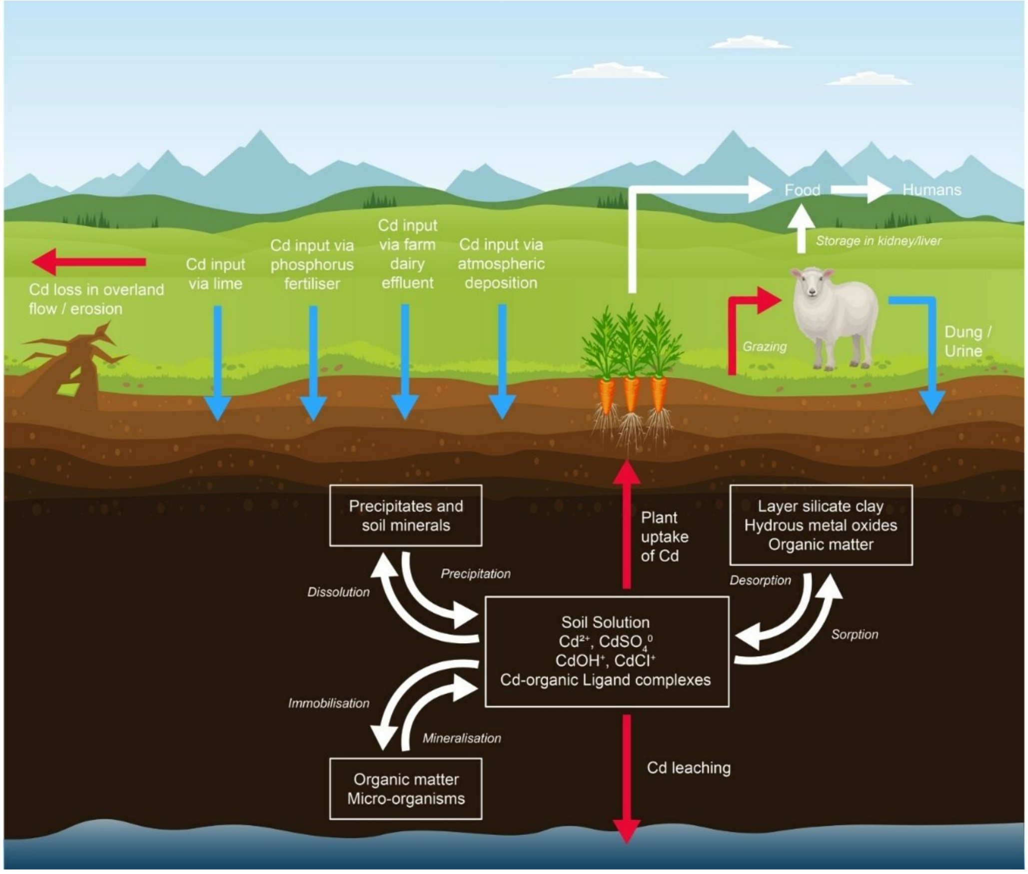


Figure 2.2: A summary of the main cadmium (Cd) inputs, losses, and transformations in New Zealand agricultural soils (Gray & Cavanagh, 2022)

2.4.1. Adsorption, Desorption and Redox processes

Soils contain clays and metal oxyhydroxides that can adsorb Cd (Kubier et al., 2019). As a general rule, any solid surface in soils or aquifers can be a potential adsorption site. Solids with larger specific surface areas have higher adsorption capacities (Appelo & Postma, 2004). The fate and transport of Cd in soils, pastures, and aquifers are controlled by three sorption processes: adsorption, desorption, and ion exchange. Adsorption occurs when ions adhere to the surface of a solid. Adsorption results in the formation of a molecular layer of the adsorbate on the surface. In the ion-exchange process, an ion is exchanged with another one at the surface of the solid (Figure 2.3). A pure ion exchange process releases the same number of ions as it takes up. However, pure adsorption and ion exchange are rare in nature, and most often, a mixture of the two occurs (Appelo & Postma, 2004).

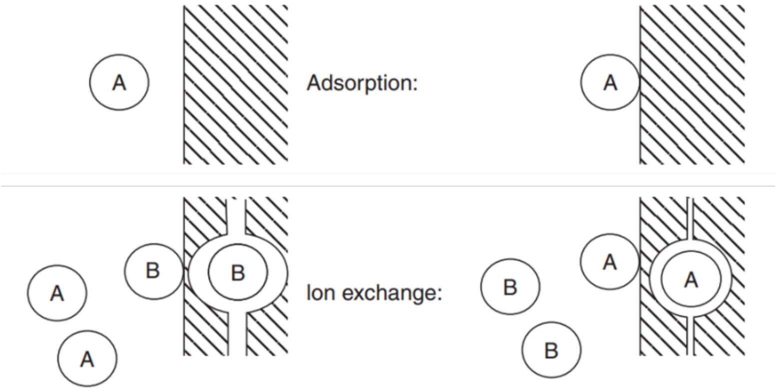


Figure 2.3: Pictorial definition of adsorption (A: adsorbate, Patterned substance: adsorbent) and ion exchange (A and B: ions, Patterned substance: adsorbent) processes (Appelo & Postma, 2004)

Moreover, trace metals can bind to oxide surfaces as well as to organic matter (Welikala et al., 2021). Oxides and hydroxides can have positive or negative surface charges based on the pH, so they can trap positively charged heavy metals, such as Pb^{2+} and Cd^{2+}, and oxyanions, such as $HAsO_4^{2-}$ and $H_2PO_4^-$ depending on the ambient aquatic chemical conditions. Hence, the surface charge is the key factor in controlling adsorption (Appelo & Postma, 2004).

Sorption comprises a set of continuous reactions from adsorption to solid solution formation. The continuum goes from one stage to another sequentially. The rate of trace metal adsorption on solid surfaces is typically highest in the first few minutes, followed by a plateau after a few hours (Davis et al., 1987; Lodygin et al., 2020; Rangel-Porras et al., 2010; Stipp et al., 1992). When molecules become weakly immobilised on a surface, due to the formation of van der Waals forces, they are said to be physically adsorbed, or physisorbed. The forces holding physisorbed molecules to the surface are not strong enough to break chemical bonds within the adsorbed molecule. Because physisorption requires no activation energy, equilibrium between the surface and absorbate is achieved very quickly (Appelo & Postma, 2004; Bikerman, 2013). Then, metals start to adsorb to strong sites and diffuse into the internal mineral structure, which is known as chemical adsorption, or chemisorption. This process continues as long as the internal structure has not been saturated. There must be a chemical bond between the adsorbent and the adsorbate for chemisorption to occur and it requires high activation energy. Chemisorption depends on the surface area. Increasing adsorbent surface area also increases chemisorption (Appelo & Postma, 2004; Bikerman, 2013). Desorption also follows the same pattern, but usually takes more time than adsorption. The desorption process starts with an initial fast step desorbing labile species, followed by a slow step where the absorbed solid solution starts to desorb (Mohammadi et al., 2018).

Reduction and oxidation are also important processes controlling the fate and transport of pollutants like heavy metals and oxyanions in agricultural fields. Redox processes in groundwater occur through electron transfer from one atom to another by adding an oxidant (electron acceptor), like $O_{2,}$ to an aquifer containing a reductant (electron donor) like organic carbon. These reactions are often very slow and may only proceed when mediated by bacterial catalysis. The presence of an external reductant, such as dissolved organic matter (DOM) from landfill leachates, can enhance the reduction process (Appelo & Postma, 2004). Redox conditions control Cd release and retention in soil and groundwater, although Cd is not redox-sensitive. The redox environments in an aquifer must be considered in order to evaluate Cd mobility, specifically, oxic, suboxic, nitrate reducing, Mn(IV) reducing, Fe(III) reducing, reducing sulfate, and methanogenic environments. The redox condition in groundwater systems depend on chemical composition of soil and groundwater. Cd is highly mobile in oxic and acidic waters. When groundwater systems change from anoxic to oxic, Cd can get released from sulfide minerals (Kubier & Pichler, 2019). The concentrations of Cd decrease in suboxic, methanogenic, manganese-, iron-, and sulfate-reducing conditions, which lead to precipitation of sulfides such as pyrite, and thus, Cd immobilization (Carrillo-González et al., 2006).

2.4.2. Soil Properties

In a pH range of about 2 pH units, metal cations exhibit a rapid increase in sorption from almost zero to almost 100%. The position of this pH region, also known as "sorption-edge", is determined by the properties of sorbent (soil), and also by the soil-solution interaction. Different soils have varying capacities to hold or release Cd. Differences in soil properties and soil solution chemistry, such as organic matter content, clay minerals content, pH, cation exchange capacity (CEC), and particle size, mean that Cd concentrations vary across gradients of soil type (Gray et al., 1998; Kubier et al., 2019; Naidu et al., 1994). High clay content, basic pH conditions, high organic matter content and low Cl^- concentration tend to favor Cd adsorption in soil (Kubier et al., 2019). Higher acidities favor heavy metal mobility in soil, and Cd can become mobilised in soils by even slightly acidic conditions (Shahid et al., 2016). Soil treatments can change the average pH of the sorption edge, for example, phosphate enrichment of oxide enhances its capability to retain Cd (Kuo & McNeal, 1984).

The capacity of particles to adsorb cations is expressed as CEC, in meq/kg. The CEC of soil minerals (Table 2.2) varies due to the differences in mineral structure, structural substitutions and the specific surface of the minerals accessible to water. The CEC of oxyhydroxides and organic matter is a function of pH since the surface oxygen groups behave as amphoteric acids (Davis & Kent, 2018). The cation exchange concept works well for major cations and trace metals when the pH is constant. However, trace metals behave differently when pH varies (Stumm, 1992). Figure 2.2 shows that metal adsorption decreases at lower pH. H^+ ions are responsible for this trend as they compete with heavy metals for adsorption sites at low pH. It should be noted that the pH where half of a specific metal is adsorbed, called pH_{50} or the 'adsorption edge', varies for different metal ions. Hence, the pH of the groundwater and subsurface environment greatly influences the mobility of metal ions. Gray et al. (1999) Found that increasing soil pH from 5.5 to 7.0 significantly decreased the Cd uptake by four crops (ryegrass, clover, carrots, lettuce). It is also important to note that metal ion stability is strongly controlled by $[OH^-]$ at high pH, which leads to a strong pH dependence on metal hydroxide formation (Paripurnanda Loganathan et al., 2012).

Table 2.2: Cation exchange capacities of common soil and sediment materials (Davis & Kent, 2018)

	CEC (meq/kg)
Kaolinite	30–150
Halloysite	50–100
Montmorillonite	800–1200
Vermiculite	1000–2000
Glauconite	50–400
Illite	200–500
Chlorite	100–400
Allophane	up to 1000
Goethite and hematite	up to 1000
Organic matter (C)	1500–4000

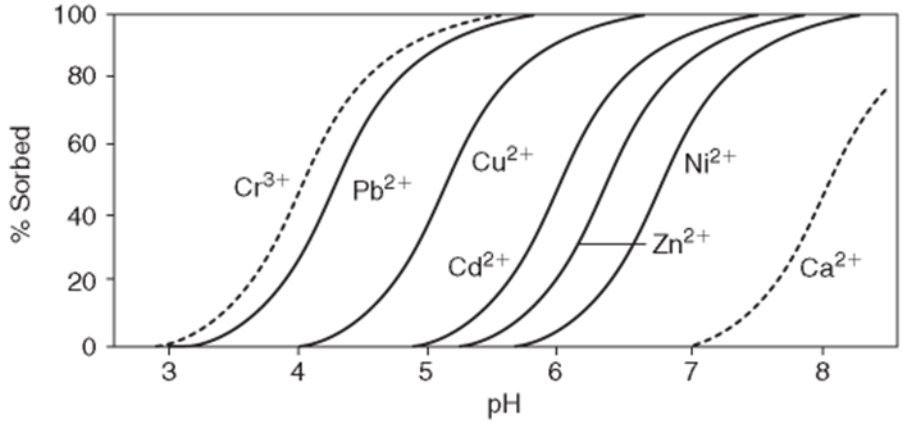


Figure 2.4: Adsorption of heavy metals on the surface of ferrihydrite as a function of pH (Stumm, 1992)

2.4.3. Organic Matter

Organic matter and related substances such as humic acids (HA) and fulvic acids (FA) are widely distributed in soils and water bodies, and they may be strongly adsorbed to particle surfaces. Sedimentary organic matter contributes most of the organic matter in groundwater, which primarily consists of plant remains in terrestrial sediments, along with plankton and animal remains in marine and lacustrine sediments (Appelo & Postma, 2004). The organic matter content of soil varies based on the soil type, which is commonly high in clay and silt, and lower in sand deposits and chalk. The dissolved organic carbon (DOC) concentrations in soil water and groundwater are typically 0.1−3 mM and 0.01−1 mM, respectively (Shen et al., 2015; Thurman, 2012).

Dissolved organic matter (DOM) plays an important role in ion exchange and metal complexation (chelation). The type and content of DOM can have a significant impact on the fate, transportation, and bioavailability of heavy metals (Gao et al., 2018; Welikala et al., 2021). The binding of these contaminants to DOM greatly increases the leaching potential of metals into the subsoil. However, metal cations can be released when attracted to stronger electrical charges (Pettit, 2004). In general, organic matter contains carboxyl groups (COOH), which confer high complexation capacities with metal ions (Mohammadi et al., 2019). Hence, the stability of organic matter-contaminant complexes, contaminant speciation, and soil properties determine the fate and transport of heavy metals in the environment.

2.4.4. Land Management Strategies

Farm management strategies have traditionally been focused on ensuring a high pasture yield. With the introduction of the TFMS in NZ, farmers adopted novel tools and recommendations to ensure sustainable farming by optimising fertiliser application rates, thereby reducing nutrient losses to the subsurface via percolation or drains. Various land management strategies, including farm effluent management, irrigation, fertiliser type and timing, pasture type, cow urine, and grazing cycles can increase Cd movement through topsoil due to increased infiltration and fertiliser input (Gray et al., 2017, 2021; Salmanzadeh, Schipper, et al., 2017). However, the combined effects of land management strategies on metal mobilisation in the subsurface are still not fully understood.

Forage species and cultivars play a major role in determining how much feed can be yielded from pasture. When cultivars and species are matched to the farm system, climate, soil, and pests, the best results can be achieved. The choice of plant species directly affects the amount and timing of fertiliser applications. Research studies have explored strategies for reducing the nitrogen loading potential of urine patches by introducing alternative forage species into cow diets (Minnée et al., 2020). For instance, cows fed plantain have been found to excrete urine with less nitrogen than cows fed ryegrass (Box et al., 2017; Bryant et al., 2018).

Farm dairy effluent (FDE) is increasingly being applied to land instead of being discharged directly to waterways, in response to regulations for protecting the NZ environment from eutrophication. A eutrophic environment is characterised by excessive plant and algal growth caused by an increase in access to one or more growth factors needed for photosynthesis (Payen et al., 2020). Several studies have shown that leaching of P may enrich groundwater by between 2–20%, especially when FDE is applied to soils with low sorption capacities (McDowell et al., 2019; Monaghan et al., 2010). Waterlogging also affects Cd mobility in soil solution, hence spraying FDE on waterlogged soil is prohibited. Therefore, farmers must have adequate storage ponds to delay spraying until the conditions are suitable (Taranaki Regional Council, 2012).

2.4.5. Chloride

In column tests, the leaching of Cd under the influence of $CaCl_2$ has been found to increase with corresponding increases in Cl^- concentration. Hence, in view of the abundance of Cl^- in a wide range of soils, Cd may move deeper in the soil profile as a result of additional Cl^- (Zanders, 1998). The Cl^- concentration of rainwater may therefore be expected influence the leaching of Cd from soil to groundwater. While there are multiple sources of Cl^- in rainwater, sea-salt has the greatest contribution. Hence, Cl^- concentrations of rainwater (found near the coast) decrease exponentially inland and are expected to have a exponentially diminishing effect on Cd mobilisation (Kubier et al., 2019). High Cl^- concentration was also found in cow urine (Miah et al., 2017), which can enhance the mobility of Cd is soil (Ondrasek et al., 2020; Smolders et al., 1998).

2.4.6. Waterlogging

Under waterlogged soils, pH and Eh are two key factors that are sensitively affected by the degradation of soil organic matter. It has been reported that Fe^{2+} and amorphous iron oxide content increases when soil pH and Eh decrease in flooded soil (Glinski et al., 1996). Additionally, the formation of sulfide (S^{2-}) has led to a reduction in SO_4^{2-} and a decrease in soil Eh, leading to CdS precipitation (Huang et al., 2013). As a result, the dissolved Cd concentration significantly decrease in a strongly reducing soil. Currently, limited information is available regarding the relationship between waterlogging and Cd mobility through soil and possible leaching to groundwater.

2.4.7. Flow and Transport in Porous Media

Leachate from fertilisers may percolate into underlying aquifers. The question is, how fast the fertiliser-derived Cd travel through the subsoil, and where and when these waters may intersect with aquifers further downstream. To understand the fate and transport of Cd from soil to groundwater, it is imperative to have a perception of the groundwater flow path and chemical controls on mobilisation. Contaminants can go down through soil by dissolution in water. However, the observed displacement of contaminants is not always equal to the displacement of water in soil. Along the flow line, contaminants may re-bind to soil, which retards their transport to groundwater. Or sometimes, infiltration may be enhanced along preferential flow paths through macro-fissures (Travelletti et al., 2012), or in the root zone, where water bypasses the porous matrix to reach greater depths via root channels (Mallants et al., 2011). Water percolates vertically downward in the unsaturated zone. Infiltrating water pushes the old water ahead, a process named 'piston flow'. Hence, excessive irrigation and infiltration makes shallow groundwater and drinking-water wells more vulnerable (Nolan & Hitt, 2006). Detailed information about the hydraulic conductivity and porosity of different soils is presented in Table 2.3. Groundwater velocity in the saturated zone can be calculated using Darcy's law:

$$\nu_D = -k.\frac{dh}{dx} \qquad \text{Equation 2.1}$$

where, V_D is the velocity of water (m/day), k is the hydraulic conductivity (m/day) and dh/dx is the hydraulic gradient. Hence, a first approximation of the actual distance travelled in different soil types can be achieved using Equation 2.1 and Table 2.3. According to Table 2.3, clay and peat are considered impermeable (aquicludes) and loam is considered almost impermeable (aquitards).

In saturated zones, groundwater can also flow horizontally through soils. Maps of water table heights measured in piezometers (i.e., 'the piezometric surface') can indicate the direction of flow. For instance, in Figure 2.5, points with the same groundwater elevation are connected to each other with lines, named isohypses (equipotential lines). Groundwater flows from high potentials to low potentials, and the flow direction is perpendicular to the isohypses (Dogramaci & Herczeg, 2002). However, it has been proven that permeability variations have a large influence on flow paths. Thus, predicting the actual flow lines is difficult.

Table 2.3: Hydraulic conductivity and porosity of different sediments.

Soil Type	Saturated Hydraulic Conductivity (ks, m/day)	Porosity (ε, %)
Gravel	200–2000	0.15–0.25
Sand	10–300	0.20–0.35
Loam	0.01–10	0.30–0.45
Clay	$1.0\text{x}10^{-5}$–1	0.30–0.65
Peat	$1.0\text{x}10^{-5}$–1	0.60–0.90

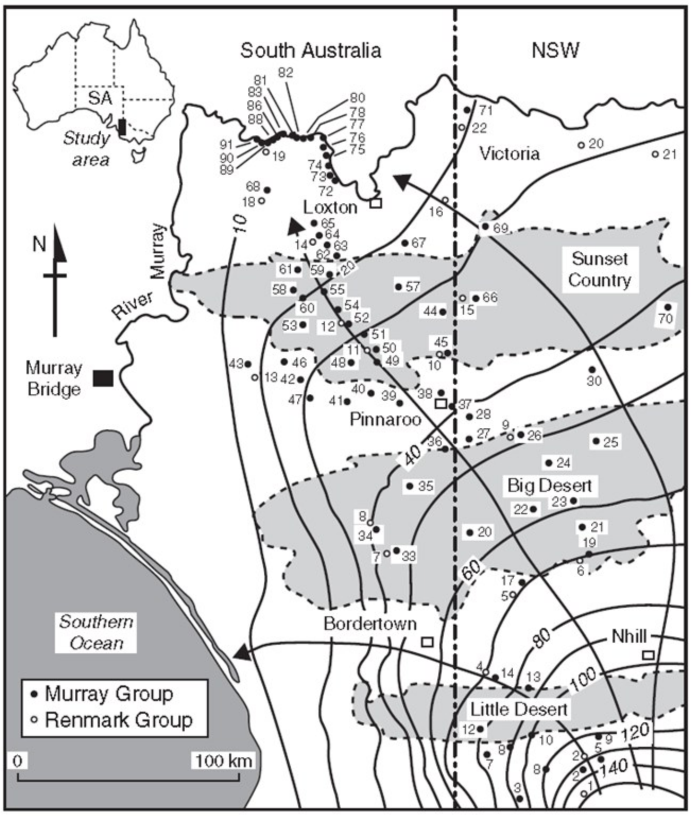


Figure 2.5: Groundwater potential and groundwater flow direction. The contours represent the hydraulic head (isohypses), and the arrows indicate the inferred direction of groundwater flow (Dogramaci & Herczeg, 2002)

Flow conditions in porous media are often inhomogeneous with water flowing in certain parts of the media and being stagnant within particle aggregates, cemented clusters or organic clods (Weber & Smith, 1987). Afterward, a diffusive exchange of ions will take place between the stagnant zones and the mobile flow region. Figure 2.6 gives an overview of the reaction orders in a porous media. The fastest reaction happens in the bulk phase, followed by a slow film diffusion through a boundary layer of stagnant water that surrounds the particles. Lastly, the chemical reaction happens (Weber & Smith, 1987).

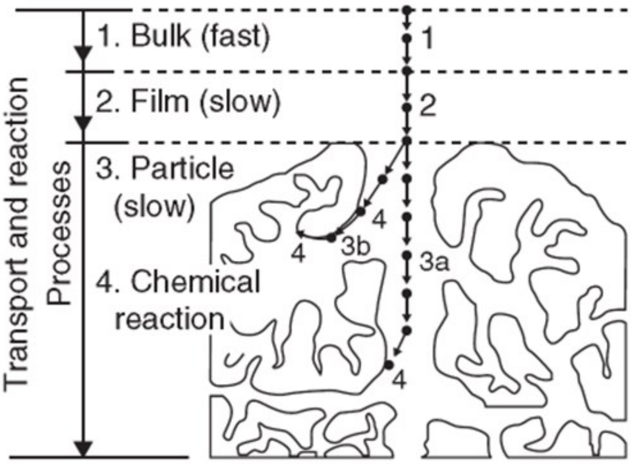


Figure 2.6: Rate determining processes for reactions in a porous media (Weber & Smith, 1987)

2.4.8. Plant Uptake

While Cd is not an essential nutrient for plants, plants take it up and accumulate it in roots, straws, and shoots, depending on its availability and concentrations (Wiggenhauser et al., 2016). Several factors affect the availability of Cd to plants, such as soil pH and structures, the rhizosphere, and organic matter content (Benavides et al., 2005). In acidic soils, Cd is found as free Cd^{2+} cations, making them readily available for plant uptake (Figure 2.4). However, at $pH > 7$, most of the Cd^{2+} exist in strongly-bound complexes. Long-term field studies, such as lysimeter trials, are necessary to better understand Cd mobility in soil−pasture−groundwater systems in which the various complexities can be integrated to determine the effects of farm management on the fate of Cd (Gray et al., 2021).

2.5. Co-contaminants

Increasing concentrations of nitrate and phosphate in NZ agricultural soil and groundwater is of great concern. These contaminants originate in groundwater from different point and non-point sources, of which the main sources are the urine patches and the excessive application of fertilisers and manure by agriculture. As a result of grazing, large amounts of nitrogen (N) are deposited in urine- and dung patches on a limited area of land. The crops can only use a limited amount of N, so large amounts of mineral N (ammonium-N and nitrate-N) can be accumulated under urine patches, causing nitrate leaching (Corré et al., 2014). Nitrogen is an important component in the biogeochemical cycle and the only way for in-situ nitrate removal from groundwater is by reduction to N_2 (denitrification). The reduction series of nitrogen during denitrification is given below, where NO_3^- known as the most oxidised species, and NH_4^+ known as the most reduced species (Xin et al., 2019).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2(g)} \rightarrow NH_4^+$$

Denitrification is largely affected by organic matter content of the environment as the predominant electron donor, as well as the presence of dissolved oxygen. NO_2^- and N_2O are often found at trace levels and used as evidence of denitrification.

A wide range of toxic elements, such as Zn, Pb, and U, are present in P-fertilisers (Khan et al., 2017; Loganathan et al., 2003; Mortvedt, 1995). Hence, there are concerns about the enrichment of these elements in NZ agricultural soil (Schipper et al., 2011). In environmental impact assessments, Zn and Cd can be considered together, since they have similar chemical properties (Hooda, 2010; Phillips, 1999; Welikala et al., 2018). Unlike Cd, Zn is essential for cellular processes, to help the plant produce chlorophyll. The Zn:Cd ratio has been widely used in soil studies, with the typical Zn:Cd ratio being 200:1 (Hooda, 2010). Significant changes in this ratio suggest that an external source has affected their concentrations in soil. Given that the accumulation trend of Cd in NZ agricultural soil is continuing, a lower ratio is expected in fertilised soil due to the dominant influence of Cd inputs from P-fertiliser. However, it should be noted that other Zn sources are present in the agricultural environment (e.g., facial eczema remedies).

2.6. Principles of the Methodology

In an environmental impact assessment of Cd, both the sampling and analytical methods should be adjusted to obtain accurate results. This thesis introduces a combination of innovative methods can be used to determine the actual concentrations and mobility of Cd in fertilised soils, pastures, and groundwater systems.

2.6.1. Groundwater Sampling

Groundwater sampling is perhaps the most important step in groundwater quality assessments to ensure the representativeness of the samples that reflect the chemical composition of groundwater. There are two types of sampling approaches commonly used in groundwater monitoring: active sampling (also known as grab sampling) and passive sampling (Valenzuela et al., 2020).

2.6.1.1 Active (Grab) Sampling

Most groundwater sampling methods involve capturing discrete grab samples at specific times. However, Cd in groundwater is typically below the detection limit of standard methods, requiring pre-concentration before analysis. Therefore, it requires large volume (> 1 L) samples to be taken. Despite its laborious and time-consuming nature, this method only provides a snapshot of contaminant levels at the time of sampling. Data from groundwater sampling may therefore be misleading where contaminant concentrations fluctuate appreciably over time due to hydrological factors or other anthropogenic factors (Górecki & Namieśnik, 2002). Increasing the frequency of sampling or installing automatic grab sampling systems that can take numerous samples of water within a certain time intervals might solve this problem (Corbett et al., 2020), however, analysing large number of samples is time consuming and expensive.

In addition, there are multiple aspects concerning sample collection and conservation. Samples may contain suspended solids or colloids that need to be removed before analysis. The size range of colloids is 10^{-9}–10^{-4} m, hence, filtering the sample through standard 0.45 µm membrane filters could remove some, but not all colloids from suspension (Stumm & Morgan, 2012). Filtering large volume samples is also time-consuming, in addition to any pre-concentration prior to analysis. Sample preparation to avoid changes in the chemical composition is typically achieved by acidification (to pH<2 with HNO_3), which ceases bacterial growth and prevents adsorption or precipitation of Cd. Comparisons of field measurements of pH with those performed in the laboratory have shown that in most cases, the pH of the sample rises during the period of storage. Since pH variations even on a small scale could affect the geochemical analysis, care should be taken to obtain reliable pH measurements.

Pumping rate, duration, and frequency may also affect the chemical composition of samples. While the absence of pumping results in the presence of stagnant water above the screen, excessive pumping may result in overestimation of real-time data by drawing waters with different compositions towards the screen. Hence, the period of pumping and the number of well volumes to be emptied before taking samples in sampling methods is important. Previous research have suggested that samples could be taken after reaching the stationary condition for measured parameters such as temperature, pH and electrical conductivity (EC). Lloyd and Heathcote (1985) demonstrated that the required number of well volumes to be emptied is 2−3 to reach stable readings for temperature, pH, Eh and EC. In addition, any disturbance in natural conditions such as drilling operations may affect the accuracy of samples. It may take a long time before the influence of disturbance is diminished, which depends on a wide range of parameters such as hydraulic conductivity.

2.6.1.2 Passive Sampling

In situ pre-concentration via passive sampling is a popular method for determining trace elements in the environment (Greenwood et al., 2007; Salim & Górecki, 2019). A passive sampling device collects chemicals continuously from water and provides time weighted averages (TWA) of the concentration of pollutants over a defined period. Passive samplers capture and retain analytes in a media known as the receiving phase, which can be a solvent, chemical reagent, or porous adsorbent. Often passive samplers take samples, isolate selective analytes, concentrate, and preserve analytes in one step (Vrana et al., 2005). Hence, they offer a number of advantages over other conventional sampling methods (Kot-Wasik et al., 2007). The development of a passive groundwater sampling method should include the following improvements: (a) reducing sample handling time through in-situ preconcentration, (b) reducing cross-contamination during sampling, (c) providing high-resolution accuracy in comparison to high-frequency grab sampling. Numerous passive sampling techniques have been developed for water sampling, e.g., Chemcatcher (Vrana et al., 2006), ceramic dosimeter (Martin et al., 2000), membrane–enclosed sorptive coating (Vrana et al., 2001), polyethylene diffusion bags (Vroblesky & Hyde, 1997), and diffusive gradients in thin films (DGT) (Davison & Zhang, 1994). DGT is fundamentally similar to a range of passive samplers developed for monitoring organic compounds in water (Greenwood et al., 2007). However, DGT has been used more extensively than other devices for the measurement of inorganic solutes worldwide (French et al., 2021; Han et al., 2013; Viana et al., 2022) and is a well-validated and understood method.

2.6.2. Principles of Diffusive Gradients in Thin-films (DGT)

DGTs consist of two essential parts: (1) a binding layer which selectively binds the analytes of interest, and (2) a diffusion layer (diffusive gel + membrane filter, together name material diffusion layer (MDL)) which controls the diffusion of the analytes prior to binding (Figure 2.7). The diffusive gel (hydrogel) allows unimpeded diffusion of analytes. The binding layer selectively binds analytes (e.g., cations, anions, organic compounds) based on the type of absorbent. Chelex resins is widely used to measure a range of cations (e.g., Ca^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}) (Panther et al., 2012; Y. Wang et al., 2016; Zhang &

Davison, 1995). DGT has proven to be very versatile, for example, ferrihydrate and A520E resin are increasingly used for phosphate and nitrate measurement in water, respectively (Corbett et al., 2020; J. Huang et al., 2017; Santner et al., 2010). The robust design of DGT devices allows them to be deployed directly into water bodies. DGTs provide TWA concentrations for the deployment time, and no calibration is usually required when the diffusion coefficient of the solute is known. These features make DGTs a popular passive sampling method for chemical measurements in water.

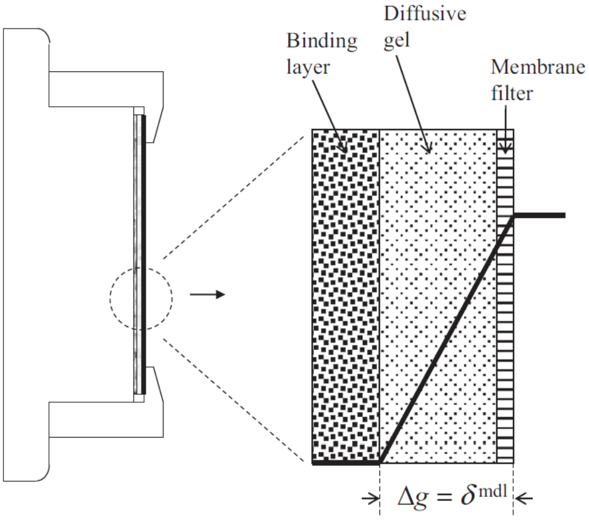


Figure 2.7: Schematic diagram of a DGT piston assembly, with an exploded view of the binding and diffusion layers, showing the concentration gradient of the analyte (Davison, 2016).

Essentially, at the surface of any submerged solid, there will be a stagnant layer close to the surface, known as diffusive boundary layer (DBL) (Figure 2.8), where the transport of analytes is restricted (Warnken et al., 2006). In vigorously stirred solutions, even though the DBL gets thinner as the flow rate increases, there will still be a thin residual layer. To ensure an accurate and quantitative assessment, the thickness of this layer must be taken into account (Section 2.7.2.1). Following a DGT deployment and subsequent analysis of the eluted resin gel layer, the concentration of the analyte(s) in the solution is determined as follows:

$$C_{DGT} = \frac{M}{A_E t}\left(\frac{\delta^g}{D^g} + \frac{\delta^f}{D^f} + \frac{\delta^{dbl}}{D^w}\right) = \frac{M}{A_E t}\left(\frac{\delta^{mdl}}{D^{mdl}} + \frac{\delta^{dbl}}{D^w}\right) \qquad \text{Equation 2.2}$$

where, C_{DGT} is the DGT-measured concentration; M is the mass of analyte in the binding layer; A_E is the effective exposure window area (3.8 cm^2 for standard solution devices); t is deployment time; δ^g is the diffusion gel thickness; D^g is the gel diffusion coefficient; δ^f is the filter membrane thickness; D^f is filter membrane diffusion coefficient; δ^{dbl} is the diffusive boundary layer thickness; D^w is water diffusion coefficient; δ^{mdl} is the material diffusion layer thickness; D^g is the material diffusion layer diffusion coefficient. Diffusion Coefficients in the standard DGT gel (agarose crosslinked polyacrylamide, APA) from 1 to 35°C can be found online in the DGR research website (https://www.dgtresearch.com/diffusion-coefficients/). Table 2.4 shows that for most measurements in well-stirred solutions, δ^{dbl} lies within the range of 0.14–0.25 mm.

Table 2.4: Values of the DBL thickness, δ^{dbl}, measured in the laboratory and in situ using DGT devices with several MDL thicknesses

δ^{dbl} (mm)	Analyte	Deployment	Time	DGT	Ref.
0.23 ± 0.03[a] 1.5 ± 0.13[b]	Cd	On plastic mounts in 2.5 L solution stirred at 100–800[a], 0 rpm[b]	50 h	Chelex	(Warnken et al., 2006)
0.14 ± 0.03[c] 1.15 ± 0.10[d]	Cd	In situ; river; on a plastic sheet in a net; high[c] and lower[d] flow	14 d	Chelex	(Buzier et al., 2014)
0.37–1.41	U	In situ, edge of variable flow stream mounted on a plastic sheet	7 d	Metsorb	(Turner et al., 2014)
0.39	P	In situ, mounted on cords 20 cm below surface of a small pond	8 h	Ferrihydrate	(Zhang et al., 1998)
0.67 ± 0.07	As	In situ; coastal marina, 30 cm below surface, on plastic sheet on a line	4 d	Metsorb	(Bennett et al., 2010)
0.48 ± 0.36[e] 0.58 ± 0.19[f] 0.64 ± 0.92[g]	Co	In situ; channel of treated wastewater. DGTs placed at three flow rates: 0.07[e]; 1[f]; 3[g] cms^{-1}	15 d	Chelex	(Uher et al., 2013)
2.09–3.03	NO_3^-	In situ, denitrifying bioreactors monitoring piezometer	1 d	A520E	(Corbett et al., 2020)

M, the mass of analyte, is calculated as below:

$$M = \frac{c_e(V^{bl}+V_e)}{f_e} \qquad \text{Equation 2.3}$$

where, c_e is the measured concentration of analyte; V^{bl} is the binding layer volume; V_e is the eluent volume; and f_e is the elution factor.

The ability of the binding layer to accumulate the analyte of interest (uptake) as well as the efficacy of the eluent solution in extracting the analyte from the binding layer (elution) can be determined via immersion of binding gel disks in solutions with known concentrations. The uptake efficiency is determined by measuring the mass of analyte in the solution. The adsorbed mass of analyte to the binding gel disks is used to determine the elution efficiency. The uptake efficiency can be calculated as follow:

$$f_u = \frac{M_i - M_f}{M_i} \qquad \text{Equation 2.4}$$

where, f_u is the uptake factor; M_i is the initial mass of analyte in the solution; M_f is the remaining mass of analyte in the solution after the experiment. The elution efficiency can be calculated as below:

$$f_e = \frac{M_e}{M_i - M_f} \qquad \text{Equation 2.5}$$

where, f_e is the elution factor and M_e is the mass of analyte in the eluent solution. In general, >85% for fu and >75% for f_e are typical values for successful DGT methods (Davison, 2016).

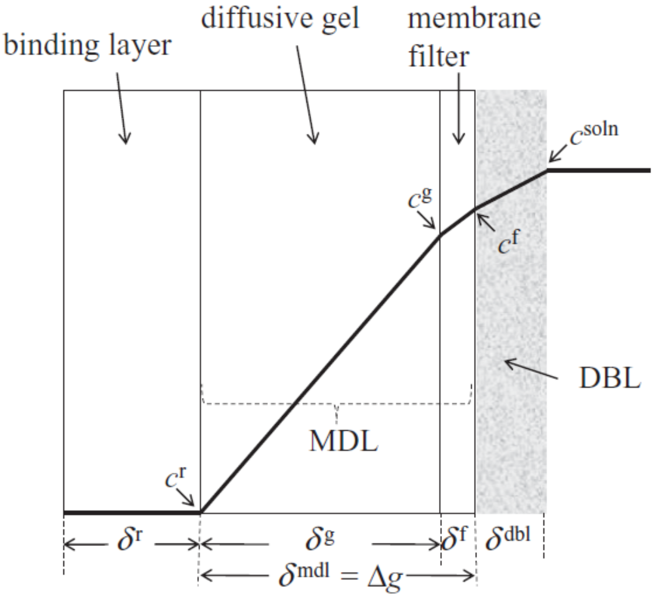


Figure 2.8: Schematic representation of the steady state concentration gradient of the analyte through the binding and diffusion layers within a DGT device, indicating symbols and terminology used in the text (Davison, 2016).

2.6.2.1 Apparent Diffusive Boundary Layer (ADBL)

There can be differences in the dissociation kinetics of different analyte complexes, which influence the amount of analytes accumulated by DGT resin gels and hence the measured concentrations. The diffusion of free analytes (e.g., nitrate) is faster than that of ions complexed with large ligands, such as metals bound to dissolved organic matter (Uher et al., 2013; Warnken et al., 2007). As a result, the flux of analytes to the binding layer can be restricted by diffusion and the rate of dissociation from the complex when these complexes are partially labile. Warnken et al. (2007) reported faster dissociation for Zn, Pb, and Cd, compared with Cu, Al, and Fe (Figure 2.9b). The term "apparent diffusive boundary layer" (ADBL) describes the characteristics of metal-organic complexes and therefore provides information about their lability. The ADBL thickness is often thicker than the physical DBL (Davison, 2016). As a consequence, each component's ADBL value must be analyzed in relation to the DBL. DGT devices with a range of MDL thicknesses can be used to determine the thickness of the DBL, enabling accurate solution concentration measurements. Plotting 1/M versus δ^{mbl} enables estimation of δ^{dbl}:

$$\delta^{adbl} = \frac{b}{a}(\frac{D^{w}A_{p}}{D^{w}A_{e}}) \qquad \text{Equation 2.6}$$

where b is the intercept; c is the slope of the linear relationship of 1/M versus δ^{mbl}; A_p is the physical exposure window area (3.14 cm^2 for standard solution devices). The intercept (b) is influenced by metal complex formation, where the b values are greater for kinetically limited complexes (Warnken et al., 2007).

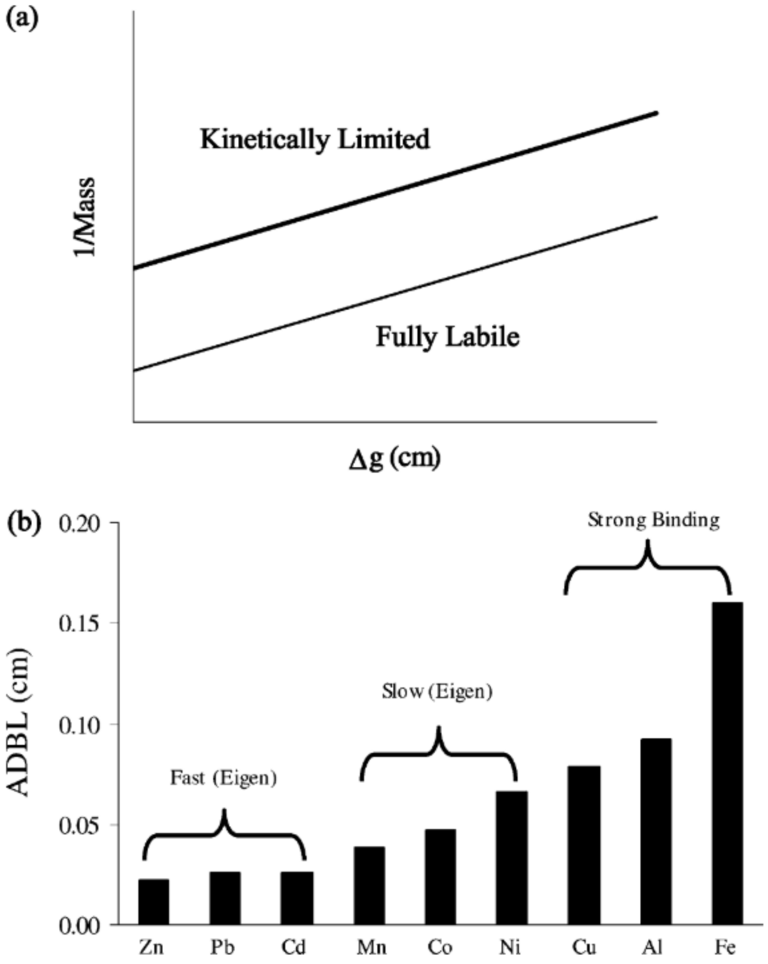


Figure 2.9: (a) Explanation of the effect of kinetic limitation on plots, (b) Thicknesses of the apparent diffusive boundary layer (ADBL) in the River Wyre at Garstang, Lancashire (Warnken et al., 2007)

2.6.2.2 Application of DGT in Groundwater Quality Monitoring

While there have been numerous investigations related to DGT monitoring in freshwater bodies, there are only a few studies focused on improving DGT performance in stagnant water bodies, like groundwater. Most of the previous research was conducted by measuring the DBL in a slowly-flowing solutions at laboratory scale (Santos et al., 2022; Uher et al., 2013). For example, Lucas et al. (2014) assessed the distribution of dissolved

Au, As and Sb in groundwater using DGTs. In their study, despite the fact that As and Sb often fell below detection limits, the DGT technique showed methodological improvements for groundwater monitoring over grab sampling. Corbett et al. (2020) used A520E-DGTs to monitor nitrate concentrations in bioreactor monitoring piezometers. They reported that nitrate concentrations determined by DGTs were consistent with high frequency grab sampling, however data collection via DGTs was significantly easier than the latter approach. Despite these advances, further research is needed to test and understand the application of DGT in monitoring groundwater quality.

2.6.3. Soil and Plant Digestion

Testing methods for metal and nutrient concentrations in soil and plants have evolved continuously to improve environmental assessments. Various techniques have been developed over the years; however, no universal soil test to accurately assess soil contamination by heavy metals exists. For soil digestion, US EPA 3050B (US EPA, 1996a), US EPA 3051A (US EPA, 2007), US EPA 3052b (US EPA, 1996b), mixture of $HClO_4$ and HNO_3, and mixtures of HF and HNO_3, , $Ca(NO_3)_2$, and Aqua Regia ($HCl:HNO_3$, 1:3, v:v) methods have been used in previous research to measure total or acid digestible Cd concentration of soil and plant matter (Gray et al., 1999; McDowell, 2018; Reiser et al., 2014; Roberts et al., 1994; Welikala et al., 2021; Wiggenhauser et al., 2016). Digestion using $HNO_3:HClO_4$ (87:13, v:v) in a heating block, microwave assisted HNO_3 digestion, microwave assisted HF and HNO_3, and $HNO_3-H_2SO_4-H_2O_2$ digestion methods have been used previously to measure total or acid digestible Cd concentration in plant samples (H. Chen et al., 2018; Wiggenhauser et al., 2016; Wu et al., 2004; Zhong et al., 2021).

2.6.4. Lysimeters: A Direct Method for Measuring Drainage

Accurate and appropriate methods in the field are needed in order to measure the controlling factors on Cd mobilisation and preferential flowpaths. Lysimeters are a device that allows measurement of the soil−water balance, or the volume and quality of water percolating vertically (Figure 2.10). Lysimeters collect leachate, which can be analysed for metal and nutrient concentrations to measure the effects of various farm management strategies on groundwater quality. Lysimeter sampling and subsequent analysis can indicate if fertilisers are applied in appropriate amounts and with correct timing (Cameron et al., 1996).

Lysimeters come in many different forms and sizes, ranging from simple buckets filled with soil to several meter-sized containers planted with trees. Undisturbed soil in lysimeters allows hydraulic pressure to be adjusted to match surrounding soil pressure. Aluminum oxide, glass sinter, ceramic, Teflon, acrylic copolymers with nylon internal supports, stainless steel and plastic "organic" polymers such as PVC, PP, PVDF are some of the materials used in lysimeters (DeVivo et al., 2017). Depending on the cup material, these samplers can cause sorption problems (sorption of solutes). Water sampling may be compromised by the absorption, precipitation, or release of solutes from the cup material (DeVivo et al., 2017).

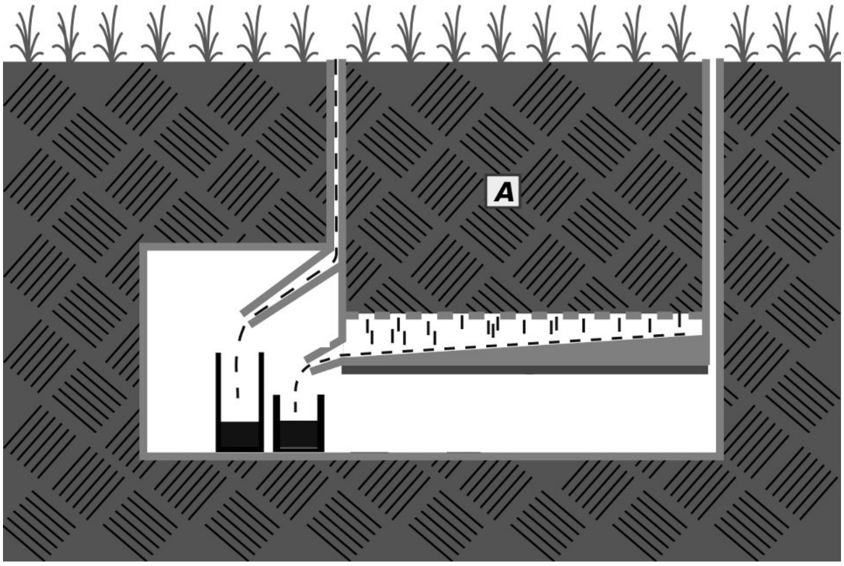


Figure 2.10: Schematic of a lysimeter and sample collection system

2.6.5. Stable Isotope Ratio Analysis

An assessment of the mobility of fertiliser-derived Cd in soil and groundwater must include an estimation on the amount of naturally occurring Cd in the media from the parent material. A knowledge of the history of fertiliser use is also necessary to estimate the impact of Cd accurately, however, the amount and type of fertiliser used in the past is not always known. Previously, unfertilised-sites adjacent to the site of interest were taken as a benchmark (Loganathan et al., 2003). In other research, samples from sites with land-uses including reserve, tussock, bush, indigenous forest and plantation forestry were used to derive the mean background concentration of Cd (Taylor et al., 2007). However, the potential differences in soil types and land-uses may cause a failure in accurately assessing background Cd concentrations.

In geochemistry, the stable isotope ratio approach has been increasingly applied to study the origin of contaminants in water, sediment, and soil. More specifically, isotope ratios can be applied to study the fate of fertiliser-derived Cd in agricultural soils and the underlying aquifers. Stable isotope ratio analysis provides a means to differentiate fertiliser-derived Cd from native Cd sources in groundwater, potentially providing a definitive assessment of Cd leaching from fertilised soil to groundwater (Salmanzadeh et al., 2017; Wiggenhauser et al., 2019). While this technique can meet the need for accurate and precise estimates of Cd partitioning in soil−pasture−groundwater systems, analytical and experimental challenges hinder the direct application of the stable isotope ratio analysis in these systems. For example, the role of soil and groundwater heterogeneity in the transport of contaminants through the subsurface can be significant (Baily et al., 2011; McDowell et al., 2013; A. D. Stafford et al., 2018). Such variations are caused by changes in soil hydrogeochemical properties. To conduct stable isotope ratio measurements, large volume samples (up to several litres) are required because of low Cd concentrations in groundwater (Gray & Cavanagh, 2022). Therefore, experimental designs should consider soil and hydrogeological heterogeneity, as well as analytical challenges.

Stable isotope ratios are normally expressed as the ratio of the most abundant isotope over an isotope that is less abundant, relative to a standard. The criteria to choose between isotopes is based on: (1) feasibility to measure the isotope ratios with a mass spectrometer, and (2) the mass difference between two isotopes, the greater this difference the greater the influence of mass fractionation effects. δ notation is expressed as the deviation of an isotopic ratio in a sample to the isotopic ratio of a standard (Equation 2.7). δ values are reported in units of parts per thousand or permil (‰).

$$\delta^{114/110}Cd = \left[\frac{(^{114}Cd/^{110}Cd)_{Sample}}{(^{114}Cd/^{110}Cd)_{Standard}} - 1\right].1000 \qquad \text{Equation 2.7}$$

Stable isotopes behave differently in physical, chemical, and biological processes due to differences in mass. Without anthropogenic sources, the variations in Cd isotopic ratios in nature is small. Isotopic fractionation is defined as the partitioning of heavier and lighter isotopes between coexisting phases (source and sink) (Tiwari et al., 2015). The apparent isotopic fractionation between source and sink is described as:

$$\Delta^{114/110}Cd_{sink-source} = \delta^{114/110}Cd_{sink} - \delta^{114/110}Cd_{source} \qquad \text{Equation 2.8}$$

During leaching from soil to groundwater or during uptake by plants, the stable isotopes of Cd may become fractionated. The resulting small variation may cause misinterpretation of data yielded from sampling methods. However, isotope fractionation may help to elucidate the geochemical processes and reactions affecting the composition of groundwater. For instance, Salmanzadeh et al. (2017) showed how mass-balance modelling of soil isotope ratios could be used to predict the δ^{114}Cd of soil leachate (accounting for fractionation terms).

2.7. Principles of Data Analysis

Understanding how to analyse and interpret results is an important consideration if one is to unravel the primary drivers of Cd in these agricultural settings. To explain the key differences between controlling factors, datasets are usually evaluated using single-factor analysis of variance, ANOVA. Paired t-tests assuming unequal variances can also be used to compare the means of different treatments.

From a classical point of view, anomalous data is an observation which deviates so much from other observations as to arouse suspicions that it was generated by a different mechanism (Hawkins, 1980). Depending on the particular scenario or the analyst's interest, outliers in datasets can have two different meanings: (1) erroneous, or unwanted data due to human mistakes or malfunctions in analytical instruments, and (2) unusual but interesting phenomena (Figure 2.11). Anomalies in datasets can be an intrinsic feature of environmental assessments. The presence of extreme values in a dataset can for example, indicate high mobilisation events. Identifying and dealing with these anomalies is an integral part of working with data, and a possible shift in the governing process (e.g., matrix to preferential flow). There are numerous methods available for detecting anomalies and transforming data. For example, the modified Z-score and Box-Cox non-linear transformation methods can be used to detect data anomalies and smoothen the effect of skewed data distribution.

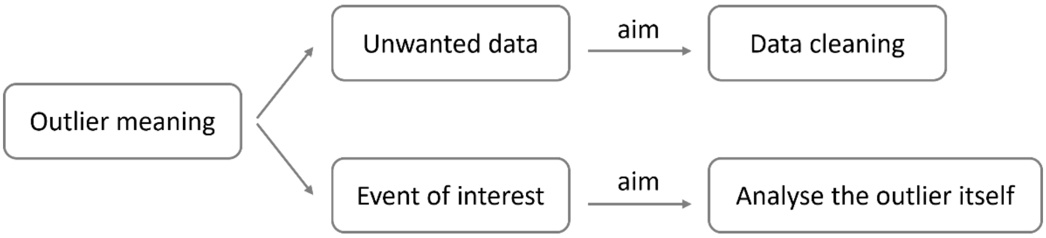


Figure 2.11: Meaning of outliers in datasets depending on the aim of the analyst (Blázquez-García et al., 2021)

The Z-score method computes the number of standard deviations of a data point from the dataset’s mean (Equation 2.9). The Z-score of a data point is defined as:

$$Z_i = \frac{Y_i - \bar{Y}}{s} \qquad \text{Equation 2.9}$$

where Y_i is the value of the datapoint, $\bar{Y}$ is the dataset mean value, and s is the standard deviation of the dataset. Iglewicz and Hoaglin recommended using the modified Z-score method (Iglewicz & Hoaglin, 1993), in which the median value is used (Equation 2.10), since the median is less sensitive to the effects of extreme values. The modified Z-score is therefore defined as:

$$M_i = \frac{0.6745(Y_i - \tilde{Y})}{MAD} < \beta \qquad \text{Equation 2.10}$$

where $\tilde{Y}$ is the dataset median value, MAD is the median absolute deviation, and β is the rejection criterion. The median absolute deviation is defined as the median of the absolute deviations from the dataset's median (Equation 2.11).

$$MAD = median(\left|Y_i - \tilde{Y}\right|) \qquad \text{Equation 2.11}$$

Iglewicz and Hoaglin suggested the rejection criterion of greater than 3.5 based on the results of a simulation of datasets of 10, 20, and 40 samples (Iglewicz & Hoaglin, 1993).

The second method employed herein to smooth the effect of skewness is Box-Cox non-linear transformation (Box & Cox, 1964). Such non-linear data transformation smooths the shape of skewed distributions and makes the dataset conform to a more normal distribution (Fu et al., 2010). The Box-Cox transformation is defined as:

$$w_i = \begin{cases} \frac{X_i^{\lambda} - 1}{\lambda}, & if\ \lambda \neq 0 \\ \ln(X_i), & if\ \lambda = 0 \end{cases} \qquad \text{Equation 2.12}$$

where X_i is the value of the datapoint and λ is the transformation parameter that provides the best approximation for the normal distribution of the datasets. The value of λ differs for different datasets.

2.8. Summary and Hypothesis

This study focuses on the effects of soil type and land management strategies on Cd and co-contaminants mobility. To understand the factors controlling Cd leaching rates, samples of soil, groundwater and pasture need to be analysed for their chemical and isotopic composition, across different soil types and land-uses. We hypothesize that, (H_1) different soil types have different intrinsic contaminant leaching potentials; and (H_2) that different land management strategies have different effects on Cd and other contaminants mobility in soil, pasture, and groundwater systems.

According to an extensive literature review, researchers have reported contrasting conclusions relating to the distribution and transport of Cd in soil, groundwater, and pasture of agricultural sites. The potentially detrimental impacts of Cd mobilisation are the subject of a continuous debate, which currently has minimal scientific grounding. Some research indicates minor mobility or leaching of Cd through these systems, but other studies found significant translocation. In most of the previous studies, Cd concentrations in groundwater were below the detection limit (Gray & Cavanagh, 2022). Hence, the extent to which Cd leaches from soil into groundwater is unknown. As shown by the literature review, one of the main advantages of passive sampling is its ability to detect low level contaminants, such as Cd. Therefore, the first part of this thesis addresses the need for an in-situ passive sampling technique that can provide information on the exact Cd concentrations, as well as the speciation and behavior of Cd and co-contaminants in groundwater.

In agricultural soils, the most important pathway for metal and nutrient loss is likely to be via transport in infiltration water. A number of laboratory studies have been conducted in New Zealand to provide insights into the effect of individual management factors on nutrient loss. However, field trials are needed to assess the combined effects of farm management strategies on metals and nutrients leaching. Therefore, the second part of this thesis aimed at assessing the individual and combined effects of farm dairy effluent (FDE) and cow urine (CU) on the leaching of metals and nutrients in Eyre (excessively-drained) and Templeton (well-drained) soils. Additionally, this chapter explores controlling factors of high mobilisation events, such as soil types and farm management strategies.

Another gap which this thesis aims to fill is to develop an isotopic view of Cd partitioning and fractionation between soil, groundwater and pasture systems. The application of stable isotope ratios could provide further insight into the fluxes of fertiliser-derived Cd, including a better understanding of Cd leaching (to groundwater) and bioaccumulation (into plants). This thesis explores how Cd isotopes fractionate during desorption from soil and during transport into groundwater and uptake by pasture. Additionally, soil type and waterlogging affects are assessed through isotopic analyses. Therefore, Cd stable isotope ratios ($\delta^{114/111}$Cd) were employed to assess whether this is a suitable tracer of Cd in agricultural systems. Because of analytical and experimental challenges hindering the direct application of the stable isotope ratio analysis in groundwater, DGT was developed as a tool for monitoring Cd in shallow groundwater. The novel combination of isotope tracing and passive sampling may offer the potential to better understand Cd dispersion in aquifers and the wider environment. Plant and fertilised soil samples were also analysed alongside an unfertilised soil to provide information on Cd fractionation patterns in the agricultural systems.

This research can be used by researchers, authorities, regional councils, and consulting companies to better understand the mobilisation of Cd in agricultural systems and to assist farmers with long term sustainable land use management.

References

Appelo, C. A. J., & Postma, D. (2004). *Geochemistry, groundwater and pollution*. CRC press.

Baily, A., Rock, L., Watson, C. J., & Fenton, O. (2011). Spatial and temporal variations in groundwater nitrate at an intensive dairy farm in South-East Ireland: Insights from stable isotope data. *Agriculture, Ecosystems and Environment*, *144*(1), 308–318. https://doi.org/10.1016/j.agee.2011.09.007

Benavides, M. P., Gallego, S. M., & Tomaro, M. L. (2005). Cadmium toxicity in plants. *Brazilian Journal of Plant Physiology*, *17*(1), 21–34.

Bennett, W. W., Teasdale, P. R., Panzther, J. G., Welsh, D. T., & Jolley, D. F. (2010). New diffusive gradients in a thin film technique for measuring inorganic arsenic and selenium (IV) using a titanium dioxide based adsorbent. *Analytical Chemistry*, *82*(17), 7401–7407.

Bikerman, J. J. (2013). *Surface chemistry: theory and applications*. Elsevier.

Blázquez-García, A., Conde, A., Mori, U., & Lozano, J. A. (2021). A review on outlier/anomaly detection in time series data. *ACM Computing Surveys (CSUR)*, *54*(3), 1–33.

Box, G. E. P., & Cox, D. R. (1964). An analysis of transformations. *Journal of the Royal*

Statistical Society: Series B (Methodological), *26*(2), 211–243.

Box, L. A., Edwards, G. R., & Bryant, R. H. (2017). Milk production and urinary nitrogen excretion of dairy cows grazing plantain in early and late lactation. *New Zealand Journal of Agricultural Research*, *60*(4), 470–482.

Bryant, R. H., Welten, B. G., Costall, D., Shorten, P. R., & Edwards, G. R. (2018). Milk yield and urinary-nitrogen excretion of dairy cows grazing forb pasture mixtures designed to reduce nitrogen leaching. *Livestock Science*, *209*, 46–53.

Buzier, R., Charriau, A., Corona, D., Lenain, J.-F., Fondanèche, P., Joussein, E., Poulier, G., Lissalde, S., Mazzella, N., & Guibaud, G. (2014). DGT-labile As, Cd, Cu and Ni monitoring in freshwater: toward a framework for interpretation of in situ deployment. *Environmental Pollution*, *192*, 52–58.

Cadmium Working Group. (2011). Cadmium and New Zealand agriculture and horticulture: A strategy for long term risk management. *Ministry of Agriculture and Forestry, Wellington, NZ*.

Cameron, K. C., Rate, A. W., Noonan, J., Moore, S., Smith, N. P., & Kerr, L. E. (1996). *Lysimeter study of the fate of nutrients following subsurface injection and surface application of dairy pond sludge to pasture*. *58*, 187–197.

Carrillo-González, R., Šim\uunek, J., Sauve, S., & Adriano, D. (2006). Mechanisms and pathways of trace element mobility in soils. Advances in Agronomy, 91, 111–178.

Cavanagh, JE, Munir, K., Gray, C., Wakelin, S., Okafor, C., Jeyakumar, J., Anderson, C., Mamun, S., & Robinson, B. (2015). *Assessing cadmium uptake in New Zealand agricultural systems, Landcare Research Report LC2366 for the Fertiliser Association* *of New Zealand*.

Cavanagh, Jo. (2014). Status of cadmium in New Zealand soils: 2014. *Landcare Research*.

Chen, H., Yang, X., Wang, P., Wang, Z., Li, M., & Zhao, F. J. (2018). Dietary cadmium intake from rice and vegetables and potential health risk: A case study in Xiangtan, southern China. *Science of the Total Environment*, *639*, 271–277. https://doi.org/10.1016/j.scitotenv.2018.05.050

Corbett, T. D. W., Dougherty, H., Maxwell, B., Hartland, A., Henderson, W., Rys, G. J., & Schipper, L. A. (2020). Utility of 'Diffusive Gradients in Thin-Films' for the measurement of nitrate removal performance of denitrifying bioreactors. *Science of the Total Environment*, *718*, 135267. https://doi.org/10.1016/j.scitotenv.2019.135267

Corré, W. J., Van Beek, C. L., & Van Groenigen, J. W. (2014). Nitrate leaching and apparent recovery of urine-N in grassland on sandy soils in the Netherlands. NJAS-Wageningen Journal of Life Sciences, 70, 25–32.

Daughney, C., & Randall, M. (2009). *National Groundwater Quality Indicators Update : State and Trends 1995-2008*. *September*.

Davis, J. A., Fuller, C. C., & Cook, A. D. (1987). A model for trace metal sorption processes at the calcite surface: Adsorption of Cd2+ and subsequent solid solution formation. *Geochimica et Cosmochimica Acta*, *51*(6), 1477–1490.

Davis, J. A., & Kent, D. B. (2018). Surface complexation modeling in aqueous geochemistry. In *Mineral-water interface geochemistry* (pp. 177–260). De Gruyter.

Davison, W. (2016). *Diffusive gradients in thin-films for environmental measurements*.

Cambridge University Press.

Davison, W., & Zhang, H. (1994). In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature*, *367*(6463), 546–548.

DeVivo, B., Belkin, H., & Lima, A. (2017). Environmental geochemistry: site characterization, data analysis and case histories. Elsevier.

Dogramaci, S. S., & Herczeg, A. L. (2002). Strontium and carbon isotope constraints on carbonate-solution interactions and inter-aquifer mixing in groundwaters of the semi-arid Murray Basin, Australia. *Journal of Hydrology*, *262*(1–4), 50–67.

Environment Waikato. (2005). *Cadmium Accumulation in Waikato Soils, Waikato Regional Council*.

Fertiliser Matters. (2005). Cadmium in New Zealand--an update. *Auckland, New Zealand Fertiliser Manufacturer's Research Association. Newsletter*, *34*.

French, A. D., Ragg, N. L. C., Ericson, J. A., Goodwin, E., McDougall, D. R., Mohammadi, A., & Vignier, J. (2021). Balancing essential and non-essential metal bioavailability during hatchery rearing of Greenshell mussel (Perna canaliculus) larvae. *Ecotoxicology and Environmental Safety*, *216*, 112194.

Fu, W., Tunney, H., & Zhang, C. (2010). Spatial variation of soil nutrients in a dairy farm and its implications for site-specific fertilizer application. *Soil and Tillage Research*, *106*(2), 185–193.

Gao, J., Lv, J., Wu, H., Dai, Y., & Nasir, M. (2018). Impacts of wheat straw addition on dissolved organic matter characteristics in cadmium-contaminated soils: Insights from fluorescence spectroscopy and environmental implications. *Chemosphere*, *193*, 1027–1035. https://doi.org/10.1016/j.chemosphere.2017.11.112

Glinski, J., Stahr, K., Stepniewska, Z., & Brzezinska, M. (1996). Changes of redox and pH conditions in a flooded soil amended with glucose and manganese oxide or iron oxide under laboratory conditions. *Journal of Plant Nutrition and Soil Science*, *June*, 297–304.

Górecki, T., & Namieśnik, J. (2002). Passive sampling. *TrAC Trends in Analytical Chemistry*, *21*(4), 276–291.

Gray, C., McLaren, R., Roberts, A., & Condron, L. (1999). Solubility, sorption and desorption of native and added cadmium in relation to properties of soils in New Zealand. *European Journal of Soil Science*, *50*(1), 127–137.

Gray, C. W., McLaren, R. G., Roberts, A. H. C., & Condron, L. M. (1999). Effect of soil pH on cadmium phytoavailability in some New Zealand soils. *New Zealand Journal of Crop and Horticultural Science*, *27*(2), 169–179. https://doi.org/10.1080/01140671.1999.9514093

Gray, C W, & Cavanagh, J. E. (2020). Redevelopment of the cadmium balance model. *Report for the Fertiliser Association of New Zealand: RE450/2020/039.(Accessed 20 January 2021)*.

Gray, C W, & Cavanagh, J. E. (2022). The state of knowledge of cadmium in New Zealand agricultural systems : 2021. *New Zealand Journal of Agricultural Research*, *May*, 1–51. https://doi.org/10.1080/00288233.2022.2069130

Gray, C W, McLaren, R. G., Roberts, A. H. C., & Condron, L. M. (1998). Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time.

Soil Research, *36*(2), 199–216.

Gray, Colin William, Chrystal, J. M., Monaghan, R. M., & Cavanagh, J. A. (2017). Subsurface cadmium loss from a stony soil—effect of cow urine application. *Environmental Science and Pollution Research*, *24*(13), 12494–12500. https://doi.org/10.1007/s11356-017-8865-0

Gray, Colin William, Lucci, G. M., Cavanagh, J., & Gray, C. W. (2021). *Can the application of farm dairy effluent enhance cadmium leaching from soil ?* 50919–50929.

Greenwood, R., Mills, G., & Vrana, B. (2007). *Passive sampling techniques in environmental monitoring*. Elsevier.

Hamon, R., Wundke, L., McLaughlin, M., & Naidu, R. (1997). Availability of zinc and cadmium to different plant species. *Australian Journal of Soil Research*, *35*, 1267–1277.

Han, S., Naito, W., Hanai, Y., & Masunaga, S. (2013). Evaluation of trace metals bioavailability in Japanese river waters using DGT and a chemical equilibrium model. *Water Research*, *47*(14), 4880–4892.

Hawkins, D. M. (1980). *Identification of Outliers*. Springer.

Hooda, P. S. (2010). *Trace elements in soils*.

Huang, J., Bennett, W. W., Teasdale, P. R., Kankanamge, N. R., & Welsh, D. T. (2017). A modified DGT technique for the simultaneous measurement of dissolved inorganic nitrogen and phosphorus in freshwaters. *Analytica Chimica Acta*, *988*, 17–26.

Huang, J. H., Wang, S. L., Lin, J. H., Chen, Y. M., & Wang, M. K. (2013). Dynamics of cadmium concentration in contaminated rice paddy soils with submerging time. *Paddy and Water Environment*, *11*(1–4), 483–491. https://doi.org/10.1007/s10333-012-0339-x

Iglewicz, B., & Hoaglin, D. C. (1993). *How to detect and handle outliers* (Vol. 16). Asq Press.

Kabata-Pendias, A. (2000). *Trace elements in soils and plants*. CRC press.

Khan, M. N., Mobin, M., Abbas, Z. K., & Alamri, S. A. (2017). Fertilizers and their contaminants in soils, surface and groundwater. In *Encyclopedia of the Anthropocene* (Vols. 1–5). Elsevier Inc. https://doi.org/10.1016/B978-0-12-809665-9.09888-8

Kot-Wasik, A., Zabiegała, B., Urbanowicz, M., Dominiak, E., Wasik, A., & Namieśnik, J. (2007). Advances in passive sampling in environmental studies. *Analytica Chimica Acta*, *602*(2), 141–163.

Kubier, A., & Pichler, T. (2019). Cadmium in groundwater − A synopsis based on a large hydrogeochemical data set. Science of the Total Environment, 689, 831–842. https://doi.org/10.1016/j.scitotenv.2019.06.499

Kubier, A., Wilkin, R. T., & Pichler, T. (2019). Cadmium in soils and groundwater: A review. *Applied Geochemistry*, *108*(February). https://doi.org/10.1016/j.apgeochem.2019.104388

Kuo, S., & McNeal, B. L. (1984). Effects of pH and phosphate on cadmium sorption by a hydrous ferric oxide. Soil Science Society of America Journal, 48(5), 1040–1044.

Liu, Z., Ji, X., Guan, D., Xie, Y., Zhu, J., Peng, J., & others. (2017). Effects of timing and duration of waterlogging on Cd absorption and accumulation by rice under cadmium stress. *Journal of Ecology and Rural Environment*, *33*(12), 1125–1131.

Lloyd, J. W., & Heathcote, J. A. A. (1985). *Natural inorganic hydrochemistry in relation to ground water*.

Lodygin, E. D., Alekseev, I. I., Vasilevich, R. S., & Abakumov, E. V. (2020). Complexation of lead and cadmium ions with humic acids from arctic peat soils. *Environmental Research*, *191*, 110058.

Loganathan, P. A., Hedley, M. J. A., Grace, N. D. B., Lee, J. B., Cronin, S. J. A., & Bolan, N. S. A. (2003). *Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine : a review*. 501–532.

Loganathan, P, & Hedley, M. J. (1997). Downward movement of cadmium and phosphorus from phosphatic fertilisers in a pasture soil in New Zealand. *Environmental Pollution*, *95*(3), 319–324.

Loganathan, Paripurnanda, Vigneswaran, S., Kandasamy, J., & Naidu, R. (2012). Cadmium sorption and desorption in soils: a review. *Critical Reviews in Environmental Science and Technology*, *42*(5), 489–533.

Longhurst, R. D., Roberts, A. H. C., & Waller, J. E. (2004). Concentrations of arsenic, cadmium, copper, lead, and zinc in New Zealand pastoral topsoils and herbage. *New Zealand Journal of Agricultural Research*, *47*(1), 23–32.

Lucas, A. R., Reid, N., Salmon, S. U., & Rate, A. W. (2014). *Quantitative Assessment of the Distribution of Dissolved Au, As and Sb in Groundwater Using the Di ff usive Gradients in Thin Films Technique*.

Mallants, D., Genuchten, M. T., Šim\uunek, J., Jacques, D., Seetharam, S., & others. (2011). Leaching of contaminants to groundwater. In *Dealing with Contaminated Sites* (pp.

787–850). Springer.

Mann, S. S., Rate, A. W., & Gilkes, R. J. (2002). Cadmium accumulation in agricultural soils in Western Australia. *Water, Air, and Soil Pollution*, *141*(1), 281–297.

Martin, H., Piepenbrink, M., & Grathwohl, P. (2000). Ceramic dosimeters for time-integrated contaminant monitoring. *Groundwater 2000*, 39–40.

McDowell, R. W. (2012). The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. *New Zealand Journal of Agricultural Research*, *55*(2), 133–146.

McDowell, R. W. (2018). *The rate of accumulation of cadmium and uranium in a long-term grazed pasture : implications for soil quality*. *8233*(January). https://doi.org/10.1080/00288233.2012.662901

McDowell, R. W., & Gray, C. W. (2022). Do soil cadmium concentrations decline after phosphate fertiliser application is stopped: A comparison of long-term pasture trials in New Zealand? *Science of the Total Environment*, *804*, 150047. https://doi.org/10.1016/j.scitotenv.2021.150047

McDowell, R. W., Gray, C. W., Cameron, K. C., Di, H. J., & Pellow, R. (2019). The efficacy of good practice to prevent long-term leaching losses of phosphorus from an irrigated dairy farm. *Agriculture, Ecosystems and Environment*, *273*(September 2018), 86–94. https://doi.org/10.1016/j.agee.2018.12.007

McDowell, R. W., Taylor, M. D., & Stevenson, B. A. (2013). Natural background and anthropogenic contributions of cadmium to New Zealand soils. *Agriculture, Ecosystems and Environment*, *165*, 80–87.

https://doi.org/10.1016/j.agee.2012.12.011

Miah, M. N. A., Miah, M. R. U., & Alam, M. Z. (2017). Determining chemical composition of cattle urine and indigenous plant extracts. *International Annals of Science*, *3*(1), 23–26.

Ministry for Primary Industries. (2019). *Managing cadmium in food crops in New Zealand*.

Ministry for the Environment. (2011). *Methodology for Deriving Standards for Contaminants in Soil to Protect Human Health*.

Ministry of Agriculture & Forestry. (2011). *Review of , and recommendations for , the proposed New Zealand Cadmium Management Strategy and Tiered Fertiliser Management System* (Vol. 9, Issue February).

Minnée, E. M. K., Leach, C. M. T., & Dalley, D. E. (2020). Substituting a pasture-based diet with plantain (Plantago lanceolata) reduces nitrogen excreted in urine from dairy cows in late lactation. *Livestock Science*, *239*(December 2019), 104093. https://doi.org/10.1016/j.livsci.2020.104093

Mohammadi, A, Sohrabi, B., Rashidi, M., & Saeedi, M. (2019). The extracted saponin from ginseng as an efficient renewable biosurfactant for desorption enhancement of phenanthrene and nickel. *International Journal of Environmental Science and Technology*, *16*(1), 181–190.

Mohammadi, Amir, Saeedi, M., & Mollahoseini, A. (2018). Simultaneous desorption and desorption kinetics of phenanthrene, anthracene, and heavy metals from kaolinite with different organic matter content. *Soil and Sediment Contamination: An International Journal*, *27*(3), 200–220.

Monaghan, R. M., Houlbrooke, D. J., & Smith, L. C. (2010). The use of low-rate sprinkler application systems for applying farm dairy effluent to land to reduce contaminant transfers. *New Zealand Journal of Agricultural Research*, *53*(4), 389–402.

Mortvedt, J. J. (1995). Heavy metal contaminants in inorganic and organic fertilizers. *Fertilizer Research*, *43*(1), 55–61. https://doi.org/10.1007/BF00747683

Naidu, R., Bolan, N. S., Kookana, R. S., & Tiller, K. G. (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science*, *45*(4), 419–429.

Nokes, C., & Weaver, L. (2014). Cadmium in Groundwater : review of regional council data. *Ministry of Health, Wellington*, *May*.

Nolan, B. T., & Hitt, K. J. (2006). Vulnerability of shallow groundwater and drinking-water wells to nitrate in the United States. *Environmental Science \& Technology*, *40*(24), 7834–7840.

Ondrasek, G., Romic, D., & Rengel, Z. (2020). Interactions of humates and chlorides with cadmium drive soil cadmium chemistry and uptake by radish cultivars. *Science of the Total Environment*, *702*, 134887.

Panther, J. G., Bennett, W. W., Teasdale, P. R., Welsh, D. T., & Zhao, H. (2012). DGT measurement of dissolved aluminum species in waters: comparing Chelex-100 and titanium dioxide-based adsorbents. *Environmental Science \& Technology*, *46*(4), 2267–2275.

Payen, S., Falconer, S., Carlson, B., Yang, W., & Ledgard, S. (2020). Eutrophication and climate change impacts of a case study of New Zealand beef to the European market.

Science of the Total Environment, *710*, 136120. https://doi.org/10.1016/j.scitotenv.2019.136120

Pettit, R. E. (2004). *Organic matter, humus, humate, humic acid, fulvic acid and humin: their importance in soil fertility and plant health*.

Phillips, I. R. (1999). Copper, lead, cadmium, and zinc sorption by waterlogged and air-dry soil. *Soil and Sediment Contamination*, *8*(3), 343–364. https://doi.org/10.1080/10588339991339379

Rangel-Porras, G., Garcia-Magno, J. B., & González-Muñoz, M. P. (2010). Lead and cadmium immobilization on calcitic limestone materials. *Desalination*, *262*(1–3), 1–10.

Reiser, R., Simmler, M., Portmann, D., Clucas, L., Schulin, R., & Robinson, B. (2014). *Cadmium Concentrations in New Zealand Pastures: Relationships to Soil and Climate Variables*. 917–925. https://doi.org/10.2134/jeq2013.09.0367

Roberts, A. H. C., & Longhurst, R. D. (2005). A cadmium balance model for New Zealand pastoral systems. *AgResearch, Hamilton, New Zealand, Report Prepared for the New Zealand Fertiliser Manufacturer's Research Association*.

Roberts, A. H. C., Longhurst, R. D., & Brown, M. W. (1994). Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research*, *37*(1), 119–129. https://doi.org/10.1080/00288233.1994.9513048

Salim, F., & Górecki, T. (2019). Theory and modelling approaches to passive sampling. *Environmental Science: Processes \& Impacts*, *21*(10), 1618–1641.

Salmanzadeh, M., Balks, M. R., Hartland, A., & Schipper, L. A. (2016). Cadmium accumulation in three contrasting New Zealand soils with the same phosphate fertilizer history. *Geoderma Regional*, *7*(3), 271–278. https://doi.org/10.1016/j.geodrs.2016.05.001

Salmanzadeh, M., Hartland, A., Stirling, C. H., Balks, M. R., Schipper, L. A., Joshi, C., & George, E. (2017). *Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil*. https://doi.org/10.1021/acs.est.7b00858

Salmanzadeh, M., Schipper, L. A., Balks, M. R., Hartland, A., Mudge, P. L., & Littler, R. (2017). The effect of irrigation on cadmium, uranium, and phosphorus contents in agricultural soils. *Agriculture, Ecosystems and Environment*, *247*(June), 84–90. https://doi.org/10.1016/j.agee.2017.06.028

Santner, J., Prohaska, T., Luo, J., & Zhang, H. (2010). Ferrihydrite containing gel for chemical imaging of labile phosphate species in sediments and soils using diffusive gradients in thin films. *Analytical Chemistry*, *82*(18), 7668–7674.

Santos, C. A., Gemeiner, H., Menegário, A. A., Galceran, J., Zanatta, M. B. T., & Chang, H. K. (2022). A new approach to improve the accuracy of DGT (Diffusive Gradients in Thin-films) measurements in monitoring wells. *Talanta*, *238*, 123044.

Schipper, L. A., Sparling, G. P., Fisk, L. M., Dodd, M. B., Power, I. L., & Littler, R. A. (2011). Agriculture , Ecosystems and Environment Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer. *"Agriculture, Ecosystems and Environment,"* *144*(1), 95–101. https://doi.org/10.1016/j.agee.2011.08.002

Shahid, M., Dumat, C., Khalid, S., Niazi, N. K., & Antunes, P. (2016). Cadmium bioavailability, uptake, toxicity and detoxification in soil-plant system. *Reviews of Environmental Contamination and Toxicology Volume 241*, 73–137.

Shen, Y., Chapelle, F. H., Strom, E. W., & Benner, R. (2015). Origins and bioavailability of dissolved organic matter in groundwater. *Biogeochemistry*, *122*(1), 61–78.

Shi, T., Zhang, Y., Gong, Y., Ma, J., Wei, H., Wu, X., Zhao, L., & Hou, H. (2019). Status of cadmium accumulation in agricultural soils across China (1975--2016): From temporal and spatial variations to risk assessment. *Chemosphere*, *230*, 136–143.

Smolders, E., Lambregts, R. M., McLaughlin, M. J., & Tiller, K. G. (1998). *Effect of soil solution chloride on cadmium availability to Swiss chard*.

Sneath, G. (2020). Revision of the tiered fertiliser management system for soil cadmium. *Nutrient Management in Farmed Landscapes. Occasional Report*, *33*.

Stafford, A. D., Palmer, A. S., Jeyakumar, P., Hedley, M. J., & Anderson, C. W. N. (2018). Soil cadmium and New Zealand dairy farms: Impact of whole-farm contaminant variability on environmental management. *Agriculture, Ecosystems and Environment*, *254*(August 2017), 282–291. https://doi.org/10.1016/j.agee.2017.11.033

Stafford, Aaron, Jeyakumar, P., Hedley, M., & Anderson, C. (2018). Influence of soil moisture status on soil cadmium phytoavailability and accumulation in plantain (Plantago lanceolata). *Soil Systems*, *2*(1), 9.

Stafford, AD. (2017). *Distribution of cadmium in long-term dairy soils, its accumulation in selected plant species, and the implications for management and mitigation*. Massey University.

Stipp, S. L., Hochella Jr, M. F., Parks, G. A., & Leckie, J. O. (1992). Cd2+ uptake by calcite, solid-state diffusion, and the formation of solid-solution: Interface processes observed with near-surface sensitive techniques (XPS, LEED, and AES). *Geochimica et Cosmochimica Acta*, *56*(5), 1941–1954.

Stumm, W. (1992). *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*. Wiley.

Stumm, W., & Morgan, J. J. (2012). *Aquatic chemistry: chemical equilibria and rates in natural waters* (Vol. 126). John Wiley \& Sons.

Syers, J. K., Mackay, A. D., Brown, M. W., & Currie, L. D. (1986). Chemical and physical characteristics of phosphate rock materials of varying reactivity. *Journal of the Science of Food and Agriculture*, *37*(11), 1057–1064.

Taranaki Regional Council. (2012). Future directions for the management of farm dairy effluent. In *Taranaki Regional Council*.

Taylor, M., Caldwell, J., Sneath, G., & Council, W. R. (2017). *CURRENT STATE AND TREND OF CADMIUM LEVELS IN SOIL , FRESHWATER AND SEDIMENTS ACROSS THE WAIKATO REGION*. *30*, 1–11.

Taylor, M., Gibb, R., Willoughby, J., Hewitt, A., & Arnold, G. (2007). *Soil Maps of Cadmium in New Zealand*. *June*.

Thurman, E. M. (2012). *Organic geochemistry of natural waters* (Vol. 2). Springer Science \& Business Media.

Tiwari, M., Singh, A. K., & Sinha, D. K. (2015). Stable isotopes: Tools for understanding past climatic conditions and their applications in chemostratigraphy. In *Chemostratigraphy* (pp. 65–92). Elsevier.

Tóth, G., Hermann, T., Da Silva, M. R., & Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International*, *88*, 299–309.

Travelletti, J., Sailhac, P., Malet, J.-P., Grandjean, G., & Ponton, J. (2012). Hydrological response of weathered clay-shale slopes: Water infiltration monitoring with time-lapse electrical resistivity tomography. *Hydrological Processes*, *26*(14), 2106–2119.

Turner, G. S. C., Mills, G. A., Bowes, M. J., Burnett, J. L., Amos, S., & Fones, G. R. (2014). Evaluation of DGT as a long-term water quality monitoring tool in natural waters; Uranium as a case study. *Environmental Sciences: Processes and Impacts*, *16*(3), 393–403. https://doi.org/10.1039/c3em00574g

Uher, E., Tusseau-Vuillemin, M. H., & Gourlay-France, C. (2013). DGT measurement in low flow conditions: Diffusive boundary layer and lability considerations. *Environmental Sciences: Processes and Impacts*, *15*(7), 1351–1358. https://doi.org/10.1039/c3em00151b

Uraguchi, S., Mori, S., Kuramata, M., Kawasaki, A., Arao, T., & Ishikawa, S. (2009). Root-to-shoot Cd translocation via the xylem is the major process determining shoot and grain cadmium accumulation in rice. Journal of Experimental Botany, 60(9), 2677–2688.

US EPA. (1996a). *Method 3050b: Acid Digestion of Sediments, Sludges, and Soils*.

US EPA. (1996b). *Method 3052b: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices*.

US EPA. (2007). *Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*.

Valenzuela, E. F., Menezes, H. C., & Cardeal, Z. L. (2020). Passive and grab sampling methods to assess pesticide residues in water. A review. *Environmental Chemistry Letters*, *18*(4), 1019–1048.

Viana, J. L. M., de Souza, A. F., Hernández, A. H., Elias, L. P., Eismann, C. E., Rezende-Filho, A. T., Barbiero, L., Menegario, A. A., & Fostier, A. H. (2022). In situ arsenic speciation at the soil/water interface of saline-alkaline lakes of the Pantanal, Brazil: A DGT-based approach. *Science of The Total Environment*, *804*, 150113.

Vrana, B., Allan, I. J., Greenwood, R., Mills, G. A., Dominiak, E., Svensson, K., Knutsson, J., & Morrison, G. (2005). Passive sampling techniques for monitoring pollutants in water. *TrAC - Trends in Analytical Chemistry*, *24*(10), 845–868. https://doi.org/10.1016/j.trac.2005.06.006

Vrana, B., Mills, G. A., Dominiak, E., & Greenwood, R. (2006). Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water. *Environmental Pollution*, *142*(2), 333–343.

Vrana, B., Popp, P., Paschke, A., & Schüürmann, G. (2001). Membrane-enclosed sorptive coating. An integrative passive sampler for monitoring organic contaminants in water. *Analytical Chemistry*, *73*(21), 5191–5200.

Vroblesky, D. A., & Hyde, W. T. (1997). Diffusion samplers as an inexpensive approach to monitoring VOCs in ground water. *Groundwater Monitoring \& Remediation*, *17*(3), 177–184.

Wang, Y., Ding, S., Gong, M., Xu, S., Xu, W., & Zhang, C. (2016). Diffusion characteristics of agarose hydrogel used in diffusive gradients in thin films for measurements of cations and anions. *Analytica Chimica Acta*, *945*, 47–56.

Warnken, K. W., Davison, W., Zhang, H., Galceran, J., & Puy, J. (2007). In situ measurements of metal complex exchange kinetics in freshwater. *Environmental Science and Technology*, *41*(9), 3179–3185. https://doi.org/10.1021/es062474p

Warnken, K. W., Zhang, H., & Davison, W. (2006). *Accuracy of the Diffusive Gradients in Thin-Films Technique : Diffusive Boundary Layer and Effective Sampling Area Considerations*. *78*(11), 3780–3787. https://doi.org/10.1021/ac060139d

Weber, W. J., & Smith, E. H. (1987). Simulation and design models for adsorption processes. *Environmental Science \& Technology*, *21*(11), 1040–1050.

Welikala, D., Hucker, C., Hartland, A., Robinson, B. H., & Lehto, N. J. (2018). Trace metal mobilization by organic soil amendments: insights gained from analyses of solid and solution phase complexation of cadmium, nickel and zinc. *Chemosphere*, *199*, 684–693. https://doi.org/10.1016/j.chemosphere.2018.02.069

Welikala, D., Robinson, B. H., Moltchanova, E., Hartland, A., & Lehto, N. J. (2021). Soil cadmium mobilisation by dissolved organic matter from soil amendments. *Chemosphere*, *271*, 129536. https://doi.org/10.1016/j.chemosphere.2021.129536

Wiggenhauser, M., Bigalke, M., Imseng, M., Keller, A., Rehkämper, M., Wilcke, W., & Frossard, E. (2019). Using isotopes to trace freshly applied cadmium through mineral phosphorus fertilization in soil-fertilizer-plant systems. *Science of the Total Environment*, *648*, 779–786. https://doi.org/10.1016/j.scitotenv.2018.08.127

Wiggenhauser, M., Bigalke, M., Imseng, M., Müller, M., Keller, A., Murphy, K., Kreissig, K., Rehkämper, M., Wilcke, W., & Frossard, E. (2016). Cadmium isotope fractionation in soil-wheat systems. *Environmental Science and Technology*, *50*(17), 9223–9231. https://doi.org/10.1021/acs.est.6b01568

World Health Organization. (2011). Guidelines for drinking-water quality. *WHO Chronicle*, *38*(4), 104–108.

Wu, Q. T., Xu, Z., Meng, Q., Gerard, E., & Morel, J. L. (2004). Characterization of cadmium desorption in soils and its relationship to plant uptake and cadmium leaching. *Plant and Soil*, *258*(1), 217–226. https://doi.org/10.1023/B:PLSO.0000016552.12451.95

Xin, J., Liu, Y., Chen, F., Duan, Y., Wei, G., Zheng, X., & Li, M. (2019). The missing nitrogen pieces: a critical review on the distribution, transformation, and budget of nitrogen in the vadose zone-groundwater system. *Water Research*, *165*, 114977.

Zanders, J. M. (1998). *Studies on the origin, distribution and mobility of cadmium in pastoral soils: a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Soil Science at Massey University*. Massey University.

Zhang, H., & Davison, W. (1995). Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Analytical Chemistry*, *67*(19), 3391–3400. https://doi.org/10.1021/ac00115a005

Zhang, H., Davison, W., Gadi, R., & Kobayashi, T. (1998). In situ measurement of dissolved phosphorus in natural waters using DGT. *Analytica Chimica Acta*, *370*(1), 29–38.

Zhong, S., Li, X., Li, F., Liu, T., Huang, F., Yin, H., Chen, G., & Cui, J. (2021). Water Management Alters Cadmium Isotope Fractionation between Shoots and Nodes/Leaves in a Soil-Rice System. *Environmental Science and Technology*, *55*(19), 12902–12913. https://doi.org/10.1021/acs.est.0c04713

Chapter 3 - Application of Diffusive Gradients in Thin Films for Monitoring Groundwater Quality

Amir Mohammadi, Thomas Corbett, Amanda French, Niklas J. Lehto, John Hadfield, Peter Jarman, Dean Sandwell, Ali Shokri, Louis Schipper, and Adam Hartland

ACS ES&T Water 2022 2 (4), 518-526

DOI: 10.1021/acsestwater.1c00279

Publication History:

Received 4 August 2021

Accepted 4 March 2022

Revised 2 March 2022

Published online 21 March 2022

Published in issue 8 April 2022

ACS ES&T Water

pubs.acs.org/estwater

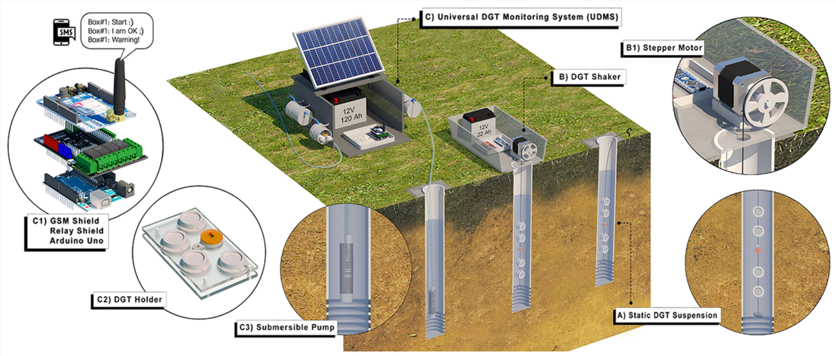
Article

Application of Diffusive Gradients in Thin Films for Monitoring Groundwater Quality

Amir Mohammadi, Thomas Corbett, Amanda French, Niklas J. Lehto, John Hadfield, Peter Jarman, Dean Sandwell, Ali Shokri, Louis Schipper, and Adam Hartland*

Cite This: https://doi.org/10.1021/acsestwater.1c00279

Read Online



ABSTRACT: Diffusive gradients in thin films (DGTs) provide time-weighted solute concentrations in well-mixed fluvial environments. However, the DGT method has rarely been applied to relatively slowly moving groundwater systems, where the increased length of the diffusive boundary layer (DBL) must be accounted for, to give accurate concentration measurements. Because the DGT method pre-concentrates trace-level solutes (e.g., Cd^{2+}) and averages out fluctuations in more dynamic contaminants (e.g., NO_3^-), it has potential advantages over conventional methods. This study evaluated the application of DGT methods for monitoring trace contaminants in groundwater, which are often present at levels below standard instrumental detection limits. We tested three different DGT deployment approaches using NO_3^- to estimate the DBL thickness: a static DGT suspension, a DGT shaker, and a pumped flow-cell unit coined the "universal DGT monitoring system" (UDMS). Unlike static and DGT shaker approaches, the UDMS reduced the DBL thickness (~0.02 cm) to values within the range of well-mixed waters (DBL $\leq$ 0.03 cm). Comparable DBL thicknesses for NO_3^- and Cd^{2+} and correlations with grab sample measurements (R^2 = 0.99 and 0.98, respectively) demonstrate the suitability of DGTs combined with the UDMS for groundwater monitoring. This approach is particularly suitable for analysis of trace-level solutes including organic contaminants.

KEYWORDS: *groundwater, passive sampling, ADBL, dissociation kinetics, grab sampling*

1. INTRODUCTION

Groundwater supplies more than half of the current global water demand.[1] Yet, declines in aquifer water quality due to intensive agriculture and industrial land uses[2,3] present challenges to the management of these resources. Among these challenges, fertilizer use affects shallow aquifers globally through nutrient and metal leaching.[4−7] However, determination of contamination trends in aquifers is difficult because many metals and nutrients exist at low levels that are analytically challenging to resolve.

Aquifer contamination with biotoxic trace-level (parts per billion, ppb or lower) contaminants such as cadmium (Cd) presents significant analytical challenges for which conventional sampling is poorly suited. Trace-level contaminants often require pre-concentration between sample collection and analysis.[8] Moreover, many analytes must be preserved upon collection and/or analyzed within a short time to provide a representative measure of concentrations at the time of sampling.[9,10] Regulators and researchers need robust, practical methods for routine groundwater quality monitoring for a range of emerging non-threshold contaminants, that is, which may be biologically active at ng L^{-1} levels.[11] Passive sampling can circumvent these issues by accumulating the target analyte in situ on an analyte-selective absorbent where it is effectively preserved until analysis, thereby providing representative time-

Received: August 4, 2021
Revised: March 2, 2022
Accepted: March 4, 2022

weighted average (TWA) concentrations, when theoretical preconditions are met.[12,13] This effect is also advantageous for other types of analysis, for example, stable metal isotope ratios[14] and organic micro-pollutant analysis.[15] Passive sampling is also more compatible with long-term environmental management by reducing groundwater monitoring costs and by better representing the average concentration.[16] This final point is pertinent where estimates of contaminant fluxes into receiving environments must faithfully account for temporal variability.

Diffusive gradients in thin films (DGT) is increasingly being viewed as a robust sampling technique for in situ measurement of solutes in freshwater environments.[17] Continuous development of DGT methods for both inorganic and organic determinants also provides for an ever-widening range of potential analytes and research applications.[18] When deployed in water, the DGT solution probe accumulates the analyte(s) of interest on a binding layer, which is separated from the bulk solution by an agarose cross-linked polyacrylamide (APA) hydrogel and filter membrane, together termed the ″material diffusion layer" (MDL).[19] These layers are contained in an inert plastic holder with a circular exposure window. Within around 1 h of deployment commencement, a diffusive gradient between the binding layer and the bulk solution establishes, leading to a steady flux of solute from the solution into the binding layer. At the end of the deployment, the accumulated solute mass can be measured and used to estimate the average concentration at the water−filter membrane interface over the deployment period.

In early DGT studies, the probe−water interface concentration was thought to be equivalent to the bulk solution concentration.[20] However, subsequent studies showed that in all solution deployments, a stagnant layer of water next to the probe interface exists that has a lower concentration compared to the rest of the solution.[18,21,22] The thickness of this ″diffusive boundary layer" (DBL) increases with the decreasing flow rate of the adjacent solution, which can confound the use of DGT for measuring solute concentrations in quiescent environments, such as groundwater monitoring wells.[22−24] Under such conditions, the thickness of the DBL can be determined by using several DGT devices with a range of MDL thicknesses to enable accurate solution concentration measurements with DGT.[18]

In addition to purely physical effects, the amount of analytes accumulated by the DGT resin gel and hence the reported concentrations can be affected by differences in the dissociation kinetics of different analyte complexes. Free analytes (e.g., NO_3^-) diffuse faster than ions that are complexed with large ligands, such as those found in dissolved organic matter.[23,25,26] Moreover, when these complexes are partially labile, the flux of analytes to the binding layer can be limited by diffusion and the rate of dissociation from the complex. The term ″apparent diffusive boundary layer" (ADBL) reflects the different properties of metal−organic complexes and therefore provides information on the lability of contaminants.[25] Where complexes are present, the ADBL is often thicker than the physical DBL;[25] therefore, the DBL must be quantified in order to assess ADBL values of the various components.

To date, few papers have investigated the application of DGT in groundwater studies.[24,27,28] To our knowledge, there have been no investigations of (a) the limitations associated with the static DGT suspension in bores and piezometers, (b) DBL effects in stagnant groundwater, and (c) kinetically limited dissociation of metal complexes in groundwater. Therefore, this research is aimed to test the application of DGT in monitoring groundwater quality by testing three different approaches to DGT deployment. In these tests, NO_3^- was used as a conservative tracer (i.e., non-kinetically limited) to evaluate approaches to minimize the DBL effect. With knowledge of DBL effects based on simultaneous nitrate DGT deployments, the different kinetic restrictions between trace metals (ADBL) were further evaluated.

2. MATERIALS AND METHODS

2.1. Study Area. Eight small-diameter (90−100 mm) piezometers and seven large-diameter ($D \geq 900$ mm) bores were selected around the Waikato region of Aotearoa New Zealand. The selection was based on a range of soil types, land uses, and logistical factors. Locations, dimensions, water table depths, and details of these piezometers/bores are given in the Supporting Information (Table S2).

2.2. Gel Preparation and DGT Assembly. All solutions were prepared using ultrapure (type I, resistivity 18.2 MΩ) water (Milli-Q Direct, Merck, Massachusetts, USA). All chemicals were of the analytical reagent grade or higher. DGT housings and cross-linkers (0.3%) were supplied by DGT Research Ltd (Lancaster, UK). All experimental components were acid-washed in 10% (v/v) HCl for 24 h, followed by 10% (v/v) HNO_3 for 24 h, before being thoroughly rinsed with ultrapure water. For some parts of this experiment, the HNO_3 washing step was skipped to minimize contamination where the analyte of interest was NO_3^-. All laboratory and field tests were conducted in triplicate at a minimum.

APA, Chelex-100 (Bio-Rad, California, USA), ferrihydrite, and Purolite A520E (Purolite, Pennsylvania, USA) binding gels were prepared separately under clean conditions within a laminar flow cabinet to minimize contamination. The procedure of preparation of APA and Chelex gels was similar to that by Zhang and Davison (1995).[19] Ferrihydrite and A520E binding gels were prepared as described by Huang et al. (2016)[29] and Corbett et al. (2020).[16]

All binding gels were prepared by mixing gel solution (10 mL, 15% acrylamide, and 0.3% cross-linker) with the required amount of binding resin: 2 g of Chelex-100, 2 g of ferrihydrite slurry, or 4 g of ground A520E powder (≤125 μm particle diameter) were used to achieve final binding material contents of 12.5 mg (Chelex-100 and ferrihydrite) and 60 mg (A520E) per DGT sampler. To this mixture, 70 μL of freshly prepared 10% ammonium persulfate solution and 25 μL of TEMED were added while stirring. The solution was pipetted immediately between glass plates separated by 0.25, 0.4, and 0.5 mm spacers for Chelex, ferrihydrite, and A520E, respectively. The gels were then cured at 45 °C for 90 min, followed by a 24 h hydration period in ultrapure water and stored at 4 °C. Three different thicknesses of diffusion gels were cast: 0.4, 0.64, and 0.8 mm. The preparation procedure was the same for the APA diffusive gels, with the exception that the hydrating water was changed at least three times during the hydration period. After hydration, the APA gels were stored in 0.01 mol L^{-1} NaCl until probe assembly. 12 types of DGT devices were assembled, comprising one set of replicates for each binding gel-diffusive gel combination. Polyethersulfone filter membranes (pore size: 0.45 μm and thickness: 0.14 mm) were used to protect the gels. The assembled probes were

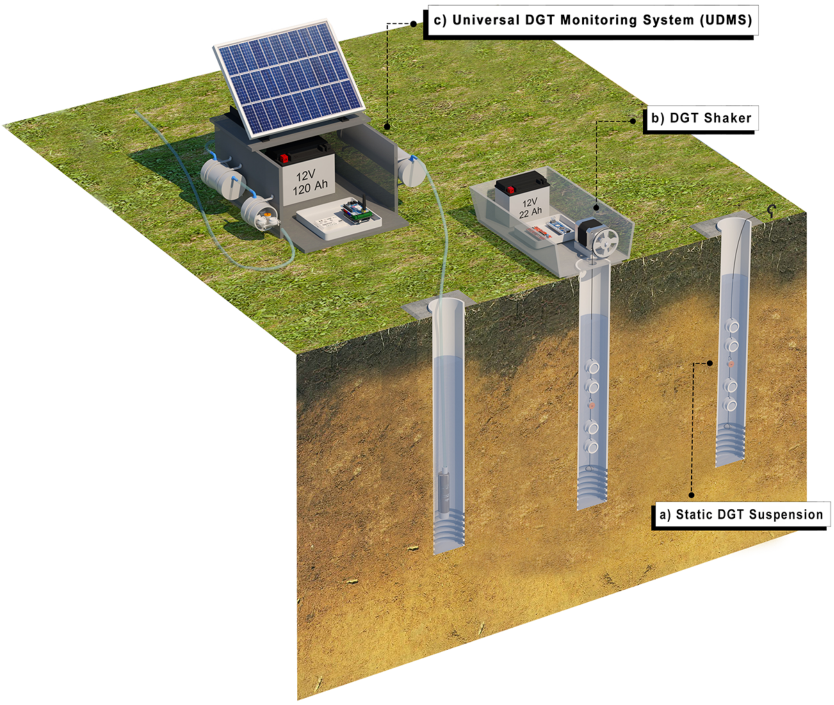


Figure 1. Schematic of three DGT deployment approaches for groundwater monitoring, (a) static DGT suspension, (b) DGT shaker, and (c) UDMS.

stored at 4 °C in resealable plastic bags with a few drops of ultrapure water until deployment.

2.3. Sample Analysis and Calculations. Temperature, pH, Eh, electrical conductivity (EC), and dissolved oxygen (DO %) were measured in each borehole after purging (two times the borehole volume) prior to DGT deployment and upon the retrieval using a YSI ProDSS (YSI Incorporated, Ohio, USA) handheld multiparameter water quality meter. All sensors were calibrated on the day before measurements were taken. General groundwater quality data for all sites are included in the Supporting Information (Table S3). Three grab samples were taken daily alongside all DGT deployments for comparison (Section 2.5). All grab samples were filtered to 0.45 μm immediately after collection. The samples intended for metal analysis were acidified with 2% (v/v) trace-element grade HNO_3 (69% Merck, Massachusetts, USA), while the samples for NO_3^- analysis were stored on ice at 4 °C. All samples were either analyzed on the same day or refrigerated at 4 °C until subsequent instrumental analysis.

Nitrate concentrations were determined using a Dionex ICS-2000 ion chromatograph (Dionex, California, USA). Metals measurements were conducted using an Agilent 8900 ICP−MS (Agilent Technologies, California, USA) controlled using a MassHunter Workstation (version 4.5). Phosphorus measurements were performed using Dynamica Halo Vis-20 (Dynamica Scientific, Livington, UK). Instrumental limits of quantification (LOQs) were 0.1 μg L^{-1} (Co, Ni, Cu, Cd, and Pb), 1.0 μg L^{-1} (P and Zn), 10 μg L^{-1} (Al), and 0.1 mg L^{-1} (NO_3^-). A five-point calibration curve for nitrate and metals and a ten-point calibration curve for phosphorus were performed alongside each measurement. Check standards, type I water, and DGT blanks were analyzed every 10−20 samples to ensure minimal drift and carryover between samples. Sc was used as the internal standard for major cations, while Ge was used as the internal standard for the transition metals.

After each deployment period, DGT devices were retrieved and handled cautiously to avoid cross-contamination. All DGT devices were rinsed with type I water and packaged in sealable plastic bags. Binding gels were eluted for at least 24 h using 1 mL of 1 mol L^{-1} HNO_3, 10 mL of 0.25 mol L^{-1} H_2SO_4, and 4 mL of 2 mol L^{-1} NaCl for Chelex, ferrihydrite, and A520E DGTs, respectively, before being analyzed.

The accumulated masses of the analytes on the binding layers were then calculated using the analyte concentrations in the eluents. The TWA concentrations were determined using eq 1.[18]

$$C_{\mathrm{DGT}} = \frac{M}{A_e t}\left(\frac{\delta^g}{D^g} + \frac{\delta^f}{D^f} + \frac{\delta^{\mathrm{DBL}}}{D^w}\right) \quad (1)$$

where C_{DGT} is DGT concentration (μg L^{-1}), M is accumulated mass of analytes (μg), A_e is the effective area (3.8 cm^2), t is deployment time (sec), and δ^g, δ^f, and δ^{DBL} are the thicknesses of the diffusive gel, filter membrane and physical DBL, respectively (cm). D^g, D^f, and D^w are the analyte diffusion coefficients through the diffusive gel, filter membrane, and water (cm^2 s^{-1}), respectively.[18] Due to lateral diffusion occurring close to the edge of DGT caps, the effective area (A_e = 3.8 cm^2) is slightly larger than the physical area of the exposure window (A_p = 3.14 cm^2).[22] All diffusion coefficients were obtained from Davison (2016),[18] except NO_3^- which was obtained from Huang et al. (2016).[29] The temperature dependence of the diffusion coefficients was corrected based on the Stokes−Einstein equation and diffusion coefficients of analytes at 25 °C.[30]

To ensure an accurate and quantitative assessment of DGT concentrations, accounting for the background mass of the analytes in gels is essential.[18] Blank DGTs were analyzed alongside the deployed DGTs to monitor cross-contamination during laboratory preparation and field deployment. Each binding layer blank mass was subtracted from the measured masses of the deployed DGTs.

The operating performance of DGTs, including the uptake and elution efficiency, and the binding capacity of the binding disks are summarized in the Supporting Information (section S.1). To make our approach accessible to practitioners, we estimated the minimum and maximum deployment times for each analyte based on in-field conditions, and on this basis, recommendations are made in Section 4.5. Using eq 1, we based our estimates on (a) the typical concentration ranges of analytes in shallow aquifers (9 mg L^{-1} NO_3^-, 1 μg L^{-1} Cd, and 140 μg L^{-1} P),[3,5] (b) the LOQ of the analytical instruments, and (c) the binding capacity of absorbents. Calculations were performed for standard DGT devices for solution deployments, with a diffusive gel thickness of 0.8 mm, and a 0.2 mm DBL thickness, an exposure window of 3.14 cm^2, and a temperature of 15 °C (typical global shallow groundwater temperature[31]) were assumed.

2.4. ADBL. The ADBL for each analyte was determined by deploying DGTs with different diffusive layer thicknesses (δ^{MDL}) from 0.13 to 0.93 mm, where δ^{MDL} was the sum of the thickness of diffusive gel (δ^{gel}) and the filter membrane (δ^{f}). The ADBL thickness (δ^{ADBL}) was then calculated by plotting M^{-1} versus δ^{MDL} using eq 2, where b is the intercept and c is the slope of the linear relationship of M^{-1} versus δ^{MDL}.

$$\mathrm{ADBL} = \frac{b}{a}\left(\frac{D^{w}A_{p}}{D^{g}A_{e}}\right) \qquad (2)$$

2.5. DGT Deployment Approaches. Three different approaches have been tested in this study to modify the application of DGTs for stagnant and semi-stagnant solution scenarios. A video of all three types of field deployments is available online (https://youtu.be/JoTGFwwlwng). The DBL thicknesses were measured and compared using the different approaches to minimize the DBL effect on the accuracy of determined concentrations. Three grab samples were taken daily from each site to compare against the passive sampling methods. All boreholes were purged two−to−three times the volume of each borehole prior to grab sampling and DGT deployment using the following approaches. Chelex, ferrihydrite, and A520E DGTs were deployed alongside each other to observe the kinetic restrictions of different analytes. Nitrate was assumed to act as a conservative tracer, and hence, its ADBL was used to estimate the physical DBL to be estimated for the other analytes. In each case, the deployed DGT devices were inspected to confirm that there was no significant biofilm formation ("biofouling") on the probes.

2.5.1. Static DGT Suspension. DGTs were arranged on a fishing line with a temperature data logger (HOBO TidbiT v2, Onset, Massachusetts, USA) and a weight. River stones were used as weights to minimize cross-contamination, compared to metal weights. The assembly was then suspended within the borehole/piezometer (Figure 1a). Because groundwater levels had the potential to fluctuate during deployments due to groundwater abstraction, DGTs were deployed at least 1 m below the groundwater table to ensure that they were submerged throughout the deployment period.

2.5.2. DGT Shaker. DGTs and a temperature data logger were arranged on a nylon fishing line. The fishing line was attached to a motorized assembly, "DGT shaker" (Figure 1b). The DGT shaker consisted of a pulley attached to a stepper motor, which was controlled by a microcontroller (Arduino Nano, Arduino, Somerville, USA), stepper motor driver circuits, and a battery. DGT shaker was designed to steadily move the DGTs up and down over a 30 cm height range in the bore/piezometer and minimize the DBL effect of stagnant water. The effective velocity of the water at the DGT interface was ~15 cm s^{-1} for the pulley dimensions used here (radius 4 cm). All DGTs were positioned at least 1.3 m below the groundwater table to ensure that DGTs were continuously submerged throughout the deployment time. The setup was easy to transport, and it could be deployed for up to a month with a full battery charge (12 V and 22 Amp-hour). All programming, schematics, and details for the DGT shaker are given in the Supporting Information.

2.5.3. Universal DGT Monitoring System. The universal DGT monitoring system (UDMS) consisted of a submersible pump, relays, an Arduino Uno microcontroller, an Arduino compatible cellphone to communicate errors, warning sensors, batteries, a solar panel, a solar panel regulator, and three different DGT flowcells for Chelex, A520E, and ferrihydrite DGTs (Figure 1c).

UDMS pumped groundwater to the surface, which was then passed through opaque flowcells loaded with DGTs and temperature data loggers mounted on acrylic holder plates. The pump was controlled by the microcontroller and the relay shield and was programmed to sequentially turn the pump on and off to allow recharge in the sampling well. The UDMS was programmed to pump the groundwater for 1 min before going into the sleep mode for several minutes (1−9 min). The submersible pump used in the UDMS setup was capable of pumping 6−9 L min^{-1}: the flow rate was dependent on numerous factors, including groundwater table depth and bore/piezometer recharge rates. The water velocity in the cell generally varied between 10 and 15 cm s^{-1}.

Bore recharge rates were tested individually before each deployment by recording the time that it took for the pump to empty the bore. The submersible pump was then reprogrammed at the site. Hence, the water extraction was at a low enough rate to achieve stable drawdown and avoid emptying the bore. In piezometers with lower recharge rates, the pump was programmed for a shorter working period (20 s on) to ensure that the pump stopped before emptying the piezometer.

For all the UDMS deployments, the ratio of the number of deployed DGTs to the total volume of flowcells (4 DGTs:2L) was consistent. In a no-water extraction scenario, that is, where the pump stops working, it was calculated (using eq 1) that DGTs in UDMS flowcells would lower the target analyte concentrations by no more than 6−12% over 24 h. For comparison, the maximum duration of water residence in the flowcells under normal operation was 9 min.

UDMS was equipped with a water sensor within the case to warn about water leakage; a voltage monitoring sensor monitored the performance of the battery and the pump, and a magnetic reed switch warned about tampering. The solar panels charged the battery (12 V and 120 Amp hour), enabling UDMS to run continuously. All programming, schematics, and other relevant details are given in the Supporting Information.

3. RESULTS

The pH of all sites was within the operational range of Chelex 100 (pH 5.0−8.3),[19] A520E (pH 3.5−8.5),[29] and ferrihydrite

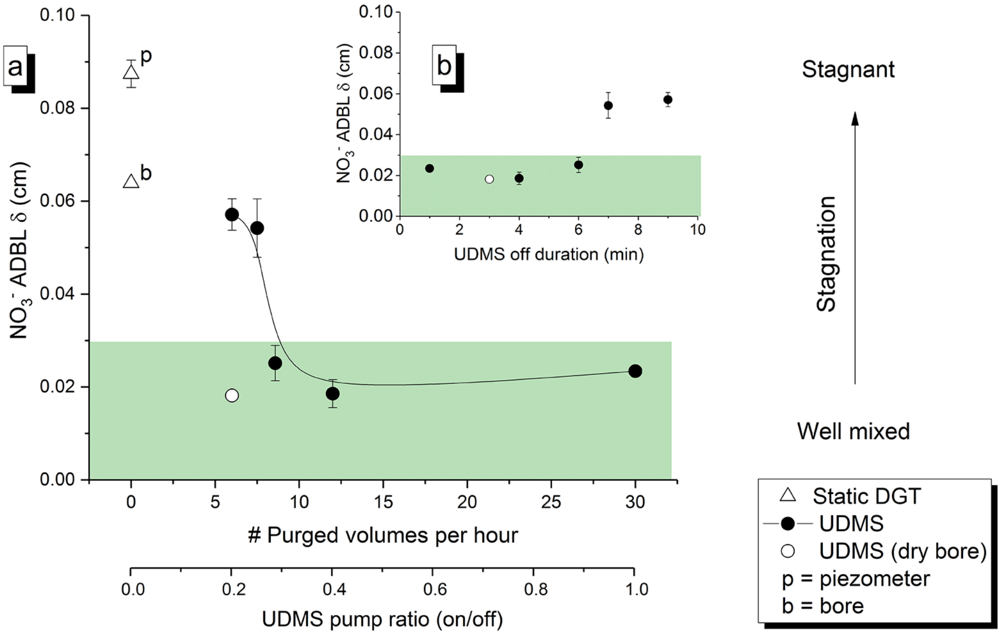


Figure 2. Average nitrate DBL (cm) values in groundwater using different DGT deployment approaches. (a) All approaches are shown relative to the rate of groundwater extraction and the UDMS on/off ratio. Zero for DGT shaker and static deployments. (b) Groundwater nitrate DBL values based on UDMS off-duration (min). b = bore and p = piezometer. Error bars are 1σ based on multiple deployments (n = 2 to 3). Green boxes show the range of DBL values for well-stirred and fast-flowing systems.

(pH 3.2–6.9).[32] During the UDMS deployment period, there were no major changes in groundwater properties, including water table depth, pH, EC, Eh, DO %, and temperature. Although excessive pumping could conceivably result in changes in groundwater properties (e.g., water table depth and solute concentrations) and flow paths on the subsurface,[28] the stability of the groundwater parameters in this study suggests that groundwater abstraction with the UDMS was low enough to avoid such issues.

3.1. Nitrate DBL Thicknesses Using Different Approaches. A static suspension of A520E DGTs in a large-diameter bore ($D \geq 900$ mm) and an average of small-diameter piezometers ($D \leq 100$ mm) returned nitrate δ^{DBL} of 0.076 and 1.05 cm, respectively (Figure 2). A DGT shaker deployment in a large-diameter bore returned a nitrate δ^{DBL} of 0.061 cm. Bores and piezometers were only purged before deployment and after retrieval while using the static DGT and the DGT shaker.

In Figure 2a, nitrate δ^{DBL} versus the pumping rate of UDMS is shown. For reference, the number of extracted flow cell volumes (primary x-axis) was equal to the total min h^{-1} of UDMS pumping. The secondary x-axis shows the UDMS pump ratio (on/off), which was the ratio of the working period to the stopped period of the submersible pump. $\mathrm{NO_3}^-$ DBL thicknesses decreased with the working period/stopped period ratio of the submersible UDMS pump. Increasing that ratio above 0.2 significantly lowered the DBL thickness to the range previously observed in well-stirred and fast-flowing systems.[25,33,34] Comparing DBL versus UDMS off-duration (Figure 2b) showed that applying UDMS off-durations below 6 min would likely result in low nitrate DBL values (≤0.03 cm).

3.2. ADBL Measurement. ADBL values for different analytes were calculated for the UDMS deployments. The plot of M^{-1} versus δ^{MDL} for one of the sites (site no. 7, available in Supporting Information) is shown (Figure 3a) as an example. As expected, the inverse masses of nitrate, phosphorus, and metals (e.g., Cd) linearly correlated with δ^{MDL} ($R^2 = 0.98 \pm 0.02$, being the average for all analytes at this site). The average of R^2 values for all analytes and sites was 0.87 ± 0.13. The ADBL for all analytes for each study site was calculated using eq 2. The difference between the metal ADBL and nitrate DBL value [δ^{ADBL} − ($\mathrm{NO_3}^-$ δ^{DBL})] for each analyte was then calculated and showed that differences between $\mathrm{NO_3}^-$ and the metal ADBL increased in the order Cd < Ni < Zn < Pb ∼ Co < Cu < Al < P (Figure 3b).

3.3. DGTs versus Grab Samples. The DGT-determined concentrations of Cd and $\mathrm{NO_3}^-$ were typically within 70 and 90% of concentrations detected in grab samples (Figure 4a), respectively. Nitrate DGT concentrations showed the same magnitude and trend as the grab nitrate concentrations (Figure 4c), following the 1:1 line closely. There was also a good agreement between Cd DGT and grab sample concentrations, despite the grab samples generally being below the ICP–MS LOQ (Figure 4b). The DGT: grab sample ratios of analytes decreased in the order $\mathrm{NO_3}^-$ > Cd > Al ∼ P ∼ Co ∼ Ni > Zn > Pb > Cu (Figure 4a). All metal DGT concentrations were considerably above the ICP–MS LOQ. DGTs mostly reported lower concentrations compared to grab samples, likely due to the different kinetic behavior of the non-conservative analytes.

4. DISCUSSION

4.1. Evaluating the Different DGT Deployment Approaches. The "static" DGT deployment is not technically challenging; however, it does not allow for accurate measurements in the stagnant environment due to the increased DBL thicknesses. Moreover, the method of deploying DGTs in small-diameter piezometers is also problematic because the probe interface can rest against piezometer walls, thereby restricting the free diffusion of solute from the water into the

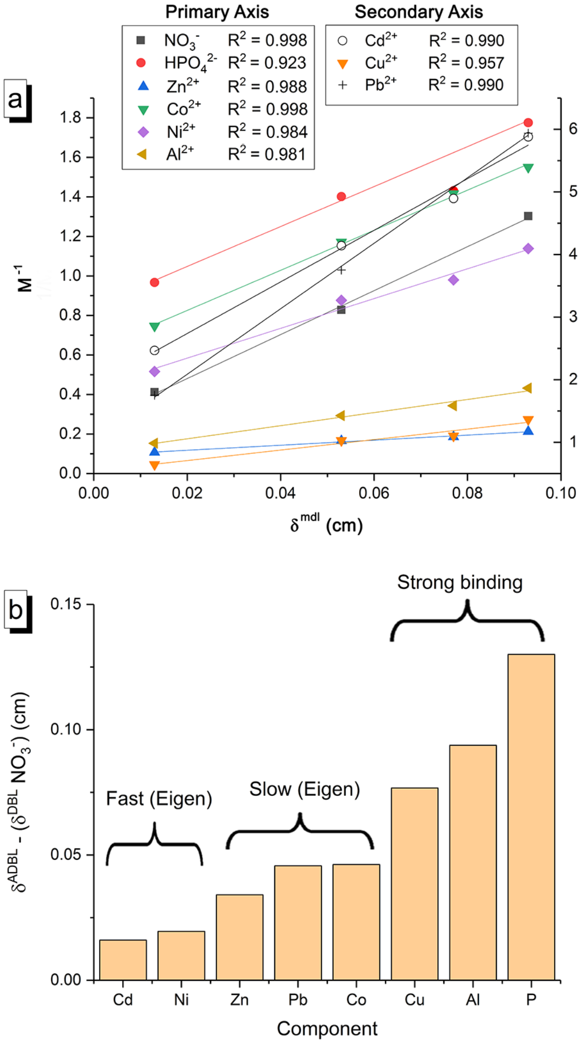


Figure 3. (a) Plots of the inverse accumulated mass of the analytes of interest versus MDF thicknesses (δ^{MDL}) for one UDMS deployment (site 7, details available in Supporting Information). All inverse mass units are μg^{-1} except for nitrate (mg^{-1}). (b) Plot of the ADBL thickness of the analytes of interest grouped based on binding strength.

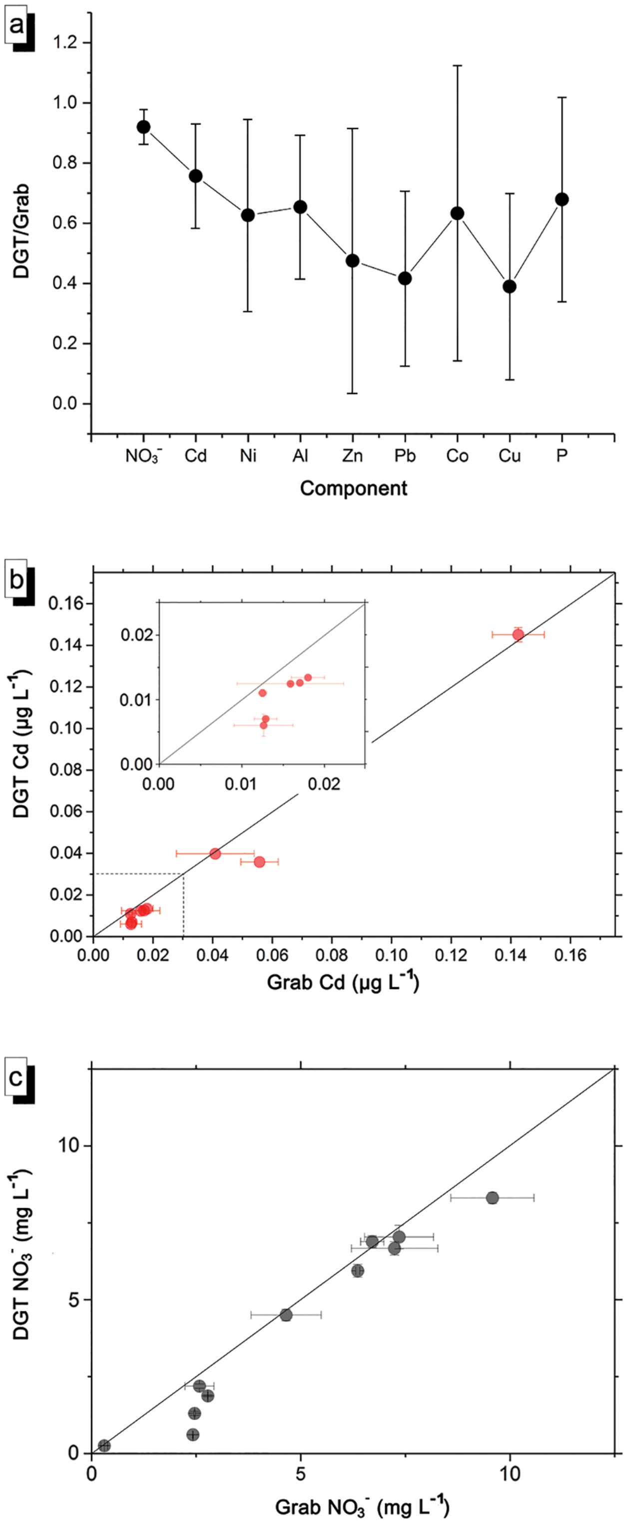


Figure 4. Performance of UDMS DGT against grab sampling. (a) Average ratio of DGT concentrations to those from grab samples. Data from individual sites (b) nitrate and (c) cadmium, where DGT *n* = 4 and grab samples *n* = 3 per day (deployment times varied). Solid line represents y = *x*.

probe. This is a random effect that will impact individual DGT devices and cannot be compensated for after the deployment.

The ″DGT shaker″ was easy to transport to sampling sites and reduced the physical DBL of the DGT. However, the nylon line was prone to be tangled or adhered to the walls of the well. As a result, motor failure of the pulley apparatus was seen in some cases and hence this method should be restricted to use only in large-diameter boreholes with minor modifications to the pulley (by increasing the pulley groove width and depth).

The UDMS approach overcame the problems seen with the static DGT and the DGT shaker deployments. Pumping water helped to ensure that DGTs were exposed to fresh groundwater throughout the deployment. Another advantage of this approach is that groundwater can be pumped from specific depths when combined with piezometer packers.[27] Moreover, UDMS as a standalone device was capable of long monitoring deployments by employing solar panels and remote communication technologies, and it was shown to be easy to transport and set up (usually <10 min after arrival on site). The UDMS enabled monitoring of groundwater with DGT devices and therefore has potential for use in long-term (monthly, seasonal, or yearly) environmental monitoring.

4.2. The Effect of UDMS Pumping Frequency on the Nitrate DBL.

Previous studies have shown the effects of flow rate and stirring on DBL thicknesses and associated DGT measurement accuracy;[18,21] however, even in a vigorously stirred system, a thin residual DBL will remain close to the surface of DGTs.[25,33,34] Because of this, an accurate and quantitative assessment of concentrations measured by DGT is ensured by determining the DBL thickness through simultaneous deployment of DGTs with a range of δ^{MDL}.

Garmo et al. (2006)[21] estimated that δ^{DBL} dependence on the velocity of ambient solution will be small when the effective flow rate exceeds 2 cm s^{-1}. Corbett et al. (2020)[16] also showed that NO_3^- DBLs in narrow piezometers that sample denitrifying bioreactors are on average ∼0.19 cm, consistent with low flow rates typical of these systems. In this study, the DBL values for static DGT deployments in piezometers (0.105 cm ± 3.3%) and the wider bore (0.076 cm) were considerably higher than the values observed in well-mixed systems (around 0.03 cm)[18] but lower than static deployments in bioreactor tube wells.[16] By comparison, the UDMS reduced the NO_3^- DBL thickness by a factor of 4.7 compared to static deployments (average UDMS DBL = 0.022 cm ± 0.004). During the UDMS pumping period, the groundwater velocity in the flowcells ranged between 10 and 15 cm s^{-1}. The minimum UDMS pump ratio needed to approach DBL values obtained in well-stirred solutions ($\delta^{DBL} \leq 0.03$ cm) was found to be 0.3 (on/off) (Figure 2a). Hence, the effective average water velocity over the UDMS deployment using >0.3 (on/off) pumping ratio settings is >3.3 cm s^{-1}. This flow rate exceeds the estimated minimum velocity (2 cm s^{-1}) for a thinner DBL than 0.03 cm based on hydrodynamic considerations.[21]

In one of the piezometers, the water table was too shallow (0.5 m deep) and the piezometer was incapable of fast recharge. The piezometer was depleted before the 1 min pumping session ended. Instead of 1 min on, UDMS was programmed to pump water for 20 s on/3 min off to avoid depleting the piezometer and abstraction from adjacent areas. Although this setup had a similar pump ratio (on/off) to the setup with 1 min on/9 min off, it drastically decreased the ADBL thickness. It was concluded that the nitrate DBL thickness depended on UDMS off-duration, hence by decreasing the off-duration, the ADBL thicknesses decreased accordingly (Figure 2b).

4.3. DGT versus Grab Sample Concentrations.

More than half of the grab sample metal concentrations were below or just above the LOQ of the analytical instruments. Almost all NO_3^- samples were above the LOQ, whereas only one grab sample was above the LOQ for Cd. DGTs accumulated analytes, such that the concentrations of analytes in binding disks after elution were all significantly above the instrument LOQ. The use of DGTs, therefore, overcame limitations associated with the LOQ of analytical instruments.

Huang et al. (2016)[35] showed that the average of DGT: grab sample ratios for NO_3^- and PO_4^{3-} were between 1.00 and 1.12 over the study deployment period. Our study showed that the average DGT: grab sample ratio for NO_3^- was 0.9. Despite the 0.7 ratio for P (i.e., DGT on average underestimated PO_4^{3-} concentrations), our results showed a great deal of variation between sites, probably reflecting a wider variability in P speciation in the aquifers studied here. Allan et al. (2007)[36] also evaluated the responsiveness of DGT devices to rapidly changing concentrations in natural river water and experimental tanks compared to the grab sampling method. Our results for metals showed similar DGT: grab sample ratios (0.45 μm-filtered) as their results in an experimental tank, with the ratio of metals decreasing in the same order (Cd > Ni > Zn > Pb > Cu). Allan et al. (2007)[36] noted that biofouling of DGT surfaces and differential dissociation kinetics of organic−metal complexes can also affect the accuracy of the DGT method for measuring metals in natural systems. Because DGTs underestimate the concentration of analytes in the presence of strong complexes, a correction factor may be applied to improve the accuracy of C_{DGT} for these determinants but should be used cautiously.[37]

In dynamic surface water systems, where concentrations will vary with time and/or depend on environmental factors, DGT has clear advantages over grab sampling because infrequent grab sampling only provides a snapshot in time whereas DGTs provide TWA concentrations. Clearly, from the perspective of capturing transient changes in solute concentration, DGT has greater relevance in settings characterized by higher flow rates or groundwater−surface water interactions, where concentrations could change more dynamically.[38] For studies targeting TWA concentrations in dynamic fluvial settings, increasing the frequency of grab sampling will reduce the discrepancies between DGTs and the average of grab samples.[16] As grab sampling frequency increases, the changes in analyte concentrations are better resolved. However, this has limitations in terms of costs and logistics. For groundwater monitoring, DGTs decreased the number of samples to one sample (excluding duplicates) for analysis and overcame detection and quantification issues for low-concentration analytes. Due to these advantages, DGTs proved suitable for monitoring cadmium in aquifers and may prove suitable for determining other trace-level contaminants, such as emerging organic contaminants,[15] where low concentration is the main impediment to determining long-term trends.

4.4. Analyte Dissociation Kinetics.

The ADBL has been used as a means to examine the extent to which trace metal complexes limit metal uptake by the DGT when dissolved ligands are present.[25,26,39,40] The pattern of the increasing ADBL (viz. decreasing dissociation rate of the complex) observed here (Figure 3b) generally agrees with the aforementioned reports, where Cd and Zn complexes were shown to dissociate quickly, while complexes of other metals (e.g., Cu and Al) were relatively inert. Metal-binding ligands in natural freshwaters are highly heterogeneous, and hence, estimation of precise dissociation rates for complexes using this approach is difficult.[41] However, using NO_3^- as a conservative (fully labile) tracer alongside measurement of metals with DGT allows the effect of the physical DBL to be measured independently. This provides a strong indicator of the net kinetic limitation imposed by the complexes on metal uptake by DGTs over the deployment period, without the need to obtain representative measurements of potential binding ligands (e.g., dissolved organic matter). The NO_3^- DBL: metal ADBL ratio could be used as an index of metal bioavailability and potential toxicity, for example, to freshwater biota. Although this application requires validation, there is evidence to support it in principle.[23,42]

4.5. Suitability of DGT for Long-Term Deployments.

The calculations for the recommended and maximum deployment length of different DGTs for monitoring groundwater quality indicated that Purolite, Chelex, and ferrihydrite DGT devices should be retrieved no sooner than 1, 14, and 14 days after deployment, respectively. These durations were usually enough to ensure that the accumulated mass of analytes in DGTs deployed in shallow groundwater were considerably above the LOQs. The maximum deployment lengths for Purolite, Chelex, and ferrihydrite DGT devices were determined to be 14 days, 5 months, and 1 year, respectively. Long DGT deployments should account for biofouling and competition effects to ensure analytes maintain steady-state diffusion. Biofouling can block the filter membrane pores, restricting analyte diffusion pathways, and has shown to affect long-term DGT deployments,[23,36] but this was not a problem here. Competition effects arise from the simultaneous presence of ions with different binding strengths.[18] This is more likely when DGT devices are deployed in saline water and/or non-circumneutral pH (<5.5 or >7.4). However, groundwater salinity and pH were not a problem here.

5. CONCLUSIONS

The application of DGTs using a static suspension in boreholes is problematic due to the stagnancy of groundwater. Monitoring of groundwater using the UDMS provided concentration data that compared well with high-frequency grab sampling and provided insights into analyte kinetics (and potential bioavailability). The UDMS overcame the limitations associated with stagnancy by pumping groundwater through DGT flowcells, and achieved around a fourfold decrease in the DBL thicknesses. Analytes with fast dissociation rates also showed lower ADBL thicknesses compared to analytes with strong binding characteristics, extending insights into these processes to quiescent aquifers. The UDMS approach is particularly suitable for monitoring of low-level contaminants such as cadmium and in settings where higher frequency changes in solute concentration are expected, such as in alluvial groundwater systems, or denitrifying bioreactors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00279.

> Video showing the UDMS components and specifications, design of the DGT shaker, and overview of deployment approaches (MP4)
>
> Uptake and elution efficiency and binding capacity tests, study area, DGT deployment methods catalogue, UDMS components and specifications, groundwater properties for the study sites, overview of three DGT deployment approaches for groundwater monitoring, cross-section of the three DGT deployment approaches for groundwater monitoring, design of the DGT shaker, design of the UDMS, arrangement of Arduino compatible electronic boards of UDMS, cross-section of a flowcell containing the DGT holder, and UDMS components and specifications (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Adam Hartland – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand;* orcid.org/0000-0002-1864-5144;
Email: adam.hartland@waikato.ac.nz

Authors

Amir Mohammadi – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand;* orcid.org/0000-0001-8201-2993
Thomas Corbett – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand;* Present Address: Department of Earth Sciences, Uppsala University, Villavägen 16 752 36 UPPSALA, Sweden; orcid.org/0000-0001-6943-0373
Amanda French – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand;* Present Address: Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington, United States
Niklas J. Lehto – *Faculty of Agriculture and Life Science, Lincoln University, Lincoln 7647, New Zealand*
John Hadfield – *Waikato Regional Council, Hamilton 3204, New Zealand*
Peter Jarman – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand*
Dean Sandwell – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand;* Present Address: BTW Company Ltd, 517 Anglesea Street, Hamilton Central, Hamilton 3204, New Zealand
Ali Shokri – *School of Engineering, University of Waikato, Hamilton 3216, New Zealand*
Louis Schipper – *Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsestwater.1c00279

Funding

This study was funded by The University of Waikato, DairyNZ, and the Ministry of Business, Innovation, and Employment (MBIE, Smart Ideas contract UOWX1804). A.H. was also supported by a Rutherford Discovery Fellowship [RDF-UOW1601]. The views expressed in this paper are those of the authors and do not necessarily reflect the views or policies of The University of Waikato, Waikato Regional Council, DairyNZ, and MBIE.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We would like to acknowledge John Hughey and Sajeewa Herath from the Waikato Regional Council for providing access to study sites across the Waikato region, Ben Fisher from DairyNZ for providing access to the Scott Farm site, Purolite Co. for supplying the A520E anionic exchange resin, Mehdi Ghorashi Nezhad for graphical design support, and Sajed Golabpars for helping in Arduino programming.

■ REFERENCES

(1) Connor, R. *The United Nations World Water Development Report 2015: Water for a Sustainable World. Vol 1*; UNESCO publishing, 2015.

(2) Xiang, T.; Malik, T. H.; Nielsen, K. The impact of population pressure on global fertiliser use intensity, 1970-2011: An analysis of policy-induced mediation. *Technol. Forecast. Soc. Change* **2020**, *152*, 119895.

(3) Burri, N. M.; Weatherl, R.; Moeck, C.; Schirmer, M. A review of threats to groundwater quality in the anthropocene. *Sci. Total Environ.* **2019**, *684*, 136−154.

(4) Dymond, J.; Ausseil, A.-G.; Parfitt, R.; Herzig, A.; Mcdowell, R. Nitrate and phosphorus leaching in New Zealand: a national perspective. *N. Z. J. Agric. Res.* **2013**, *56*, 49.

(5) Kubier, A.; Wilkin, R. T.; Pichler, T. Cadmium in soils and groundwater: A review. *Appl. Geochem.* **2019**, *108*, 104388.

(6) Belon, E.; Boisson, M.; Deportes, I. Z.; et al. An inventory of trace elements inputs to French agricultural soils. *Sci. Total Environ.* **2012**, *439*, 87−95.

(7) Zhou, Z.; Ansems, N.; Torfs, P. *A Global Assessment of Nitrate Contamination in Groundwater*; International Groundwater Resources Assessment Center, 2015; pp 1−27.

(8) Poulier, G.; Lissalde, S.; Charriau, A.; et al. Estimates of pesticide concentrations and fluxes in two rivers of an extensive French multi-agricultural watershed: application of the passive sampling strategy. *Environ. Sci. Pollut. Res. Int.* **2015**, *22*, 8044−8057.

(9) Burke, P. M.; Hill, S.; Iricanin, N.; Douglas, C.; Essex, P.; Tharin, D. Evaluation of preservation methods for nutrient species collected by automatic samplers. *Environ. Monit. Assess.* **2002**, *80*, 149−173.

(10) Worsfold, P.; Mckelvie, I.; Monbet, P. Determination of phosphorus in natural waters: A historical review. *Anal. Chim. Acta* **2016**, *918*, 8−20.

(11) Richardson, S. D. Water analysis: emerging contaminants and current issues. *Anal. Chem.* **2009**, *81*, 4645−4677.

(12) Greenwood, R.; Mills, G.; Vrana, B. *Passive Sampling Techniques in Environmental Monitoring*; Elsevier, 2007.

(13) Zabiegała, B.; Kot-Wasik, A.; Urbanowicz, M.; Namieśnik, J. Passive sampling as a tool for obtaining reliable analytical information in environmental quality monitoring. *Anal. Bioanal. Chem.* **2010**, *396*, 273−296.

(14) Salmanzadeh, M.; Hartland, A.; Stirling, C. H.; et al. Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil. *Environ. Sci. Technol.* **2017**, *51*, 7369.

(15) Wang, R.; Zou, Y.; Luo, J.; Jones, K. C.; Zhang, H. Investigating potential limitations of current diffusive gradients in thin films (DGT) samplers for measuring organic chemicals. *Anal. Chem.* **2019**, *91*, 12835−12843.

(16) Corbett, T. D. W.; Dougherty, H.; Maxwell, B.; et al. Utility of "Diffusive Gradients in Thin-Films" for the measurement of nitrate removal performance of denitrifying bioreactors. *Sci. Total Environ.* **2020**, *718*, 135267.

(17) Österlund, H.; Widerlund, A.; Ingri, J.; Davison, W.; Zhang, H. Applications in Natural Waters. *Diffusive Gradients in Thin-Films for Environmental Measurements*; Cambridge, 2016; pp 123−145.

(18) Davison, W. *Diffusive Gradients in Thin-Films for Environmental Measurements*; Cambridge University Press, 2016.

(19) Zhang, H.; Davison, W. Performance Characteristics of Diffusion Gradients in Thin Films for the in Situ Measurement of Trace Metals in Aqueous Solution. *Anal. Chem.* **1995**, *67*, 3391−3400.

(20) Davison, W.; Zhang, H. In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature* **1994**, *367*, 546−548.

(21) Garmo, Ø. A.; Naqvi, K. R.; Røyset, O.; Steinnes, E. Estimation of diffusive boundary layer thickness in studies involving diffusive gradients in thin films (DGT). *Anal. Bioanal. Chem.* **2006**, *386*, 2233−2237.

(22) Warnken, K. W.; Zhang, H.; Davison, W. Accuracy of the Diffusive Gradients in Thin-Films Technique: Diffusive Boundary Layer and Effective Sampling Area Considerations. *Anal. Chem.* **2006**, *78*, 3780−3787.

(23) Uher, E.; Tusseau-Vuillemin, M.-H.; Gourlay-France, C. DGT measurement in low flow conditions: Diffusive boundary layer and lability considerations. *Environ. Sci.: Processes Impacts* **2013**, *15*, 1351−1358.

(24) Lucas, A. R.; Reid, N.; Salmon, S. U.; Rate, A. W. Quantitative Assessment of the Distribution of Dissolved Au, As and Sb in Groundwater Using the Diffusive Gradients in Thin Films Technique. *Environ. Sci. Technol.* **2014**, *48*, 12141.

(25) Warnken, K. W.; Davison, W.; Zhang, H.; Galceran, J.; Puy, J. In situ measurements of metal complex exchange kinetics in freshwater. *Environ. Sci. Technol.* **2007**, *41*, 3179−3185.

(26) Levy, J. L.; Zhang, H.; Davison, W.; Galceran, J.; Puy, J. Kinetic signatures of metals in the presence of suwannee river fulvic acid. *Environ. Sci. Technol.* **2012**, *46*, 3335−3342.

(27) Desaulty, A.-M.; Méheut, M.; Guerrot, C.; Berho, C.; Millot, R. Coupling DGT passive samplers and multi-collector ICP-MS: a new tool to measure Pb and Zn isotopes composition in dilute aqueous solutions. *Chem. Geol.* **2017**, *450*, 122−134.

(28) Alakangas, L. J.; Mathurin, F. A.; Åström, M. E. Diverse fractionation patterns of Rare Earth Elements in deep fracture groundwater in the Baltic Shield - Progress from utilisation of Diffusive Gradients in Thin-films (DGT) at the Äspö Hard Rock Laboratory. *Geochim. Cosmochim. Acta* **2020**, *269*, 15−38.

(29) Huang, J.; Bennett, W. W.; Welsh, D. T.; Li, T.; Teasdale, P. R. Development and evaluation of a diffusive gradients in a thin film technique for measuring ammonium in freshwaters. *Anal. Chim. Acta* **2016**, *904*, 83−91.

(30) Simpson, J. H.; Carr, H. Y. Diffusion and nuclear spin relaxation in water. *Phys. Rev.* **1958**, *111*, 1201.

(31) Benz, S. A.; Bayer, P.; Blum, P. Global patterns of shallow groundwater temperatures. *Environ. Res. Lett.* **2017**, *12*, 034005.

(32) Santner, J.; Prohaska, T.; Luo, J.; Zhang, H. Ferrihydrite containing gel for chemical imaging of labile phosphate species in sediments and soils using diffusive gradients in thin films. *Anal. Chem.* **2010**, *82*, 7668−7674.

(33) Panther, J. G.; Teasdale, P. R.; Bennett, W. W.; Welsh, D. T.; Zhao, H.; Coast, G. Titanium Dioxide-Based DGT Technique for In Situ Measurement of Dissolved Reactive Phosphorus in Fresh and Marine Waters. *Environ. Sci. Technol.* **2010**, *44*, 9419−9424.

(34) Buzier, R.; Charriau, A.; Corona, D.; et al. DGT-labile As, Cd, Cu and Ni monitoring in freshwater: toward a framework for interpretation of in situ deployment. *Environ. Pollut.* **2014**, *192*, 52−58.

(35) Huang, J.; Bennett, W. W.; Welsh, D. T.; Li, T.; Teasdale, P. R. Diffusive gradients in thin films" techniques provide representative time-weighted average measurements of inorganic nutrients in dynamic freshwater systems. *Environ. Sci. Technol.* **2016**, *50*, 13446−13454.

(36) Allan, I. J.; Knutsson, J.; Guigues, N.; Mills, G. A.; Fouillac, A.-M.; Greenwood, R. Evaluation of the Chemcatcher and DGT passive samplers for monitoring metals with highly fluctuating water concentrations. *J Environ Monit* **2007**, *9*, 672−681.

(37) Altier, A.; Jiménez-Piedrahita, M.; Uribe, R.; Rey-Castro, C.; Galceran, J.; Puy, J. Time weighted average concentrations measured with Diffusive Gradients in Thin films (DGT). *Anal. Chim. Acta* **2019**, *1060*, 114−124.

(38) Hartland, A.; Larsen, J. R.; Andersen, M. S.; Baalousha, M.; O'Carroll, D. Association of Arsenic and Phosphorus with Iron Nanoparticles between Streams and Aquifers: Implications for Arsenic Mobility. *Environ. Sci. Technol.* **2015**, *49*, 14101−14109.

(39) Warnken, K. W.; Davison, W.; Zhang, H. Interpretation of in situ speciation measurements of inorganic and organically complexed trace metals in freshwater by DGT. *Environ. Sci. Technol.* **2008**, *42*, 6903−6909.

(40) Levy, J.; Zhang, H.; Davison, W.; Groben, R. Using diffusive gradients in thin films to probe the kinetics of metal interaction with algal exudates. *Environ. Chem.* **2011**, *8*, 517−524.

(41) Zhang, H.; Davison, W. Use of diffusive gradients in thin-films for studies of chemical speciation and bioavailability. *Environ. Chem.* **2015**, *12*, 85−101.

(42) Furukawa, K.; Takahashi, Y. Effect of complexation with humic substances on diffusion of metal ions in water. *Chemosphere* **2008**, *73*, 1272−1278.

Chapter 4 - Effects of dairy farm effluent management on cadmium, metal and nutrient leaching: A lysimeter trial on two contrasting soils

Amir Mohammadi, Niklas Lehto, Ali Shokri, Louis Schipper, Richard McDowell, Adam Hartland

Science of the Total Environment

Publication History:

To be submitted on 31 May 2022

Effects of dairy farm effluent management on cadmium, metal and nutrient leaching: A lysimeter trial on two contrasting soils

[1]Amir Mohammadi, [2]Niklas Lehto, [3]Ali Shokri, [1]Louis Schipper, [2]Richard McDowell, [1*]Adam Hartland

1. Environmental Research Institute, School of Science, University of Waikato, Hamilton 3240, New Zealand
2. Faculty of Agriculture and Life Science, Lincoln University, Lincoln 7647, New Zealand
3. School of Engineering, University of Waikato, Hamilton 3240, New Zealand

* Corresponding author: adam.hartland@waikato.ac.nz

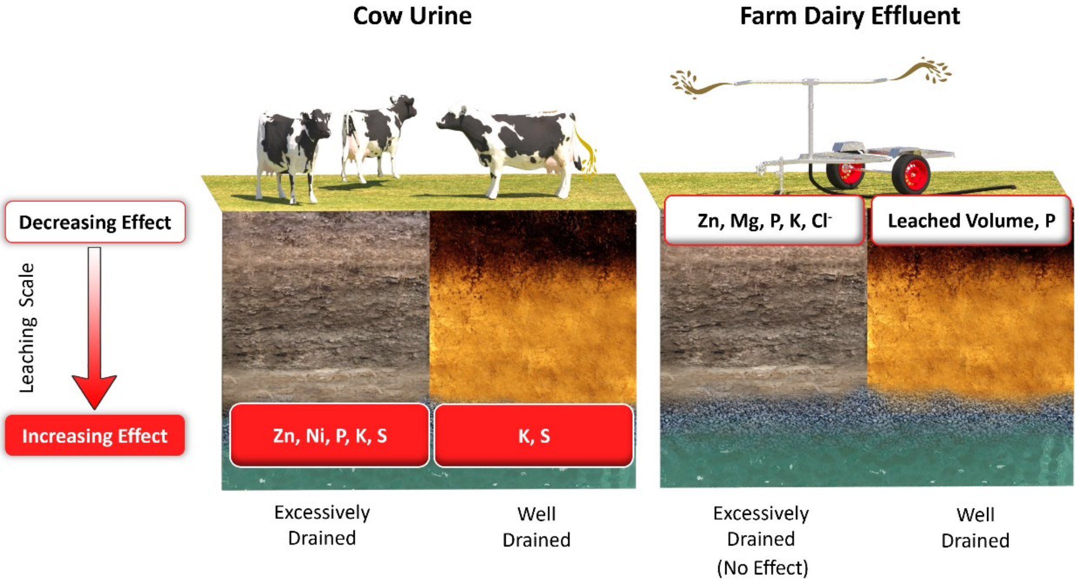
Abstract

Leaching of fertiliser-derived metals and nutrients from soil to groundwater may be impacted by effluent applications, but the effects of this common dairy farm practice remain unclear. This paper assesses the individual and combined effects of farm dairy effluent (FDE) and cow urine (CU) on the leaching of metals and nutrients in Eyre (excessively-drained) and Templeton (well-drained) soils. Leachate samples from sixty lysimeters with three treatment combinations of FDE, CU, and FDE + CU were tested. Datasets (n = 77) for nutrients, metals, and fluorescent dissolved organic matter (fDOM) were positively skewed, reflecting the importance of preferential flow events for contaminant transfer to aquifers. While high values were observed in less than 14% of samples, they were accountable on average for 63% of the leached mass. Around 88% of extreme values across all determinants coincided with CU applications. Conversely, FDE-treatments caused fewer high mobilisation events. Following normalisation, we evaluated statistical differences between soils and treatments. In the Eyre soil, CU induced greater ($p < 0.05$) leaching of Zn, Ni, Mg, P, S, and Cl^- than FDE. A similar trend was observed in the Templeton soil for Cd, Ni, Mg, P, K, S, and Cl^-. Adding FDE to CU-treated soils caused a decreasing effect on Zn, Mg, P, K, Cl^- in the Eyre soil and on P in the Templeton soil. FDE-derived organic matter tended to remain in the FDE-treated soil, but enhanced fDOM leaching following CU applications. Overall, the Eyre soil showed a higher leaching potential than the Templeton soil for all measured metals and nutrients, suggesting that soil type is the dominant control on metal and nutrient leaching from fertilised topsoil, with CU being a key driver of high mobilisation events. There are mechanistic differences in metal mobility between soil types, with Cl^- having a stronger mobilising effect in soils with a less free-draining nature, whereas excessive drainage is likely to drive higher mass transfer from soils with a more free-draining nature.

Keywords

Leaching, Farm Dairy Effluent, Cow urine, Soil, DOM

Graphical Abstract



4.1. Introduction

Population growth and shifting dietary preferences toward animal-based foods have increased the pressure on land and water resources (Drechsel et al., 2015). In Aotearoa New Zealand, phosphorus (P) and nitrogen (N) fertiliser application rates during the last two decades have been increased to maintain pasture growth on dairy farms (Foote et al., 2015). On dairy farms, effluent and manure by-products are often recycled by applying them to topsoil to increase nutrient retention and minimise damaging discharges into freshwater ecosystems. Accordingly, the dairy sector in New Zealand has experienced increased public and regulatory scrutiny over farm management practices (Rogério et al., 2020; Tilman et al., 2002).

New Zealand is now one of the largest dairy exporters in the world, following a 77% increase in dairy cattle stocking rates over the last two decades (from 3.44 million in 1990 to 6.11 million in 2020) (Statistics, 2020). The highest stocking densities occur in the Waikato and Canterbury regions, amounting to 28% and 19% of the national total, respectively (DairyNZ, 2019; Statistics, 2019, 2020). It is now widely accepted that intensive dairy farming and the historical application of fertilisers on dairy farms are responsible for the accumulation of fertiliser-derived contaminants in the soil and groundwater of these regions (Environment Waikato, 2005).

Fertilisers normally consist of six macronutrients (nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulphur (S)), and eight micronutrients (boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn) and nickel (Ni)) (Gupta et al., 2014). Unsurprisingly, long-term field trials investigating the effects of fertilisers on topsoil have also shown that fertilisers drive metal accumulation, including cadmium (Cd), nickel (Ni), uranium (U), arsenic (As), chromium (Cr), and lead (Pb) (Gray et al., 2021; McDowell, 2018; Mortvedt, 1995; Salmanzadeh et al., 2017). Cadmium is of greater concern than other metals, either because other metals are less readily absorbed by plants from P-fertilised soils or because their relative health effects are less pronounced (Mortvedt, 1995). Several factors, including soil hydrology, the amount of generated effluent (farm dairy effluent (FDE) and cow urine (CU)), farm effluent management strategies, and fertiliser application rates, control the mobilisation of fertiliser-derived contaminants (Gray et al., 2021; Houlbrooke et al., 2004; Silva et al., 2005). However, the relative importance of these factors for contaminant leaching from soils remains poorly constrained.

Previous studies have addressed the effects of individual and combined factors that enhance N and P leaching losses. For example, the application of FDE on lysimeter trial soils increased P-losses by 4–7% annually (McDowell et al., 2019); and nitrate-N leaching losses under urine-treated lysimeters were about 7–11 times more than those without urine (Malcolm et al., 2015). Other workers also report higher nitrate-N leaching losses where urine is applied alongside FDE, than urine alone (Fan et al., 2017; Silva et al., 2005). Despite these clear effects on nitrate, less is known about FDE and urine's effects on the leaching of fertiliser-derived metals from different soil types under controlled conditions, where all inputs and outputs are recorded (Gray et al., 2017; Liu et al., 2019).

In this study, we sought to evaluate the effects of urine and FDE on metal transport from soil to groundwater. Both treatments contain ligands that could potentially enhance metal leaching and transport. Dissolved organic matter (DOM) can transport metals in soil and water via the formation of stable metal-DOM complexes (Welikala et al., 2021). DOM can thereby mobilise metals into the subsurface and potentially enhance metal leaching to groundwater (Zhao et al., 2007). DOM is abundant in facultative ponds of dairy farms (Sukias et al., 2001), and this effluent-derived DOM, adds to native DOM in soil water (Zhuang et al., 2021), potentially accelerating down-profile metal losses. Additional DOM can also impair shallow groundwater quality, particularly in aquifers underlying the highly permeable soils of the Canterbury Plains, where this research was located (Hartland et al., 2011). Hence, DOM sourced from FDE may act as a vector for metal contamination, and decrease aquifer water quality by increasing the local biochemical oxidation demand (Monaghan & Smith, 2004). Likewise, chloride, another abundant component in urine (Haynes & Williams, 1993), is also known to enhance Cd mobility via formation of soluble inorganic complexes (e.g., $CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, $CdCl_4^{2-}$) (Doner, 1978; Kubier et al., 2019;

McDowell, 2019). Hence, the impact of Cl^- and DOM on metal translocation between soil and groundwater is of particular interest.

This study, therefore, focuses on the effects of applying FDE and CU on metal mobility and seeks to identify whether these impact metal transfer to aquifers. This work follows a recent analysis of P mobilisation by different farm treatments of Eyre and Templeton soils (McDowell et al., 2019), in which FDE and CU were applied to two soils with uniform fertiliser histories. Here, archived samples from the Lincoln University Dairy Farm (LUDF) lysimeter trial from two different years were investigated. Through a statistical analysis of the data, we aimed to test the hypotheses that, (H_1) adding FDE and CU to soil would synergistically increase the leaching of metals and nutrient components; and (H_2) that different soil types have different intrinsic contaminant leaching potentials.

4.2. Methodology

Study area

The Lincoln University Dairy Farm (LUDF) was established in 2001 in southwest Christchurch, New Zealand (43°38’40.13 “S, 172°26’36.02 “E) with the aim of developing and demonstrating best practice in dairy farm systems. The farm has a total of 186 ha of irrigated property, of which 160 ha is the effective area (milking platform).

The farm received an average annual rainfall of 593 mm in the past 20 years (CliFlo NIWA, 2022), and is sprayed with an additional 450 mm ha^{-1} yr^{-1} using an irrigation system with a capacity of 5.5 mm day^{-1}. The average evapotranspiration of the farm is 928 mm yr^-

^{1}. Therefore, on average, the farm receives an excess of 115 mm ha^{-1} yr^{-1}. During the past decade, the average minimum and maximum temperatures were -6 to 37 °C.

At LUDF, N- and P-fertilisers are applied at 170 kg N ha^{-1} yr^{-1} and 40 kg P h^{-1} yr^{-1}, respectively, and all paddocks are sown with a variety of ryegrass and clover. LUDF paddocks were grazed once every 20–40 days depending on the number of cows on the farm, approximately equal to 4–8 ha grazed per day. The LUDF livestock is Holstein-Friesian based (average 500 kg of live weight), which consumes approximately 20 kg dry matter (cow^{-1} day^{-1}). The number of cows on the farm varies during a year, with an average of 400–500 calved cows and heifers in 2005 and 2014 (the two years investigated in this study).

Lysimeters: soil types and treatments

In 2001, sixty lysimeters were installed in two different soil types (Eyre and Templeton soils, 30 lysimeters on each soil type) across the LUDF. Lysimeters were 50 cm in diameter and 70 cm deep with edge flow protection (Cameron et al., 1992). Farm Dairy Effluent (FDE) and cow urine (CU) were applied regularly to lysimeter trial soils from 2001 to 2015. Soil and treatment combinations evaluated in this study are listed in Table 4.1.

Farm dairy effluent was collected directly from washing down the dairy shed during the milking season and was stored in sump tanks, then applied to the receiving land (and lysimeters) every second day. The FDE area received 75% of P as superphosphate and 25% as FDE. The FDE treated lysimeters also receive 85% N as N-fertiliser and 15% as FDE (McDowell et al., 2019). Assuming 500 cows on the farm and 35 L of urine cow^{-1} day^{-1} (Minnée et al., 2020), LUDF receives about 110 L of urine ha^{-1} day^{-1}.

Table 4.1: Lincoln University Dairy Farm (LUDF) lysimeter treatments, symbols, and number of samples

Soil Type	FDE (F)	Cow urine (CU)	Symbol	Number of Samples
Eyre (E)	Yes	No	E-F	9
	No	Yes	E-CU	17
	Yes	Yes	E-F-CU	23
Templeton (T)	Yes	No	T-F	7
	No	Yes	T-CU	9
	Yes	Yes	T-F-CU	12

A deep Templeton silt loam and shallow stony Eyre silt loam were used in this study and represent of the soils used for irrigated dairy farming in the Canterbury region. Soil chemical properties is available in Table S1 in the supplementary information (SI). The Templeton and Eyre soils are classified as Typic Immature Pallic soils and Typic Orthic Recent soils, respectively, in the NZ soil classification (Hewitt, 2010), or as Typic Haplustept and Typic Dystrustept, respectively, in US Soil Taxonomy (Webb et al., 2000). The Templeton soil occurs adjacent to large rivers on the Canterbury plains (Cox, 1978). The Eyre soil is commonly associated with the Templeton soil, being essentially developed on 3,000–10,000 years old alluvial deposits in different parts of the paleo river channel and flood plain (Cox, 1978). The Templeton soil is well-drained (32–82 cm d^{-1}), and the Eyre soil is even more so, ranging from well-drained shallow silt loams to excessively-drained very stony sandy loams (115–260 cm d^{-1}) (Lee, 2019; Schwärzel et al., 2011). Hence, the Eyre soil has lower water retention capacities compared to Templeton (Cox, 1978). Both soils require irrigation to reach maximum yield production.

Leachate sample collection and preparation

The dataset consists of 77 leachate samples that were sub-sampled from frozen (-20°C) and stored samples collected from the LUDF lysimeters over two comparable months in the LUDF series: April 2005 (n = 25) and January 2014 (n = 52). Table 4.1 shows the number of samples for each treatment combination. To ensure the accuracy and homogeneity of the analyses, several samples were collected for each combination of soil treatments from different lysimeters. Samples were filtered through 0.45 µm membrane filters at the time of collection and before being frozen in polypropylene bottles.

Sample preparation and analysis were conducted in analytical laboratories at the University of Waikato. As samples were stored frozen for a long time before analysis, it is possible that organic matter and organic matter-bound metals aggregated. In order to ensure quantitative recovery of metals in thawed leachates, samples were prepared for metal analysis by adding 0.2 mL HNO_3 (65% Merck, Massachusetts, USA) and 0.2 mL H_2O_2 (30% Merck, Massachusetts, USA) to 9.6 mL of leachate, followed by overnight digestion at room temperature, before filtration and analysis (Ishak et al., 2015). This step served to liberate any metal held in DOM-metal complexes prior to filtration, thereby minimizing artefacts from sample storage.

Rainfall data were collected from New Zealand's National Climate Database (CliFlo NIWA, 2022) at Lincoln, 2.5 km away from the LUDF. Cumulative rainfall during the drainage season was similar, with 49.4 mm in April 2005 (rainfall event 12.5% > 10-year average) and 51.2 mm in January 2014 (rainfall event 5.9% > 10-year average) (CliFlo NIWA, 2022). The percentage of dry days (< 1 mm precipitation (Polade et al., 2014)) was 76% of

25 days of sampling in 2005 and 71% of 31 days in 2014. Data for each rainfall event is available in Table 4.S2 in the supplementary information (SI).

Sample analysis

An Agilent 8900 inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, California, USA) controlled by MassHunter Workstation (version 4.5), and Dionex ICS-200 Ion Chromatograph (Dionex, California, United States) were used for metal and anion measurements. Instrumental limits of quantification were 0.1 µg L^{-1} (Ni, Cd, Pb, U), 0.3 µg L^{-1} (As), 1.0 µg L^{-1} (Zn), 0.1 mg L^{-1} (P, Cl^-, NO_3^-), 10 mg L^{-1} (Mg), and 0.5 mg L^{-1} (S, K). A five-point calibration curve for metals and anions was performed alongside each set of measurements. Check standards and blanks were analyzed every 10–20 samples to ensure minimal drift and carryover between samples.

A fraction of DOM is fluorescent (fDOM). Following excitation by light between UV and visible wavelengths, characteristic spectra can be obtained and sorted into general compound classes (here classified as fulvic-like, humic-like, and protein-like). fDOM can be readily quantified using fluorescence excitation-emission matrices (EEMs) and modelled using parallel factor analysis (PARAFAC), which provides information regarding the concentration and composition of the organic molecules present (Coble, 1996; Rosario-ortiz & Korak, 2017). Characterisation of fDOM was performed using a Horiba Jobin Yvon Aqualog spectrometer equipped with a charge-coupled device detector. All samples were scanned for EEMs using a quartz cuvette (1 cm, 4 mL) across excitation wavelengths of 240–600 nm and emission wavelengths of 245–800 nm, with an increment of 3 nm and an integration time of 0.5 s. Fluorescence measurements were corrected for instrument-specific biases to ensure an accurate quantitative (signal intensity) and qualitative assessment (spectral shape) (Stedmon & Bro, 2008). All sample signals were corrected for spectral shape (inner filter effects) and signal intensity (Raman normalisation and removal of Rayleigh scatter effects) issues, using dedicated data processing software prior to PARAFAC modelling. The water-Raman scattering intensity was measured using fresh ultrapure (Type I, resistivity 18.2 MΩ) water (Milli-Q Direct, Merck, Massachusetts, USA) and used to normalise blank-subtracted EEMs before completing PARAFAC analysis. Blanks were measured every six samples to ensure minimal drift. The Rayleigh effects were removed automatically by setting the region below the Rayleigh line to zero (Stedmon & Bro, 2008).

Data analysis

In this study, a total of 77 samples were analyzed for metals, anions, fDOM, and leached volumes. Whenever possible, data were normalised based on the number of datapoints per soil treatment (Table 4.1). A non-linear transformation method (Box and Cox, 1964) was used to smooth the effect of skewness in the distributions, thereby ensuring that the dataset conformed to a normal distribution (Fu et al., 2010). The transformed datasets were then evaluated using single-factor analysis of variance, ANOVA. Paired t-tests assuming unequal variances were also used to compare the means of different treatments. The dataset null hypothesis that the means of several populations are not significantly different was tested by ANOVA and the t-test ($p < 0.05$).

The modified Z-score method (Iglewicz & Hoaglin, 1993) was also used to detect high mobilisation events in the datasets. Extreme values, thus defined, indicate higher-than-normal mass transfer to the subsurface (i.e., preferential flow events), with values falling below the Z-score cut-off being considered analogous to matrix-flow. We apply the recommended rejection criterion of 3.5 based on the results of a simulation of datasets of 10, 20, and 40 samples (Iglewicz & Hoaglin, 1993).

PARAFAC was performed in MATLAB (Math Works, USA) using the drEEM toolbox. To obtain a robust and adequate PARAFAC model, the dataset for all the samples (n=77) were analyzed together (Bro, 1997). The PARAFAC components were characterised based on the 3D contour plots, using the intensity of fluorescence peaks and their position (Coble, 1996; Gao et al., 2018). A three-component PARAFAC model was found to be most suitable for the lysimeter samples, reflecting the following generalised components: C1, typical of the humic-like peak A; C2, composed of the two overlapping humic-like peaks of A and C; and C3, matching protein-like components, referred to generally in the literature as Peak T (Figure 4.S1 in Supplementary Information) (Coble, 1996; Rosario-ortiz & Korak, 2017).

4.3. Results

All the probability curves for metals, nutrients, and fDOM components of samples were asymmetrical and positively skewed. Probability curves for the transferred mass of Cd, Ni, Mg, S, Cl^-, and the C1 component in the leachate samples are shown in Figure 4.1. The presence of extreme values affected the probability curves and the means, which in some cases, such as for Cd, Mg, and Cl^-, were strongly affected by single or multiple datapoints. The probability curves for other components are available in Figure 4.S2 in the supplementary information. Table 4.2A shows a summary of mean, standard deviation, median, maximum, minimum, and kurtosis. Extreme kurtosis coefficients demonstrate the skewed distributions of metals and other components.

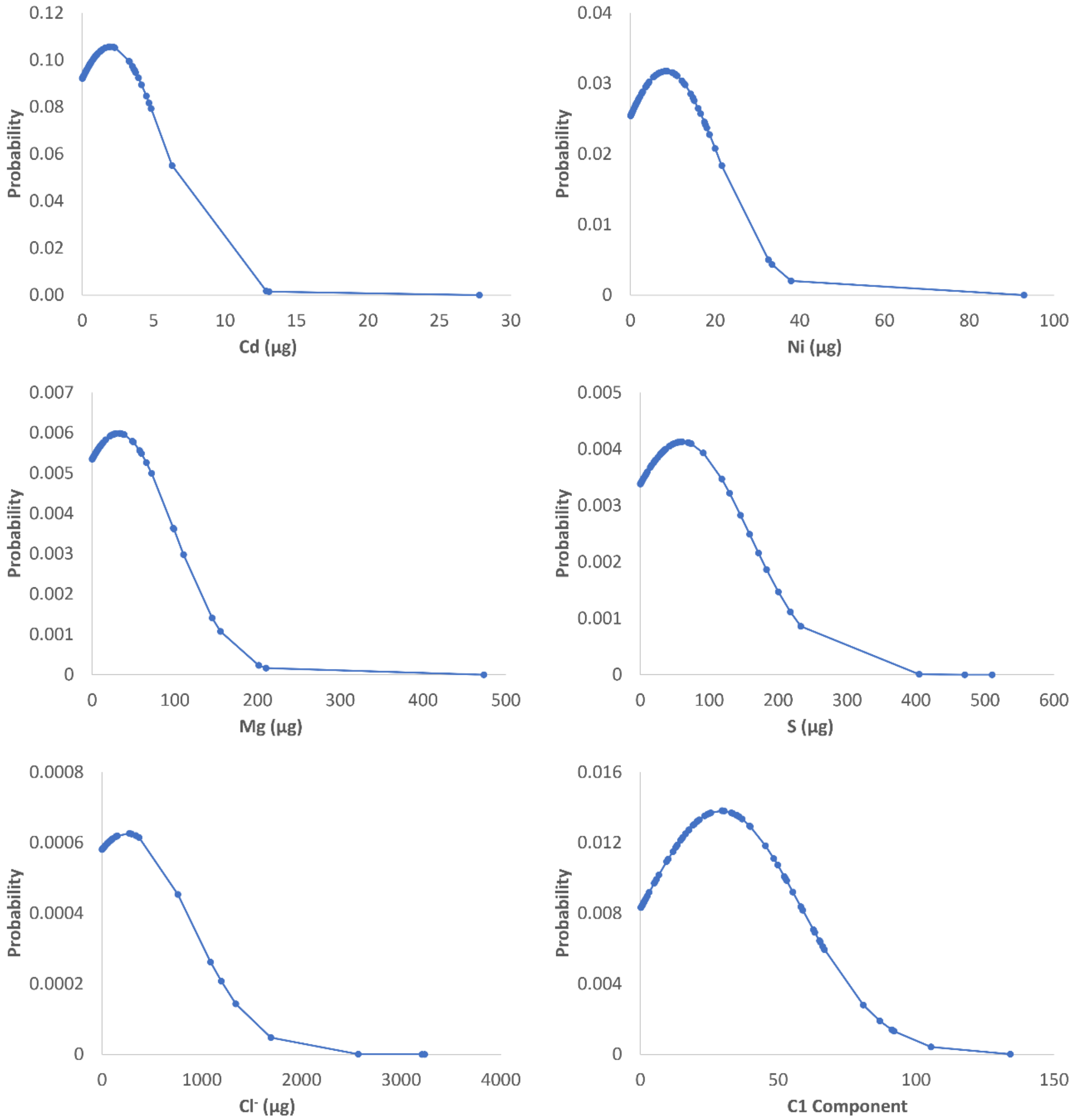


Figure 4.1: Probability curves of the original data of metals (Cd, Ni), nutrients (Mg, S, Cl^-), and fDOM component (C1) in leachate samples

Table 4.5: A: Summary of mean, standard deviation, median, max, min, and kurtosis, B: The mass transfer percentage (% of total mass transferred) and number of high mobilisation events as a function of soil and treatment combination (out of 77 samples).

A	**Leachate**	**Cd**		**Zn**		**Ni**		**Pb**		**U**		**As**		**Mg**		**P**		**K**		**S**		**Cl^-**		**NO_3^-**	
	Vol. (L)	**Conc. (µg L^{-1})**	**Mass (µg)**	**Conc. (µg L^{-1})**	**Mass (µg)**	**Conc. (µg L^{-1})**	**Mass (µg)**	**Conc. (µg L^{-1})**	**Mass (µg)**	**Conc. (µg L^{-1})**	**Mass (µg)**	**Conc. (µg L^{-1})**	**Mass (µg)**	**Conc. (mg L^{-1})**	**Mass (mg)**	**Conc. (mg L^{-1})**	**Mass (mg)**	**Conc. (mg L^{-1})**	**Mass (mg)**	**Conc. (mg L^{-1})**	**Mass (mg)**	**Conc. (mg L^{-1})**	**Mass (mg)**	**Conc. (mg L^{-1})**	**Mass (mg)**
Mean	3.02	0.72	1.98	88.2	169	2.86	8.42	25.9	16.2	0.29	0.63	1.32	3.47	9.19	31.7	0.95	1.84	32.3	104	18.6	61.1	64.8	215	74.1	248
Stdv	2.69	1.10	3.77	209	317	2.28	12.5	127	29.1	0.43	1.02	1.40	4.76	10.9	66.6	3.46	7.68	61.9	232	17.2	96.7	92.1	348	155	637
Median	2.50	0.38	0.85	27.5	68.9	2.05	4.24	1.91	3.18	0.15	0.26	1.02	2.09	3.52	8.13	0.11	0.28	11.5	21.7	13.1	31.7	16.2	29.1	20.5	29.3
Max	11.2	7.5	27.8	1372	2059	9.27	92.9	1108	142	1.99	6.41	8.81	32.4	46.9	474	19.2	61.4	384	1498	92.2	510	398	1660	891	3236
Min	0.02	< LOQ	--	5.75	0.65	0.14	0.04	< LOQ	--	< LOQ	--	< LOQ	--	0.08	0.04	< LOQ	--	< LOQ	--	< LOQ	--	0.28	0.05	< LOQ	--
Kurtosis	1.58	19.2	29.3	22.5	20.2	1.2	26.3	70.6	6.5	6.9	14.2	11.0	18.1	2.2	25.4	22.2	49.1	16.5	19.9	4.5	10.4	2.8	4.4	13.0	13.2

B	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**	**%**	**Number**
E-F	0	0	0	0	0	0	0	0	0	0	0	0	11	3	0	0	3	1	8	1	18	3	29	3
E-CU	21	2	29	4	0	0	27	7	13	3	0	0	23	6	68	5	31	6	25	4	36	10	32	6
E-F-CU	10	3	8	3	9	3	6	4	6	2	4	2	10	3	8	2	8	4	8	2	24	7	23	3
T-F	0	0	0	0	0	0	16	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
T-CU	15	1	20	2	21	1	26	2	31	3	24	2	32	2	7	1	35	2	12	2	10	2	3	1
T-F-CU	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	1	0	0
Total	46	6	57	9	30	4	75	14	50	8	28	4	76	14	82	8	77	13	54	9	90	23	87	13

Statistical differences between treatments

A Box-Cox data transformation was applied prior to statistical analysis of the transferred masses, i.e., concentrations x volume, to address the need for normally-distributed data while retaining as much information as possible. Table 4.3 summarises the significant differences between soil types and land treatments after data transformations. Additionally, Figure 4.2 shows box plots of (A) the original data' leached Cd mass and (B) after transforming the data using the Box-Cox transformation.

Statistical analysis of the Eyre soil treatments indicated that adding urine to FDE-treated Eyre soil (E-F vs E-F-CU) significantly increased Zn, Ni, P, K, and S mass transfer. Conversely, adding FDE to urine-treated Eyre soil (E-CU vs E-F-CU) showed a decreasing effect on Zn, Mg, P, K, Cl^- mass leaching. Application of urine to Eyre soil showed significantly higher leaching for Zn, Ni, Mg, P, S, and Cl^-, versus adding FDE to this soil (E-F vs E-CU). Statistical analysis also showed that CU application could significantly mobilise fDOM components (C1, C2, and C3) in Eyre soil.

The application of urine to the FDE-treated Templeton soil (T-F vs T-F-CU) significantly increased K, S, C1, C2, and C3 leaching. Conversely, the addition of FDE to urine-treated Templeton soil (T-CU vs T-F-CU) significantly decreased P leaching. Urine applications on Templeton soil also showed significantly higher leaching of Cd, Ni, Mg, P, K, S, Cl^-, and fDOM components versus adding FDE to this soil (T-F vs T-CU).

Overall, a comparison of Eyre and Templeton soils with the same treatments shows that adding FDE to Eyre soil drove higher leaching of almost all the measured components (except Zn and S) versus adding FDE to Templeton soil (E-F vs T-F). Similarly, the combination of FDE + CU on Eyre soil also showed higher leaching of almost all measured components (except Zn, Mg, NO_3^-, and C3), versus adding FDE + CU to Templeton (E-F-CU vs T-F-CU). Moreover, adding urine to Eyre soil resulted in higher leaching of Ni, P, Cl^- and C1, versus adding urine to Templeton soil (E-CU vs T-CU). Thus, overall analysis of the differences in leachate concentration between soils and treatments suggests that Eyre soil has a higher leaching potential for all the measured components than Templeton soil.

When comparing the chemical component’ concentrations in the leachate sample, fewer significant differences were observed between soils and treatments. Also, there were discrepancies between the differences of masses and concentrations in some cases. For example, when FDE was added to urine-treated Templeton soil, the concentration of Zn and S in the leachates significantly decreased, while the mass of total leached P decreased significantly.

Differentiating matrix and preferential flow

The modified Z-score method was used to identify high mobilisation (or preferential flow) events. Table 4.2B gives the percentage of mass transfer and the number of high mobilisation events as a function of soil and treatment combination. Percentages are normalised based on the number of datapoints per soil treatment. While high values were observed in less than 14% of samples, they were accountable on average for 63% of the leached mass. High mobilisation events accounted for 90, 87, and 82% of the transferred mass of Cl^-, N, and P, respectively. On the other hand, high values were less important for As and Ni, with 28 and 30% of the transferred mass due to values at the tail of the distribution, respectively. When the frequency of high mobilisation events in each dataset is considered, our results indicate that about 88% of these values were observed when urine was applied to soils. Interestingly, FDE-treatments were characterised by fewer high mobilisation events. Figure 4.2C shows high Cd mobilisation events, falling above 3.5 standard deviations from the mean. These high-concentration samples accounted for 46% of total Cd mass mobilised. Thus, high mobilisation events had a disproportionate effect on Cd mobility.

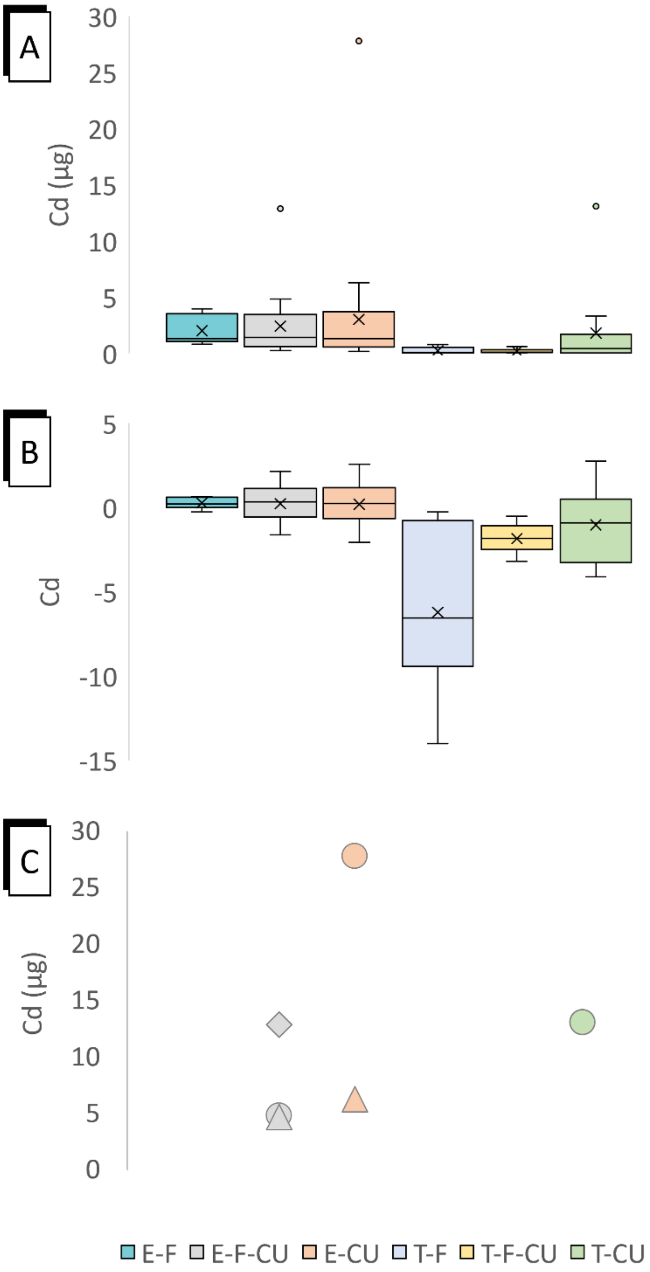


Figure 4.1: Plot of cadmium mass transferred under different soil treatments in the LUDF lysimeter trial; A: original data, B: after transformed data following the Box-Cox method (non-linear), C: high mobilisation events detected using the modified Z-score method; E: Eyre, T: Templeton, F: Farm Dairy Effluent, CU: Cow urine

Table 4.6: Significant differences in leached mass and concentrations across soil types and land treatments using the t-test method ($p < 0.05$) after data transformation using Box-Cox method. FDE: Farm Dairy Effluent, CU: Cow urine, LV: Leached Volume, C1: humic-like component (peak A); C2: humic-like component (peaks A and C); and C3 protein-like component, referred to (peak T). Eyre > Templeton: The leaching potentials of the mentioned metals and nutrients, and the leached volumes of different soil treatments of Eyre soil were significantly more than Templeton soil. FDE < CU: The leaching potentials of the mentioned metals and nutrients in urine-treated soil were significantly more than FDE-treated soil. ↑: Synergistic effect (increase), ↓: Antagonistic effect (decrease)

	Eyre			**Templeton**			**Eyre > Templeton**			
	FDE < CU	Adding FDE	Adding CU	FDE < CU	Adding FDE	Adding CU	FDE	CU	FDE + CU	Overall
Metal Mass	Zn, Ni	Zn (↓)	Zn, Ni (↑)	Cd, Ni			Cd, Ni, Pb, U, As	Ni	Cd, Ni, Pb, U, As	Cd, Zn, Ni, Pb, U, As
Nutrient Mass	Mg, P, S, Cl^-	Mg, P, K, Cl^- (↓)	P, K, S (↑)	Mg, P, K, S, Cl^-	P (↓)	K, S (↑)	Mg, P, K, Cl^-, NO_3^-	P, Cl^-	P, K, S, Cl^-	Mg, P, K, S, Cl^-, NO_3^-
fDOM Mass	C1, C2		C1, C2, C3 (↑)	C1, C2, C3		C1, C2, C3 (↑)	C1, C2, C3	C1	C1, C2	C1, C2, C3
Leached Volume				LV	LV (↓)		LV		LV	LV
Concentrations	U, Zn	No effect	Ni, S, K (↑)	K	Zn, S (↓)	K, Mg, C1, C2, C3 (↑)	Cd, Cl^-, K, C3	Cl^-, S	Cd, Zn, P	Cd, Cl^-, P, S, K

Evidence for transfer mechanisms

An *a priori* expectation was that chloride (Cl^-) would act as a vector for soft-to-intermediate Lewis acid's, such as Cd^{2+} (Gray et al., 2017; Smolders et al., 1998). Figure 4.3 shows the correlation between the mean leached masses/concentrations of Cd and Cl^- in soils with different treatments. While the data were strongly skewed, a comparison of means reveals a strong, positive correlation between Cd and Cl^- concentrations in leachate samples of both Eyre ($R^2 = 0.93$, $p < 0.05$) and Templeton ($R^2 = 0.96$, $p < 0.05$) soils (Figure 4.3A). When Cd responses to CU applications are compared between soil types, effectively, the same slope was obtained for the transferred mass of Cd versus Cl^-, with greater transferred masses in Eyre than Templeton (Figure 4.3B). The correlation between the mean leached masses/concentrations of other metals and metalloids (Ni, Pb, Zn, U, As) and Cl^- are also shown in Figure 4.S3 in the supplementary information. These results indicate overall positive correlations between Cl^- and metals leaching from Eyre soil. However, in Templeton soil, Cl^- correlated negatively with Zn, not at all with U and Ni, and positively with As and Pb.

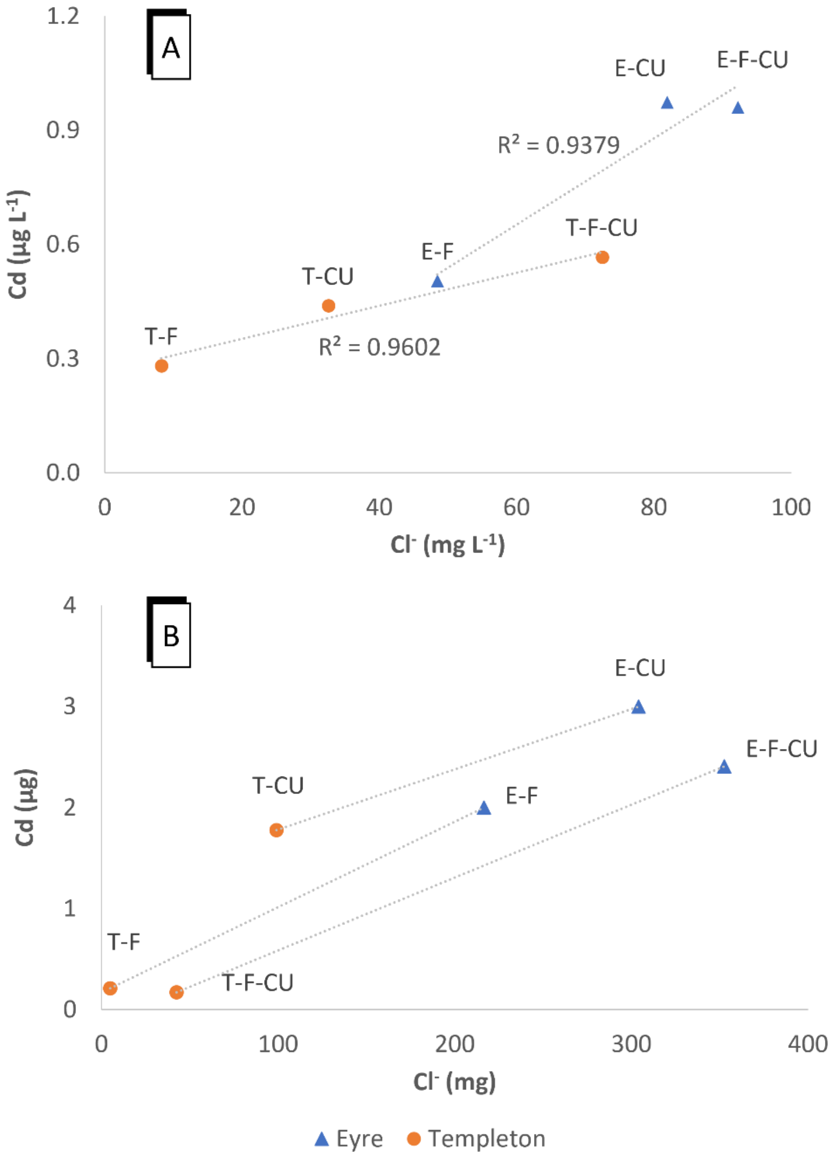


Figure 4.2: Correlation between mean cadmium and chloride in leachates from soils receiving different farm effluent treatments. E: Eyre, T: Templeton, F: Farm Dairy Effluent, CU: Cow urine.

Impacts on leached volumes

Comparing individual Eyre soil treatments with each other showed no significant differences in leached volume, with and without FDE or urine (Figure 4.4). However, there were significant differences between individual Templeton soil treatments with and without FDE. The results indicated that adding FDE to urine-treated Templeton soil (T-CU vs T-F-CU) significantly decreased the leached volume. Thus, the addition of FDE to Templeton soil resulted in lower leached volume versus adding only urine to this soil (T-F vs T-CU).

A comparison of Eyre and Templeton soils with the same treatments shows that adding FDE to Eyre soil resulted in higher leached volumes versus adding FDE to Templeton (E-F vs T-F). Also, adding the combination of FDE + CU to Eyre soil resulted in higher leached volumes versus adding FDE + CU to Templeton soil (E-F-CU vs T-F-CU). However, no significant differences were detected between the leached volumes of urine-treated Eyre and Templeton soils (E-CU vs T-CU). Unsurprisingly, when comparing soils regardless of treatments, the Eyre soil showed higher leached volumes than the Templeton soil. The average leachate volume of all Eyre soil treatments (3.74 L) was more than Templeton soil treatments (1.76 L), and this difference was statistically significant ($p < 0.001$).

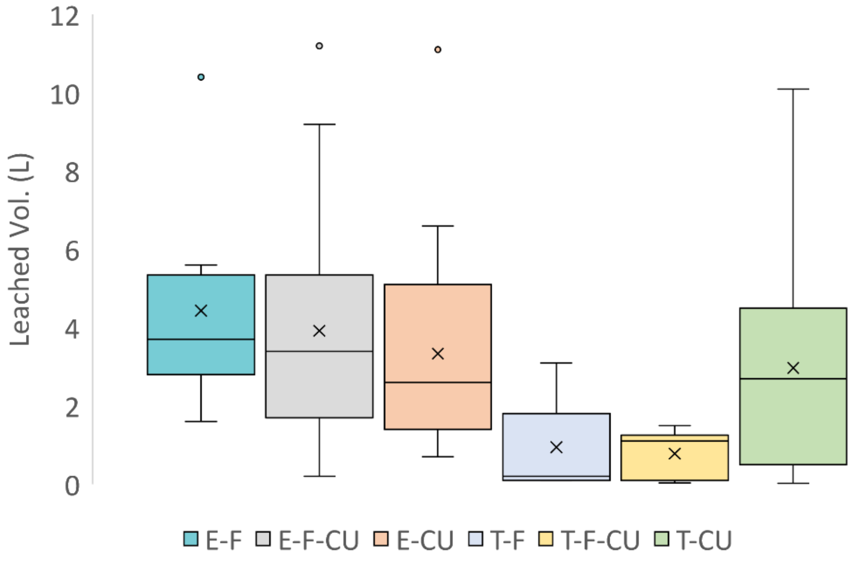


Figure 4.3: Box plot of the lysimeter trial’s leached volumes under different soil treatments; E: Eyre, T: Templeton, F: Farm Dairy Effluent, CU: Cow urine

4.4. Discussion

The results of this study suggest that differences in metal and nutrient leaching between different soil types can be enhanced or reduced by land treatments. High-concentration data points were particularly important for overall mass transfer (i.e., high mobilisation events). In addition, the positively skewed distribution of components reported here, captures information relating to mobilisation mechanisms, and how these contribute to net translocation from soil to groundwater.

Impacts of farm effluent management

This study tested the hypothesis (H_1) that FDE and urine applications cause synergistic effects on the leaching of metals and nutrients across different soil types. Results to an extent corroborate this and further suggest that the order of treatments matter. For example, our results suggest that applying urine to FDE-treated soil enhances the leaching of Zn, Ni, P, K, S and FDE-derived organic matter in the Eyre soil. Further, adding CU to FDE-treated Templeton soil increases the leaching of K, S, and fDOM. Whereas, adding FDE to urine-treated soil causes antagonistic effects on leaching (Zn, Mg, P, K, Cl^- in Eyre, and P in Templeton were all lower with this treatment combination).

We also compared FDE and urine treatments to determine which treatment resulted in mobilisation of more chemical components. Our findings showed that urine causes significantly greater ($p < 0.05$) leaching of Cd, Zn, Ni, Mg, P, K, S, Cl^-, and fDOM components than FDE. With respect to the medians and the means for Eyre soil, there were minimal differences between the treatments, but in terms of maximum recorded values, the urine treatments (E-CU and E-F-CU) produced the highest values for all metals, nutrients, and organic components. These results suggest that urine may influence the leaching of metals, nutrients and organic matter, to a greater extent than FDE.

The combined effects of dairy effluents and urine have been sparsely studied. Silva et al. (2005) conducted a lysimeter trial to investigate the effect of dairy effluent and urine on nitrate loss from Templeton soil, where they found that application of dairy effluent resulted in significantly less ($p < 0.05$) leaching than the application of urine in the second year of the trial (after 350 mm of cumulative drainage), but a different trend was observed in the first year where the total drainage volume was below 100 mm (Silva et al., 2005). They also found that combining FDE and urine causes a synergistic effect on nitrate leaching in the second year of the trial compared to FDE- and urine-treated only. However, there was no significant difference among the three treatments during the first year. Di et al. (2002) also noted that nitrate leaching between the combination of dairy effluent + urine and urine alone was not always significant. They suggest that nitrate leaching increases with increasing drainage volume. The discrepancy between these findings implies that cumulative drainage volume is an important factor affecting the leaching potential of a range of chemical components.

Soil type: a first-order control on leaching potentials

We hypothesised (H_2) that different soil types show different intrinsic leaching potentials for trace elements and the other components studied here. Overall, the application of different treatments in Eyre soil showed significantly greater ($p < 0.01$) mass transfer for all measured chemical components (Cd, Zn, Ni, Pb, U, As), nutrients (Mg, P, K, S, Cl^-, NO_3^-), and fDOM components (C1, C2, C3) compared to Templeton. The higher degree of metal and nutrient mobilisation in Eyre soil is likely an intrinsic property of the soil since Eyre soil is excessively-drained and has a smaller water retention capacity than Templeton soil. Even though the total mass transferred to the subsurface is more important than concentration, the smaller significance of leachate concentrations (Table 4.3) may indicate that the rates of chemical adsorption/desorption of both soils are within the same range, with retention capacity as the controlling factor in mass transfer. These intrinsic differences between soils were also identified by McDowell et al., (2019), who found that total P leaching from the FDE-treated Eyre soil was about six times greater over 14 years than that from the FDE-treated Templeton soil.

Considering the effect of treatments within and across soils, it was concluded that soil type is likely a more important factor for the leaching of metals and nutrients than the farm treatments and strategies. However, without control treatments, it was not possible to establish the intrinsic degree of leaching without any treatment. Therefore, further study is warranted to find and confirm the magnitude of difference between amended and unamended soils, so that the driving factors of high mobilisation events can be elucidated.

Evidence for mechanistic controls on the mobility of metals and nutrients

Adsorption and desorption ultimately control the availability and mobility of metals and nutrients in soil and groundwater (Loganathan et al., 2012). The formation of soluble metal complexes with dissolved organic matter and ligands can increase mobility by reducing adsorption (Welikala et al., 2021), but varies depending on the affinity of metal interaction with organic matter, which increases fairly predictably across the first-row transition elements from Mn to Cu (Bolan et al., 2003), but also depends on the functional properties of the DOM (Tipping et al., 2007).

The formation of soluble chloride-metal complexes can also increase mobility by reducing metal adsorption to soil (Kubier et al., 2019). For example, Cd^{2+} can form chloride complexes with different charges (e.g., $CdCl^{+}$, $CdCl_2^{0}$, $CdCl_3^{-}$, $CdCl_4^{2-}$), which can in principle act to reduce Cd adsorption substantially (Kubier et al., 2019). Our results showed that adding urine to both Eyre and Templeton soils resulted in greater chloride inputs, which likely promoted enhanced Cd mobility in both soil types (Figure 4.2). This finding is consistent with those of Gray et al. (2017), who also reported a similarly positive correlation ($r = 0.79$) between mean Cd and Cl^{-} concentrations in the leachate samples of a well-drained soil receiving cow urine treatments. Our results further suggest that high Cl^{-} also promotes leaching for other metals (i.e., As, Pb, U, Ni, Cu, Zn) in the Eyre soil.

While there is strong evidence for the impact of chloride on leaching from Eyre soil, in the Templeton soil, Cl^{-} concentration was negatively correlated with Zn, and there was no correlation with U and Ni. These results may indicate mechanistic differences in metal mobility between soil types, in which Cl^{-} has a stronger mobilizing effect in the freer-draining soil, but the excessive drainage of the Eyre soil, is likely the key factor driving higher mass transfer from the Eyre soil.

In both soils, adding urine to FDE-treated soil resulted in significantly greater ($p < 0.05$) leaching of fDOM components C1 (humic-like), C2 (humic-like), and C3 (protein-like). Urine treatment also showed significantly higher fDOM component mobilisation than FDE alone in both soils. This finding is consistent with enhanced metal leaching via the formation of metal-DOM complexes (Bolan et al., 2011; Mohammadi et al., 2022; Welikala et al., 2018).

The effect of FDE applications on soil physical properties is highly variable (Hawke & Summers, 2006). In our study, a comparison of soil types and treatments showed that the application of FDE resulted in significantly lower ($p < 0.001$) leached volumes in Templeton, compared to Eyre soil. Our results also showed the antagonistic effect of adding FDE to urine-treated soil on Zn, Mg, P, K, and Cl^- in the Eyre soil, and P in the Templeton soil. Indeed, McDowell et al. (2019) also reported that adding FDE to Templeton soil reduces the mean annual drainage volume by 12%. Whereas, adding FDE to Eyre soil increased the drainage volume by 12%, possibly reflecting increases in soil structural stability and hydraulic conductivity (Haynes & Naidu, 1998; Tisdall & Oades, 1982). Conversely, FDE may cause no significant difference (Gray et al., 2021) or even decrease the porosity, and hence hydraulic conductivity of soil (Singh & Bahadur, 1998), especially over the long-term (Arienzo et al., 2009; Y. Chen et al., 1983).

Impacts of high-mobilisation events

When comparing different soils and treatments, the leached metal concentrations varied significantly over time. Outlying values mostly coincided (88% of high values) with urine applications and with a greater proportion of these occurring in the excessively-drained Eyre soil (Figure 4.5).

High-mobilisation events may be particularly important for the water quality of shallow aquifers with potentially adverse impacts on subterranean ecosystems (Hartland et al., 2011). Several samples exceeded the trigger concentration values for the level of species protection (95%) of slightly to moderately disturbed ecosystems (ANZECC, 2018). Our results showed that 75% of Cd (> 0.2 µg L^{-1}), 40% of Pb (> 3.4 µg L^{-1}), 96% of Zn (> 8 µg L^{-1}), 13% of U (> 0.5 µg L^{-1}), and 84% of NO_3^- (> 2.4 mg L^{-1}) concentrations exceeded ecological trigger values. No data points in excess of the guideline values were observed for Ni (11 µg L^{-1}) or As (11 µg L^{-1}). However, exceedance may occur during the early stages of drainage, not captured here (Gray et al., 2021). We found fewer significant differences in leachate concentration compared with the leached masses. Despite the guidelines and standards being based on the leached concentration, the amount of mass transferred to the subsurface is of greater importance for the aggregate ecological impact.

Analysis of the raw data associated with the highest mobilisation events suggests that these events happen infrequently (<14% of samples) but can mobilise on average, 63% of mass transferred by leachates was attributed to high-mobilisation events. This observation implies that high mobilisation events are probably more important for impacts on shallow aquifers than the background leaching rate. When transgression of maximum acceptable values (MAV) frequently occurs, routine monitoring and, in some cases, remedial action may be required. This information may prove helpful in generating farm nutrient plans that optimise production while minimizing nutrient (especially NPK) losses.

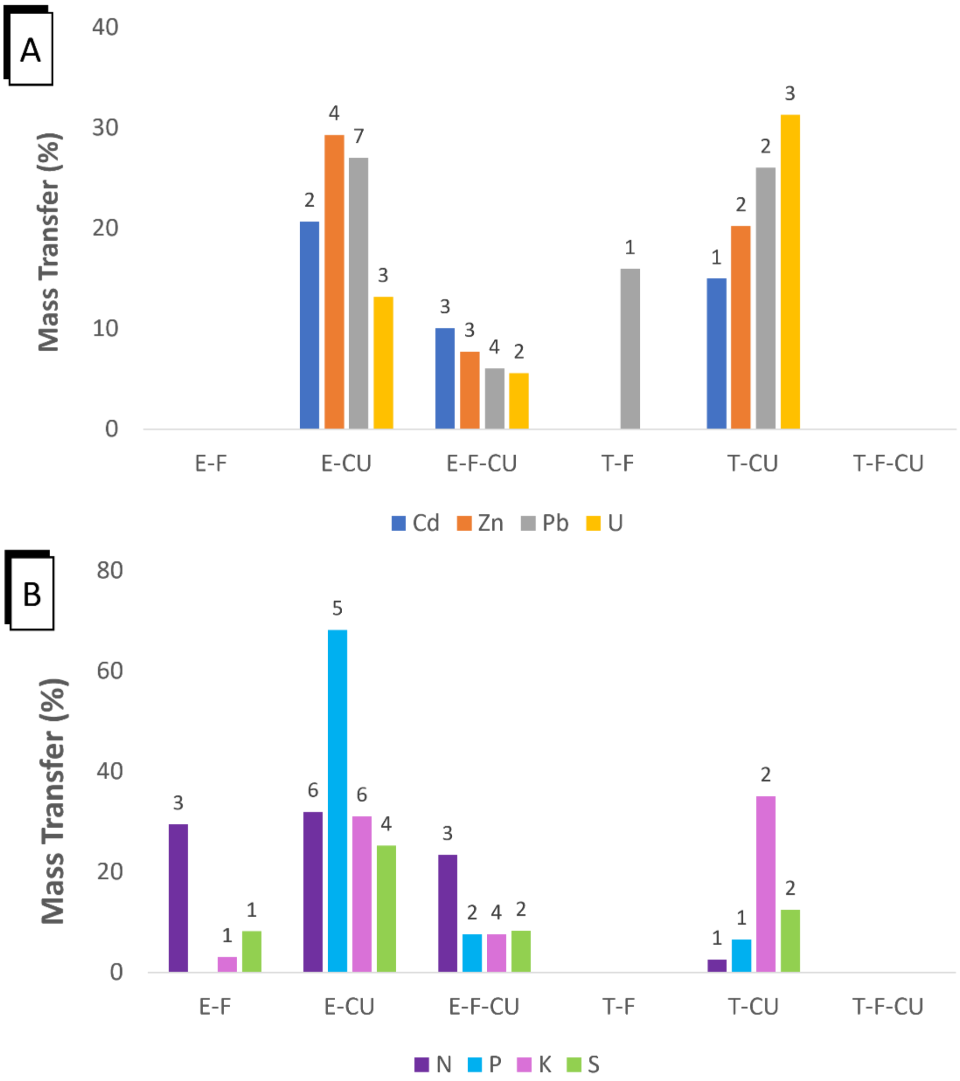


Figure 4.4: The percentage mass transfer of metal and nutrient components associated with high-mobilisation effects. Data are shown as a function of soil and treatment combination. Data labels show the number of high-mobilisation events (out of n = 77).

4.5. Conclusion

We examined the effect of the application of farm dairy effluent (FDE), cow urine (CU), and FDE + CU on the leaching of metals, nutrients, and organic components from Templeton and Eyre soils using samples from lysimeter trials. Our results illustrate that the application of CU increases the mobility of chemical components significantly more than FDE. We also observed that adding urine to FDE-treated soils synergistically increases metal mobility. But, adding FDE to urine-treated soil, results in an antagonistic independent of soil type, i.e., reducing metal and nutrient transfer to groundwater. Adding urine to soils also caused significantly greater mobilisation of organic matter, which was accompanied by higher metal leaching, suggesting a link between the leaching of fDOM and metals, including Cd and Zn. The excessively-drained Eyre soil has a significantly higher overall (metal and nutrient) leaching potential than Templeton. This may reflect the different hydraulic properties of the soils, given that adding FDE to Templeton soil resulted in a significantly lower leached volume, than FDE-treated Eyre soil. Finally, the levels of significance between soil types were greater than between treatments, implying that soil type is the first-order control on metal and nutrient leaching, and that cow urine has the overall effect of enhancing metal, DOM and nutrient leaching compared to farm dairy effluent.

Funding

This study was funded by The University of Waikato and Lincoln University. Adam Hartland was also supported by a Rutherford Discovery Fellowship [RDF-UOW1601]. The views expressed in this paper are those of the authors and do not necessarily reflect the views or policies of The University of Waikato and Lincoln University.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Acknowledgments

We would like to acknowledge Lincoln University for providing access to Lincoln Dairy Farm archived lysimeter samples; Amanda French for sample preparation and ICP-MS analysis; Mehdi Ghorashi Nezhad for graphical design; and Jonathan Nunez for providing supplementary information about LDF.

Supplementary Information Content

Rainfall data, 3D excitation-emission matrices of lysimeter leachate samples, probability curves of uncorrected data, correlation between mean metals and chloride concentrations, box plots of chemical components and components’ leaching after removing outliers using the modified Z-score, and probability chemical components and components’ leaching after Box-Cox transformation are available in the supplementary information. Table 4.S1, Figure 4.S1 – 4.S3.

References

ANZECC. (2018). Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

Arienzo, M., Christen, E. W., Quayle, W., & Kumar, A. (2009). A review of the fate of potassium in the soil-plant system after land application of wastewaters. Journal of Hazardous Materials, 164(2–3), 415–422. https://doi.org/10.1016/j.jhazmat.2008.08.095

Bolan, N. S., Adriano, D. C., Kunhikrishnan, A., James, T., McDowell, R., & Senesi, N. (2011). Dissolved organic matter: biogeochemistry, dynamics, and environmental significance in soils. Advances in Agronomy, 110, 1–75.

Bolan, N. S., Adriano, D. C., & Naidu, R. (2003). Role of phosphorus in (im) mobilization and bioavailability of heavy metals in the soil-plant system. Reviews of Environmental Contamination and Toxicology, 1–44.

Bro, R. (1997). PARAFAC . Tutorial and applications. 38, 149–171.

Cameron, K. C., Smith, N. P., McLay, C. D. A., Fraser, P. M., McPherson, R. J., Harrison, D. F., & Harbottle, P. (1992). Lysimeters without edge flow: an improved design and sampling procedure.

Chen, Y., Banin, A., & Borochovitch, A. (1983). Effect of potassium on soil structure in relation to hydraulic conductivity. In Developments in Soil Science (Vol. 12, pp. 135–147). Elsevier.

CliFlo NIWA. (2022). New Zealand’s National Climate Database. National Institute of Water and Atmospheric Research New Zealand (NIWA).

Coble, P. G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. 51, 325–346.

Cox, J. E. (1978). Soils and agriculture of part Paparua County, Canterbury, New Zealand.

DairyNZ. (2019). QuickStats about dairying – NEW ZEALAND. January, 2019.

Di, H. J., Cameron, K. C., Silva, R. G., Russell, J. M., & Barnett, J. W. (2002). A lysimeter study of the fate of 15N-labelled nitrogen in cow urine with or without farm dairy effluent in a grazed dairy pasture soil under flood irrigation. New Zealand Journal of Agricultural Research, 45(4), 235–244. https://doi.org/10.1080/00288233.2002.9513514

Doner, H. E. (1978). Chloride as a factor in mobilities of Ni (II), Cu (II), and Cd (II) in soil. Soil Science Society of America Journal, 42(6), 882–885.

Drechsel, P., Heffer, P., Magen, H., Mikkelsen, R., & Wichelns, D. (2015). Managing Water and Fertilizer for Sustainable Agricultural Intensification. International Fertilizer Industry Association (IFA), International Water Management Institute (IWMI), International Plant Nutrition Institute (IPNI), and International Potash Institute (IPI).

Environment Waikato. (2005). Cadmium Accumulation in Waikato Soils, Waikato Regional Council.

Fan, J., Xiao, J., Liu, D., Ye, G., Luo, J., Houlbrooke, D., Laurenson, S., Yan, J., Chen, L., Tian, J., & Ding, W. (2017). Effect of application of dairy manure , effluent and inorganic fertilizer on nitrogen leaching in clayey fluvo-aquic soil : A lysimeter study. Science of the Total Environment, 592, 206–214. https://doi.org/10.1016/j.scitotenv.2017.03.060

Foote, K. J., Joy, M. K., & Death, R. G. (2015). New Zealand Dairy Farming : Milking Our Environment for All Its Worth. Environmental Management, 709–720. https://doi.org/10.1007/s00267-015-0517-x

Fu, W., Tunney, H., & Zhang, C. (2010). Spatial variation of soil nutrients in a dairy farm and its implications for site-specific fertilizer application. Soil and Tillage Research, 106(2), 185–193.

Gao, J., Lv, J., Wu, H., Dai, Y., & Nasir, M. (2018). Impacts of wheat straw addition on dissolved organic matter characteristics in cadmium-contaminated soils: Insights from fluorescence spectroscopy and environmental implications. Chemosphere, 193, 1027–1035. https://doi.org/10.1016/j.chemosphere.2017.11.112

Gray, C. W., Chrystal, J. M., Monaghan, R. M., & Cavanagh, J. A. (2017). Subsurface cadmium loss from a stony soil—effect of cow urine application. Environmental Science and Pollution Research, 24(13), 12494–12500. https://doi.org/10.1007/s11356-017-8865-0

Gray, C. W., Lucci, G. M., & Cavanagh, J. (2021). Can the application of farm dairy effluent enhance cadmium leaching from soil? 50919–50929.

Gupta, D. K., Chatterjee, S., Datta, S., Veer, V., & Walther, C. (2014). Role of phosphate fertilizers in heavy metal uptake and detoxification of toxic metals. Chemosphere, 108, 134–144. https://doi.org/10.1016/j.chemosphere.2014.01.030

Hartland, A., Fenwick, G. D., & Bury, S. J. (2011). Tracing sewage-derived organic matter into a shallow groundwater food web using stable isotope and fluorescence signatures. Marine and Freshwater Research, 62(2), 119–129.

Hawke, R. M., & Summers, S. A. (2006). Effects of land application of farm dairy effluent on soil properties: A literature review. New Zealand Journal of Agricultural Research, 49(3), 307–320. https://doi.org/10.1080/00288233.2006.9513721

Haynes, R J, & Williams, P. H. (1993). Nutrient cycling and soil fertility in the grazed pasture ecosystem. Advances in Agronomy, 49, 119–199.

Haynes, RJ J, & Naidu, R. (1998). Influence of lime, fertilizer and manure applications on soil organic matter. Nutrient Cycling in Agroecosystems, 51(123), 123–137. http://link.springer.com/article/10.1023/A:1009738307837

Hewitt, A. E. (2010). New Zealand soil classification. Landcare Research Science Series, 1.

Houlbrooke, D. J., Horne, D. J., Hedley, M. J., Hanly, J. A., & Snow, V. O. (2004). A review of literature on the land treatment of farm-dairy effluent in New Zealand and its impact on water quality. New Zealand Journal of Agricultural Research, 47(4), 499–511. https://doi.org/10.1080/00288233.2004.9513617

Iglewicz, B., & Hoaglin, D. C. (1993). How to detect and handle outliers (Vol. 16). Asq Press.

Ishak, I., Rosli, F. D., Mohamed, J., & Ismail, M. F. M. (2015). Comparison of digestion methods for the determination of trace elements and heavy metals in human hair and nails. The Malaysian Journal of Medical Sciences: MJMS, 22(6), 11.

Kubier, A., Wilkin, R. T., & Pichler, T. (2019). Cadmium in soils and groundwater: A review. Applied Geochemistry, 108(February). https://doi.org/10.1016/j.apgeochem.2019.104388

Lee, M. (2019). Prescriptions for optimal management of stony soils at Te Whenua Hou in Canterbury, New Zealand. Lincoln University.

Liu, X., Bi, Q., Qiu, L., Li, K., Yang, X., & Lin, X. (2019). Increased risk of phosphorus and metal leaching from paddy soils after excessive manure application : Insights from a mesocosm study. Science of the Total Environment, 666, 778–785. https://doi.org/10.1016/j.scitotenv.2019.02.072

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2012). Cadmium sorption and desorption in soils: a review. Critical Reviews in Environmental Science and Technology, 42(5), 489–533.

Malcolm, B. J., Cameron, K. C., Edwards, G. R., & Di, H. J. (2015). Nitrogen leaching losses from lysimeters containing winter kale: The effects of urinary N rate and DCD application. New Zealand Journal of Agricultural Research, 58(1), 13–25. https://doi.org/10.1080/00288233.2014.961644

McDowell, R. W. (2018). The rate of accumulation of cadmium and uranium in a long-term grazed pasture : implications for soil quality. 8233(January). https://doi.org/10.1080/00288233.2012.662901

McDowell, R. W. (2019). The potential for potassium chloride fertiliser applications to leach cadmium from a grazed pasture soil. Geoderma, 353, 293–296.

McDowell, R. W., Gray, C. W., Cameron, K. C., Di, H. J., & Pellow, R. (2019). The efficacy of good practice to prevent long-term leaching losses of phosphorus from an irrigated dairy farm. Agriculture, Ecosystems and Environment, 273(September 2018), 86–94. https://doi.org/10.1016/j.agee.2018.12.007

Minnée, E. M. K., Leach, C. M. T., & Dalley, D. E. (2020). Substituting a pasture-based diet with plantain (Plantago lanceolata) reduces nitrogen excreted in urine from dairy cows in late lactation. Livestock Science, 239(December 2019), 104093. https://doi.org/10.1016/j.livsci.2020.104093

Mohammadi, A., Corbett, T., French, A., J. Lehto, N., Hadfield, J., Jarman, P., Sandwell, D., Shokri, A., Schipper, L., & Hartland, A. (2022). Application of Diffusive Gradients in Thin Films for Monitoring Groundwater Quality. ACS ES&T Water, 0(0). https://doi.org/10.1021/acsestwater.1c00279

Monaghan, R. M., & Smith, L. C. (2004). Minimising surface water pollution resulting from farm-dairy effluent application to mole-pipe drained soils. II. The contribution of preferential flow of effluent to whole-farm pollutant losses in subsurface drainage from a West Otago dairy farm. New Zealand Journal of Agricultural Research, 47(4), 417–428. https://doi.org/10.1080/00288233.2004.9513610

Mortvedt, J. J. (1995). Heavy metal contaminants in inorganic and organic fertilizers. Fertilizer Research, 43(1), 55–61. https://doi.org/10.1007/BF00747683

Polade, S. D., Pierce, D. W., Cayan, D. R., Gershunov, A., & Dettinger, M. D. (2014). The key role of dry days in changing regional climate and precipitation regimes. Scientific Reports, 4(1), 1–8.

Rogério, C., Augusto, J., Borges, R., Armando, J., & Machado, D. (2020). A review and some re fl ections on farmers ' adoption of sustainable agricultural practices worldwide. Science of the Total Environment, 729, 138831. https://doi.org/10.1016/j.scitotenv.2020.138831

Rosario-ortiz, F. L., & Korak, J. A. (2017). Oversimplification of Dissolved Organic Matter Fluorescence Analysis: Potential Pitfalls of Current Methods Fernando.

Environmental Science & Technology, 51, 759–761. https://doi.org/10.1021/acs.est.6b06133

Salmanzadeh, M., Hartland, A., Stirling, C. H., Balks, M. R., Schipper, L. A., Joshi, C., & George, E. (2017). Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil. https://doi.org/10.1021/acs.est.7b00858

Schwärzel, K., Carrick, S., Wahren, A., Feger, K.-H., Bodner, G., & Buchan, G. (2011). Soil hydraulic properties of recently tilled soil under cropping rotation compared with two-year pasture. Vadose Zone Journal, 10(1), 354–366.

Silva, R. G., Cameron, K. C., Di, H. J., & Jorgensen, E. E. (2005). A lysimeter study to investigate the effect of dairy effluent and urea on cattle urine N losses, plant uptake and soil retention. Water, Air, and Soil Pollution, 164(1–4), 57–78. https://doi.org/10.1007/s11270-005-2249-7

Singh, Y., & Bahadur, R. (1998). Effect of application of distillery-effluent on maize (Zea mays) crop and soil properties. Indian Journal of Agricultural Sciences (India).

Smolders, E., Lambregts, R. M., McLaughlin, M. J., & Tiller, K. G. (1998). Effect of soil solution chloride on cadmium availability to Swiss chard.

Statistics. (2019). Agricultural production statistics: June 2019. Stats NZ Tatauranga Aotearoa.

Statistics. (2020). Beef cattle continue to increase. Stats NZ Tatauranga Aotearoa.

Stedmon, C. A., & Bro, R. (2008). Characterizing dissolved organic matter fluorescence with parallel factor analysis: A tutorial. Limnology and Oceanography: Methods, 6(11), 572–579. https://doi.org/10.4319/lom.2008.6.572

Sukias, J. P. S., Tanner, C. C., Davies-Colley, R. J., Nagels, J. W., & Wolters, R. (2001). Algal abundance, organic matter, and physico-chemical characteristics of dairy farm facultative ponds: Implications for treatment performance. New Zealand Journal of Agricultural Research, 44(4), 279–296. https://doi.org/10.1080/00288233.2001.9513485

Tilman, D., Cassman, K. G., Matson, P. A., Naylor, R., & Polasky, S. (2002). Agricultural sustainability and intensive production practices. 418(August).

Tipping, E., Baker, A., Thacker, S., & Gondar, D. (2007). Relating dissolved organic matter fluorescence to functional properties. AGU Fall Meeting Abstracts, 2007, B11A--0056.

Tisdall, J. M., & OADES, J. M. (1982). Organic matter and water-stable aggregates in soils. Journal of Soil Science, 33(2), 141–163.

Webb, T. H., Claydon, J. J., & Harris, S. R. (2000). Quantifying variability of soil physical properties within soil series to address modern land-use issues on the Canterbury Plains, New Zealand. Soil Research, 38(6), 1115–1129.

Welikala, D., Hucker, C., Hartland, A., Robinson, B. H., & Lehto, N. J. (2018). Trace metal mobilization by organic soil amendments: insights gained from analyses of solid and solution phase complexation of cadmium, nickel and zinc. Chemosphere, 199, 684–693. https://doi.org/10.1016/j.chemosphere.2018.02.069

Welikala, D., Robinson, B. H., Moltchanova, E., Hartland, A., & Lehto, N. J. (2021). Soil cadmium mobilisation by dissolved organic matter from soil amendments. Chemosphere, 271, 129536. https://doi.org/10.1016/j.chemosphere.2021.129536

Zhao, L. Y. L., Schulin, R., Weng, L., & Nowack, B. (2007). Coupled mobilization of dissolved organic matter and metals (Cu and Zn) in soil columns. Geochimica et Cosmochimica Acta, 71(14), 3407–3418. https://doi.org/10.1016/j.gca.2007.04.020

Zhuang, W. E., Chen, W., Cheng, Q., & Yang, L. (2021). Assessing the priming effect of dissolved organic matter from typical sources using fluorescence EEMs-PARAFAC. Chemosphere, 264, 128600. https://doi.org/10.1016/j.chemosphere.2020.128600

Chapter 5 - Tracing fertiliser-derived cadmium in soil−pasture−groundwater systems: Coupling stable isotope ratio analysis and diffusive gradients in thin films

Amir Mohammadi, Mahdiyeh Salmanzadeh, Claudine Stirling, Ali Shokri, Matt Taylor, Adam Hartland

Environmental Science & Technology

Publication History:

To be submitted on 31 May 2022

Tracing fertiliser-derived cadmium in soil−pasture−groundwater systems: Coupling stable isotope ratio analysis and diffusive gradients in thin films

[1]Amir Mohammadi, [1]Mahdiyeh Salmanzadeh, [2]Claudine Stirling, [3]Ali Shokri, [4]Matt Taylor, [1]Adam Hartland*

1. Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand
2. Centre for Trace Element Analysis and Department of Chemistry, University of Otago, Dunedin 9016, New Zealand
3. School of Engineering, University of Waikato, Hamilton 3216, New Zealand
4. Waikato Regional Council, Hamilton 3204, New Zealand

*. Corresponding author: adam.hartland@waikato.ac.nz

Abstract

It has been difficult to trace the fate and transformation of cadmium (Cd) in fertilised soil, shallow groundwater (leaching) and biomass (bioaccumulation), limiting our ability to accurately manage soil fertiliser (P and Cd) inputs. We report Cd stable isotope ratios ($\delta^{114/111}$Cd) from two contrasting, but uniformly fertilised soils, alongside pasture and in-situ groundwater $\delta^{114/111}$Cd measurements, using diffusive gradients in thin-films (DGT). Process controls on Cd dynamics in water-logged soils were further evaluated through anaerobic incubation experiments. Variations in [Cd] and $\delta^{114/111}$Cd with depth in Te Kowhai (poorly-drained) and Horotiu (well-drained) soils and groundwater, revealed divergent fractionation likely due to anaerobic reactions associated with CdS_x formation. 56-day-long soil incubations showed this water-logging effect, with CdS_x formation operating in both soils after ~48 hrs. Isotope ratios of fertilised Te Kowhai and Horotiu soils were similar in the upper 20 cm, but diverged with depth; $\delta^{114/111}$Cd trending negatively with increasing depth from surface Horotiu ($\Delta = -0.23$) > Te Kowhai ($\Delta = -0.16$). By comparison, Cd uptake effects between topsoil and pasture were more consistent, yielding comparable fractionations in Te Kowhai ($\Delta = 0.43$) and Horotiu ($\Delta = 0.45$). These results imply that soil drainage is a key determinant of Cd mobilisation, with dissolved [Cd] in anaerobic groundwater (under Te Kowhai soil) being ~2x that under freely-drained soil with the same fertilser history. Poorly drained soils may therefore be more susceptible to Cd leaching, but redox-alteration of $\delta^{114/111}$Cd between soil and groundwater must be considered in source-apportionment studies.

Keywords

Cadmium, Stable Isotope Ratio Analysis, Diffusive Gradients in Thin films, Soil, Groundwater, Pasture, Fractionation, Redox

5.1. Introduction

Cadmium is a non-essential, toxic metal which has accumulated in agricultural topsoils around the world due to phosphate fertiliser usage. Cadmium accumulates in pasture and grazing animals, but the magnitude of fluxes to groundwater remains ambiguous. Isotopic evidence ($\delta^{114/111}$Cd) from long-term field trials suggests appreciable transfer to shallow aquifers with resulting aquifer $\delta^{114/111}$Cd compositions predicted to be negatively displaced relative to fertiliser and topsoil (Salmanzadeh et al., 2017).

Nearly three decades of research have painted a conflicting picture of Cd accumulation in New Zealand soils. Both Taylor (1997) and Kelliher et al. (2017) reported Cd accumulation in topsoil correlated with the application of P-fertilisers. But contradictory observations of stabilising (McDowell, 2012), or stable Cd concentrations (Jeng & Singh, 1995), following long-term P-fertiliser application point to declining, or steady state conditions in soil Cd mass balances (Equation 1) between systems and settings. Conflicting observations of topsoil Cd concentration with long-term P-fertiliser usage, suggest either variable rates of bioaccumulation, or leaching to groundwater. At large then, trajectories of topsoil Cd concentration remain ambiguous (Mann et al., 2002).

$$[\mathrm{Cd}]_{\mathrm{Topsoil}} = [\mathrm{Cd}]_{\mathrm{Fertiliser}} - ([\mathrm{Cd}]_{\mathrm{Biomass}} + [\mathrm{Cd}]_{\mathrm{Groundwater}}) \qquad \text{(Equation 5.1)}$$

Numerous hydrochemical and biogeochemical processes can influence transport of Cd in the sub-surface. These include complexation by organic and inorganic ligands, soil−solution pH, and redox variations associated with water-logging (Brümmer, 1986; Caporale & Violante, 2016; Z. Liu et al., 2017). Cadmium desorption from soil surfaces is favoured where Cd adsorption and precipitation is inhibited, e.g., at pH < 6.5, or where Cd forms stable dissolved complexes with inorganic and organic ligands (Welikala et al., 2021).

In well-drained soils overlying alluvial aquifers, redox transformations may be less important than soil−solution pH, which controls Cd mobility through mineral surface charge, organic matter (OM) solubility, and by enhancing metal hydrolysis/ion-pair formation (Alloway, 2012; Kubier et al., 2019). Soil management (e.g., liming, effluent irrigation) clearly can influence Cd accumulation by modifying pH and topsoil OM content (McDowell, 2012).

In non-saline groundwater, cadmium generally occurs as Cd^{2+} in the form of labile (Mohammadi et al., 2022), water−soluble complexes with dissolved organic matter (DOM) (Alloway, 2012; Bolan et al., 1999; Carrillo-González et al., 2006; Christensen & Christensen, 2000; Paripurnanda Loganathan et al., 2012; Welikala et al., 2021). Conversely, in saline groundwater, Cd forms complexes with chloride ($CdCl^{+}$) and, to a lesser extent, with sulfate ($CdSO_4^{0}$). Regardless of speciation, complexation generally facilitates Cd leaching from the topsoil to deeper soil horizons, and eventually to groundwater, by reducing the potential charge difference between Cd and immobile soil surfaces (Stumm & Morgan, 2012). In addition, redox conditions control the formation of redox-sensitive complexes, such as $CdHS^{+,}$ which are favoured under anaerobic/sub-oxic conditions, likely playing a major role in mobilising Cd in water-logged settings (Lyons & Fitzgerald, 1983).

Previous research has also shown that water-logging and flooding can affect Cd uptake by plants (Wan et al., 2018; G. Wang et al., 2020). Therefore, changes in subsurface conditions can modify Cd bioaccumulation, and possibly enhance leaching to deeper horizons and groundwater. While re-adsorption to deeper horizons can restrict the speed of Cd leaching, at some point breakthrough to near-surface aquifers is inevitable (Nokes & Weaver, 2014). Open questions of Cd breakthrough in aquifers really reflects a mismatch between the target (low-level contaminant transfer) and approach (Cd close to, or below instrumental detection limits).

In recent years, stable isotope ratio analysis has gained traction as a tool for probing contaminant cycling in agricultural systems. Based on isotopic variations between environmental samples (Arcega-Cabrera et al., 2021; Salmanzadeh et al., 2017; Wang et al., 2021; Wiggenhauser et al., 2019; Xue et al., 2009), the method exploits differences in source compositions to un-mix inputs, or where one consistent input can be assumed (e.g., fertiliser-derived Cd), to disentangle outputs (e.g., bioaccumulation vs leaching). Yet, because Cd isotopes are known to fractionate during complexation with various ligands (Ratié et al., 2021; Yan et al., 2021) and also during transferring from soils to plants (Wiggenhauser et al., 2021), further work on Cd isotope systematics in soil−groundwater−pasture systems is needed.

While the goal and approach are clearly defined, analytical and experimental challenges hinder the direct application of the stable isotope ratio analysis in these systems. For example, soil contaminant concentrations are often heterogeneous at the sub-paddock scale in dairy farms (Baily et al., 2011; McDowell et al., 2013; Stafford et al., 2018). In uniformly managed agricultural trails, such variations, result from intrinsic variations in soil hydrogeochemical properties (McDowell et al., 2013). Furthermore, low Cd concentrations in aquifers (Mohammadi et al., 2022), necessitate large volume samples (up to several litres) and laborious sample processing in order to conduct stable isotope ratio measurements. Given the considerable spatial and temporal variation of Cd in soil and the low Cd concentration in receiving aquifers, experimental designs which consider soil and hydrogeological heterogeneity, as well as analytical challenges, must be formulated (Stafford et al., 2018).

Diffusive gradients in thin-films (DGT) is a time-integrated, passive sampling technique that has been widely used for monitoring metals in water, soils, and sediments (Davison, 2016). DGT measures the dissolved labile fraction of analytes. Here, dissolved species diffuse through a well-defined diffusion layer comprising a filter membrane and hydrogel (together called the material diffusive layer (MDL)) and accumulate on a binding agent (Davison & Zhang, 1994). DGT relies on the presence of a steady-state concentration gradient from the solution to the binding agent, and typically only applies to well-mixed solutions. In reality, a stagnant layer of water, termed the diffusive boundary layer (DBL), exists close to the surface of DGTs, which restricts the diffusion of analytes to the binding resin (Davison, 2016; Garmo et al., 2006). Increasing the flow rate of the solution effectively decreases the DBL thickness (Warnken et al., 2006), to a point comparable with fluvial environments. This study used the 'universal DGT monitoring system' (UDMS) (Section 2.5.3)(Mohammadi et al., 2022) to achieve measurements of Cd and $\delta^{114/111}$Cd in groundwater. By pumping groundwater through flowcells containing DGTs and temperature data loggers mounted on acrylic holder plates, we ensured that DGTs were exposed to fresh groundwater throughout the deployments.

This study follows a recent analysis of isotope tracing of fertiliser-derived Cd in agricultural topsoil, which suggested higher-than-expected leaching rates based on the Cd isotope mass balance (Salmanzadeh et al., 2017). In order to understand the factors controlling Cd leaching rates, samples of soil, groundwater and pasture were taken at Scott Farm (Hamilton, New Zealand) and analysed for their chemical and $\delta^{114/111}$Cd compositions. DGTs were deployed using the UDMS device to monitor Cd in shallow groundwater. Given the uniform fertilisation history of this site, we hypothesised that soil type would be the controlling factor in leaching of fertiliser-derived Cd. Through a statistical analysis of the isotope ratio and batch incubation data, we aimed to test the hypotheses that, (1) cadmium isotopes fractionate during desorption from soil and transport into groundwater and pasture; (2) soil type affects the isotopic composition of cadmium in topsoil; (3) water-logging affects the solubility and isotopic properties of Cd, leading to differences between soil types in shallow aquifers.

5.2. Materials and methods

Reagents, materials, and solutions

Ultrapure (Type I, resistivity 18.2 MΩ) water (Milli-Q Direct, Merck, Massachusetts, USA) was used to prepare all solutions. All chemicals were analytical reagent grade or higher. All sample tubes and vials were thoroughly acid-washed in 10% (v/v) HCl for 24 h, followed by 10% (v/v) HNO_3 for 24 h, before being thoroughly rinsed (5 times with the ultrapure water). A Savillex DST-1000 acid purification unit was used for double-distillation of all acids. Sample preparation and elution were carried out in a class-100 laminar flow hood to avoid contamination.

Study area, sample collection and preparation

This study was conducted at Scott farm, a research dairy farm near Hamilton, New Zealand. Two paddocks with contrasting soils (Te Kowhai and Horotiu) and the same fertilisation history were sampled. Fertilised sites were relatively flat (easy slope). In addition, an unfertilised paddock (Te Kowhai soil) was studied to establish a control. The Te Kowhai−unfertilised site has historically been used as a temporary livestock holding paddock. Agricultural machinery was unable to reach the site due to its topography, making it inaccessible to P fertiliser application. The average of pasture production at this farm is 17t DM ha^{-1} annually (150 kg N ha^{-1} year^{-1}).

Te Kowhai soil (Orthic Gley soil in NZ classification, Typic Humaquept in US soil classification) is poorly drained with slowly-permeable subsoil layers. During winter and spring, Te Kowhai soils become water-logged and chemically reduced at depth. Horotiu (Orthic Allophanic soil in NZ classification, Typic Hapludand in US soil classification) is well-drained and does not have slowly-permeable subsoil layers (Soil Survery Staff, 2014).

For soil sampling, three different sides of paddock were sampled at five soil depth intervals (to a depth of 45 cm) using an automatic core hammer. Topsoil samples were taken separately from the top layer (0–7.5 cm) and then bulked together for the incubation experiments. Pasture samples were also harvested at the time of soil sampling. Samples were transferred to The University of Waikato laboratories in plastic zip-lock bags for sample preparation and preliminary analysis. Visible vegetation was removed from the soil samples and visible soil was removed from the pasture samples, followed by washing of roots and shoots with ultrapure water. All plant parts (roots, straw, grain) were mixed and milled together. Soil and pasture samples were air dried and sieved using a 2 mm sieve and preserved at 4°C until subsequent instrumental analysis.

Soil pH and P concentrations were measured (total P and plant available Olsen P)(Olsen, 1954), groundwater (total P) and pasture (total P) samples. Soil pH was measured in a suspension of distilled water with a soil/solution ratio of 1.0:2.5, after the suspensions were shaken for 24 hours on an end-over-end shaker at 20°C (Blakemore, 1987). Dry bulk density of soils were measured at the 1st depth. Calculations assume the bulk densities of the deeper horizons were similar to the A horizon.

Soil samples were digested according to the method described in Salmanzadeh et al. (2017). Briefly, 0.5 g of soil sample was weighed in a 50 mL falcon tube. Aqua regia (1 mL HNO_3 and 0.33 mL HCl) was added to each tube and left overnight on a digestion block to pre-digest, followed by a 1 h digestion at 50 °C. Digested samples were then diluted to 50 mL with ultrapure water, centrifuged, and the supernatant was pipetted out into polypropylene tubes for ICP-MS analysis. Digested samples were measured for total Cd and other metals before isotopic analysis. Soil properties and concentrations for all depth intervals are included in the supplementary information (Table 5.S2)

Pasture samples were digested using a microwave digestion system. Briefly, 0.5 g of milled pasture sample was transferred to a Teflon block, into which 4 mL of purified HNO_3 and 4 mL of H_2O_2 was added and left overnight to pre-digest, followed by digestion in microwave block. The block temperature was ramped to 90 °C and held for 10 min, followed by an increase to 180 °C and held for an additional 10 min. Digested samples were then diluted to 25 mL with ultrapure water, centrifuged, and the supernatant was pipetted into polypropylene tubes for ICP-MS analysis. Digested samples were measured for Cd before isotopic analysis.

Three piezometers in Te kowhai soil were arrayed at different depth intervals (Te Kowhai−Shallow (screen 1.1−1.9 m), Te Kowhai−Middle (screen 2.0−3.4 m), Te Kowhai−Deep (screen 5.1−6.0 m)), and one piezometer in Horotiu soil (screen 4.6−7.6 m)) were installed to monitor the groundwater using the UDMS system. The Te Kowhai−Deep site was characterised by deeply anaerobic conditions, and the results are not presented here. All groundwater properties and characterisation are rather reported for Te Kowhai−Middle, whereas measurements made in the intermittently-saturated Te Kowhai−Shallow piezometer, are presented in seasonal observation section. The details of these sites, including locations, dimensions, lithology, and water table depths are given in the supplementary information (Table 5.S1 and Figures 5.S1 & 5.S2). Temperature, pH, Eh, electrical conductivity (EC), and dissolved oxygen (DO%) were measured before and after DGT deployment, using a YSI ProDSS (YSI Incorporated, Ohio, USA) hand-held multi-parameter water quality meter. All boreholes were purged 2–3 times the volume of each borehole prior to measurements and UDMS deployments. All sensors were calibrated on the day before measurements were taken. The average groundwater quality data for all sites are included in the supplementary information (Table 5.S3). The topography of the Te Kowhai−unfertilised site prevented us from installing piezometers and monitoring the groundwater quality.

After measuring Cd concentrations of different samples, aliquots of samples containing approximately 15 ng of Cd were transferred to The University of Otago, New Zealand for isotopic analysis following a double-spike method (Gault-Ringold & Stirling, 2012).

DGT: Preparation, Deployment, Analysis

DGT preparation followed that described previously in Mohammadi et al. (2022). Briefly, the binding gel were prepared by mixing 2 g of Chelex-100 (Bio-Rad, California, USA) and 10 mL of gel solution (15% acrylamide and 0.3% cross-linker in ultrapure water); then 70 µL freshly prepared 10% ammonium persulfate solution and 25 µL TEMED were added to this mixture while stirring. The solution was pipetted immediately between glass plates and cured in the oven for 90 min, followed by a 24 h hydration period in ultrapure water. DGTs were deployed using the UDMS, in which eight DGTs and a temperature data logger were simultaneously deployed for 1–2 weeks, before retrieval (Mohammadi et al., 2022).

After each deployment period, DGT devices were retrieved, rinsed with ultrapure water, and handled cautiously to avoid cross-contamination. Chelex gels were eluted for at least 24 h using 1 mL of 1 mol L^{-1} HNO_3 before being analysed for Cd isotopes. Blank DGTs were analysed alongside the deployed DGTs to measure the background mass of the analytes in gels. Further details about diffusive gel, DGT assembly, storage, the uptake and elution efficiencies, the accumulated background masses of metals in the binding layers, DGT concentrations (C_{DGT}), and the apparent diffusive boundary layer thickness (δ^{ADBL}) were previously reported in Mohammadi et al. (2022).

Cadmium isotopes can fractionate while diffusing through the diffusive layer and binding to the binding agent. To validate the accuracy of this coupled method, DGTs need to be tested for potential introduction of Cd fractionation during diffusion through diffusive layer and accumulation onto resins, especially where variation between the isotopic composition of the natural background and the sample is low. A parallel study by our group (supplementary information, Table 5.S4) showed minor fractionation (below instrument’ standard deviation) through diffusion from solution to the Chelex gels, therefore all DGT isotope ratios were appropriately corrected.

Soil−Solution Incubation

Isotopic changes in soil−solution were measured through the course of incubation experiments aimed at understanding the effect of water-logging on $\delta^{114/111}$Cd. Te Kowhai and Horotiu topsoil samples were used in each experiment, in which soil (20 g) was placed in a centrifuge tube, and 40 mL of deionised water was added (1:2 soil/water ratio). The tubes were sealed and shaken continuously. Samples were retrieved at six time intervals (6h, 12h, 1d, 2d, 8d and 54d) under ambient conditions (∼ 20 °C). After each retrieval, the soil suspension was centrifuged, and the clear supernatants were removed and filtered through a 0.45 µm filter membrane. All experiments were conducted in triplicate, and aliquots of the filtered solutions were taken and mixed at the end of each interval. The samples were acidified to pH < 1.5 immediately after the experiments using the purified HCl (Merck, Massachusetts, USA). Cd, Zn, Mn, Fe, and S concentrations was measured separately for each interval. Instrumental limits of quantification (LOQs) were 0.1 µg L^{-1} for Cd and Mn, 500 µg L^{-1} for S, and 5.0 µg L^{-1} for Fe. All samples were refrigerated at 4°C until subsequent isotopic analysis at The University of Otago.

Cadmium isotopic composition

A multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS) was used to measure Cd isotopic composition. A DSN 100 desolvating nebuliser fitted with a ∼100 µL/min perfluor- oalkoxy (PFA) nebuliser was used as the sample introduction system. Cadmium has eight stable isotopes, among which ^{110}Cd and ^{114}Cd are mostly used to depict the Cd isotope ratio. In this study, Cd isotopic composition ($\delta^{114/110}$Cd) is expressed as the deviation of $^{114}Cd/^{110}Cd$ ratio of a sample with respect to the $^{114}Cd/^{110}Cd$ ratio of a standard in parts per-thousand (‰):

$$\delta^{114/110}Cd = \left[\frac{(^{114}Cd/^{110}Cd)_{Sample}}{(^{114}Cd/^{110}Cd)_{NIST3108}} - 1\right].1000 \qquad \text{(Equation 5.2)}$$

The $Cd_{NIST\text{-}3108}$ reference solution sourced from the National Institute of Science and Technology (Virginia, USA), was used as the "zero delta" normalising standard (Abouchami et al., 2013). The NIST3108 reference material has a $\delta^{114/110}Cd$ of −1.61 ± 0.06 ‰ (2SD, n = 23). The isotopic fractionation between two systems (sink and source) is described as:

$$\Delta^{114/110}Cd_{sink-source} = \delta^{114/110}Cd_{sink} - \delta^{114/110}Cd_{source} \qquad \text{(Equation 5.3)}$$

where sink and source denotes different systems (i.e., soil, pasture, solution, and $Ca(NO_3)_2$ extractable Cd).

Data Analysis

All sampling and lab experiments were conducted in triplicate. In the case where three independent isotope results have been processed, results are reported as the mean of three replicate analyses, with two standard errors of the values. For all other measurements, the reported error is one standard deviation of the triplicate values. Datasets were evaluated using single-factor analysis of variance, ANOVA. Paired t-tests assuming unequal variances were also used to identify significant differences between datasets ($p < 0.05$).

5.3. Results

Properties of the studied Soil−Groundwater−Pasture Systems

The properties of the studied sites varied in terms of pH, P concentration, and bulk density. Horotiu pastures total P was significantly higher than both Te Kowhai and the Te Kowhai−unfertilised site (Figure 5.1A). Total soil P in the 1st (0-7.5 cm) and 2nd (7.5-15 cm) depths were in the order of Te Kowhai > Horotiu > Te Kowhai−unfertilised site. The total P of Te Kowhai significantly decreased between topsoil and the 3rd (15-25 cm) depth, while the total P of Horotiu and the Te Kowhai−unfertilised site decreased more linearly. There was a significant difference between the P concentration in groundwater for Horotiu (24.8 $\mu g\ L^{-1}$) and Te Kowhai (9.2 $\mu g\ L^{-1}$).

All soil depths had pH values between 5.3 and 6.0 (Figure 5.1B). The pH of groundwater at Horotiu and Te Kowhai sites were close to each other throughout the study (5.6−6.1). Bulk densities of the 1st depth were 0.78, 0.86, and 1.02 g cm^3 for Horotiu, Te Kowhai, and Te Kowhai−unfertilised soils, respectively.

Across all soil depths, there was a significant correlation (R^2 = 0.92–0.95, $p < 0.05$) between total P and total Cd, which showed a stronger correlation than Olsen P (R^2 = 0.70–0.76, $p < 0.05$), especially in the 1st and 2nd depths (Figure 5.2A & 5.2B). While the 1st and 2nd depths (i.e., topsoil) had similar Cd concentrations (0.70 and 0.61 mg Cd kg^{-1} in Te Kowhai, 0.88 and 0.79 mg Cd kg^{-1} in Horotiu, 0.20 and 0.21 mg Cd kg^{-1} in Te Kowhai-unfertilised), the 1st depth was significantly enriched with Olsen P. This non-linear trend was observed across all soils.

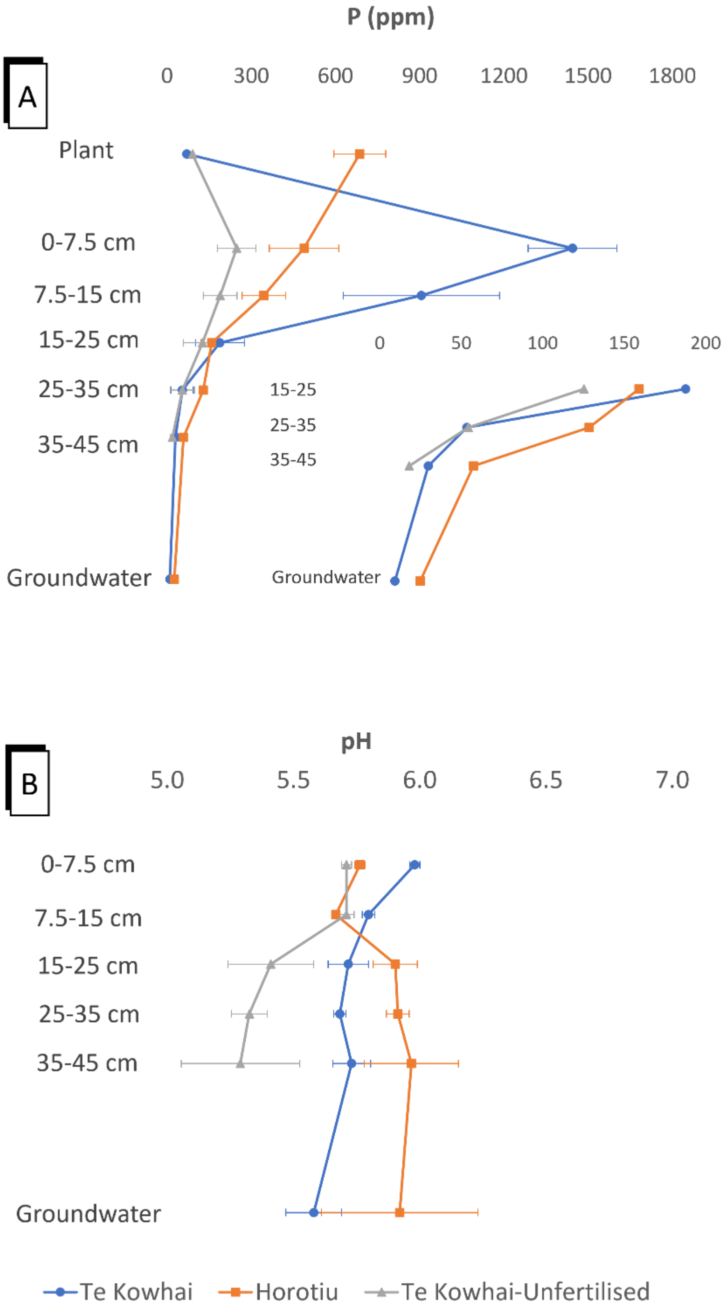


Figure 5.5: Soil, groundwater, and pasture properties, A: total P concentrations (ppm), B: pH. The error bars represent the standard error of the mean (n = 3).

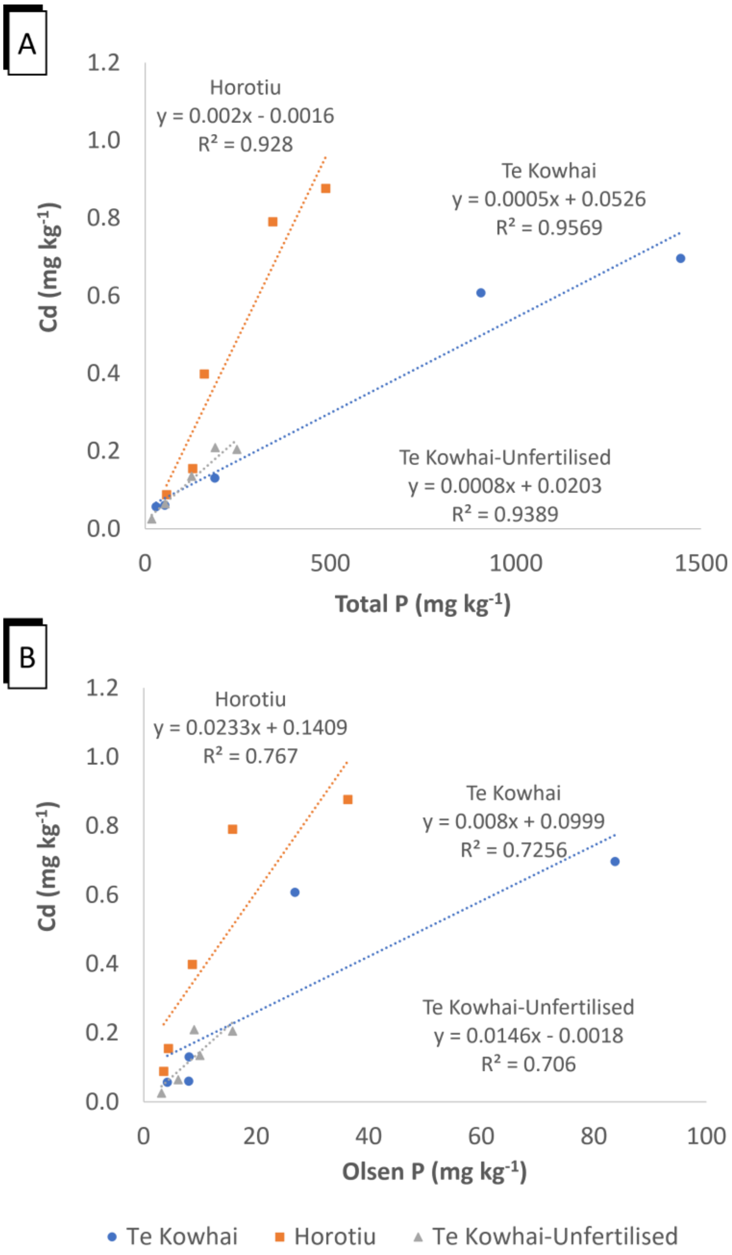


Figure 5.6: Relationship between total soil Cd (mg kg^{-1}) and A: total soil P (mg kg^{-1}), B: soil Olsen P (mg kg^{-1}), within Te Kowhai, Horotiu, and the Te Kowhai−unfertilised soils.

Cadmium Distribution among Different System Components

Cd concentrations and Cd isotope ratios ($\delta^{114/110}$Cd) were determined in five soil depths, in pasture, and groundwater. The $Ca(NO_3)_2^-$ extractable Cd was also measured in the topsoil (1st depth) of each soil (Figure 5.3). Overall, Cd concentrations decreased with depth in all soil types and showed similar trends between depths, except for Te Kowhai−unfertilised soil between the 1st and 2nd soil depths, where it slightly increased (Figure 5.3A). Cd concentrations in Horotiu exceeded Te Kowhai across all soil depths, and the $Ca(NO_3)_{2-}$ extractable fraction of Cd was also significantly higher in Horotiu soils (0.3 mg kg^{-1}), versus Te Kowhai (0.05 mg kg^{-1}) and Te Kowhai−unfertilised (0.03 mg kg^{-1}). In Horotiu, $Ca(NO_3)_{2-}$ extractable Cd contributed about 33% to the total Cd pool in topsoil, while in Te Kowhai soil the contribution was only 7%. Groundwater Cd concentration was higher in Te Kowhai (0.18 ± 0.06 µg L^{-1}) than Horotiu (0.10 ± 0.02 µg L^{-1}). Pasture Cd concentration in Horotiu (0.06 mg kg^{-1}) was higher than Te Kowhai (0.03 mg kg^{-1}) and Te Kowhai−unfertilised (0.02 mg kg^{-1}).

While Cd isotope ratios results showed different isotopic compositions between sites, they trended similarly between soil, groundwater and pasture across all sites (Figure 5.3B). The Cd isotope ratios in the groundwater was higher in Te Kowhai (0.59 ± 0.06 ‰), than in Horotiu (0.31 ± 0.10 ‰). The Cd isotope ratios in pastures of fertilised sites (Te Kowhai: 0.54 ± 0.06 ‰ and Horotiu: 0.61 ± 0.06 ‰) were lower than the unferilised site (0.84 ± 0.06 ‰). In all sites, groundwater and pastures had Cd isotope ratios that were higher than those found in soil.

The trends of Cd isotope ratio between soil depths varied between sites. Cd isotope ratios of each site were within standard errors of each other in the 1st to 3rd depths.

However, in the 4th and 5th depths, Te Kowhai and Te Kowhai−unfertilised sites were significantly more-positive (i.e., enriched) than Horotiu. In Te Kowhai soil, the isotope ratios of the 1st and 2nd depths were depleted relative to the ratios of 3rd and 4th depths. Conversely, the isotope ratios of the 1st and 2nd depths of Horotiu were enriched relative to the 3rd and 4th depths of this soil. Cadmium isotope ratios in groundwater beneath Te Kowhai and Horotiu were significantly enriched relative to the 5th depth. In all sites, the isotope ratios of $Ca(NO_3)_2^-$ extractable Cd were higher than the isotope ratios in all soil depths of respective sites. Significant differences were observed between Cd isotopes of $Ca(NO_3)_{2-}$ extractable and the topsoil (1st depths) of all sites. The Te Kowhai−unfertilised soil had lower Cd concentrations than the fertilised soils, but the trend in the isotopic composition as a function of depth was similar to the fertilised soils.

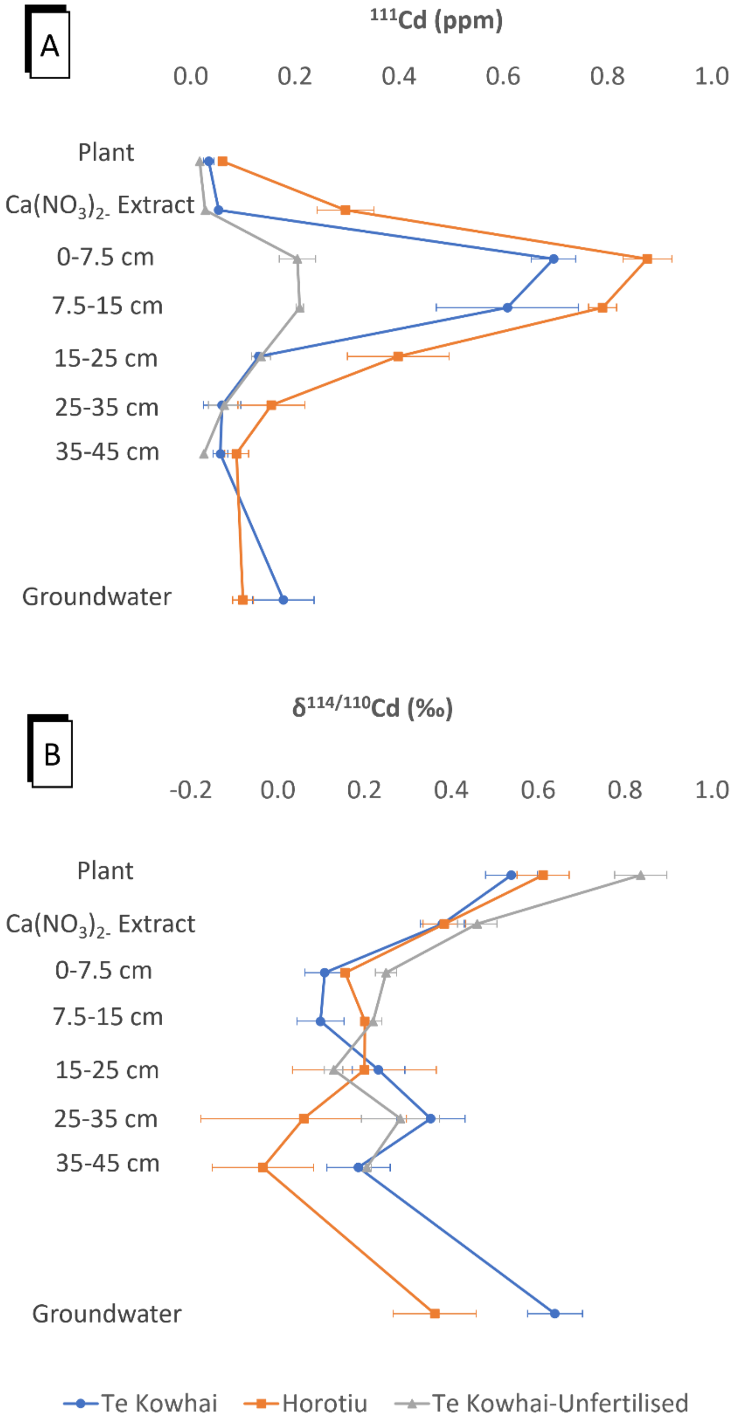


Figure 5.7: Cadmium in soil−groundwater−pasture systems, A: cadmium concentrations (ppm), B: cadmium isotopic composition (‰). The error bars of cadmium concentrations represent one standard error of the mean (n = 3). The error bars of cadmium isotopic composition represent two standard errors.

Seasonal Observations

Over the course of this study, 294.6 mm of precipitation fell (CliFlo NIWA, 2022) (Figure 5.4A). After September 11, 2019, the piezometer in the Horotiu site had become almost dry, preventing further monitoring. A major rain event occurred before September 25, 2019, raising the groundwater table, enabling the Te Kowhai−Shallow piezometer to be monitored for the first time. Mean Cd concentrations and isotopic composition were measured at the start and end of deployments. Results showed a significant mobilisation response in Te Kowhai−Middle during the rainy season (Figure 5.4B & 5.4C). The mean Cd concentrations of Horotiu and Te Kowhai−Shallow piezometers slightly decreased during this wet period. During the same deployment period, the decreasing trend in Te Kowhai−Shallow was also observed in Te Kowhai−Middle. Figure 5.4C shows an increasing trend in Cd isotope ratios of the groundwater beneath Te Kowhai−Middle and Horotiu sites. The isotope ratio of Te Kowhai−Middle increased by ~45% from 31 July 2019 (0.45 ± 0.05 ‰) to 11 September 2019 (0.66 ± 0.05 ‰). After this period, there was a slight decrease in the isotope ratio to 0.57 ± 0.06 ‰ in 25 September 2019, followed by an increase to 0.69 ± 0.06 ‰ in 9 October 2019. Similar to Te Kowhai−Middle, the isotope ratios of Horotiu increased by 42% from 0.26 ± 0.10 ‰ in 31 July to 0.36 ± 0.09 ‰ in 11 September). However, the isotope ratios of Te Kowhai−Shallow remained stable during the short period from 25 September (0.59 ± 0.08 ‰) to 9 October (0.56 ± 0.08 ‰).

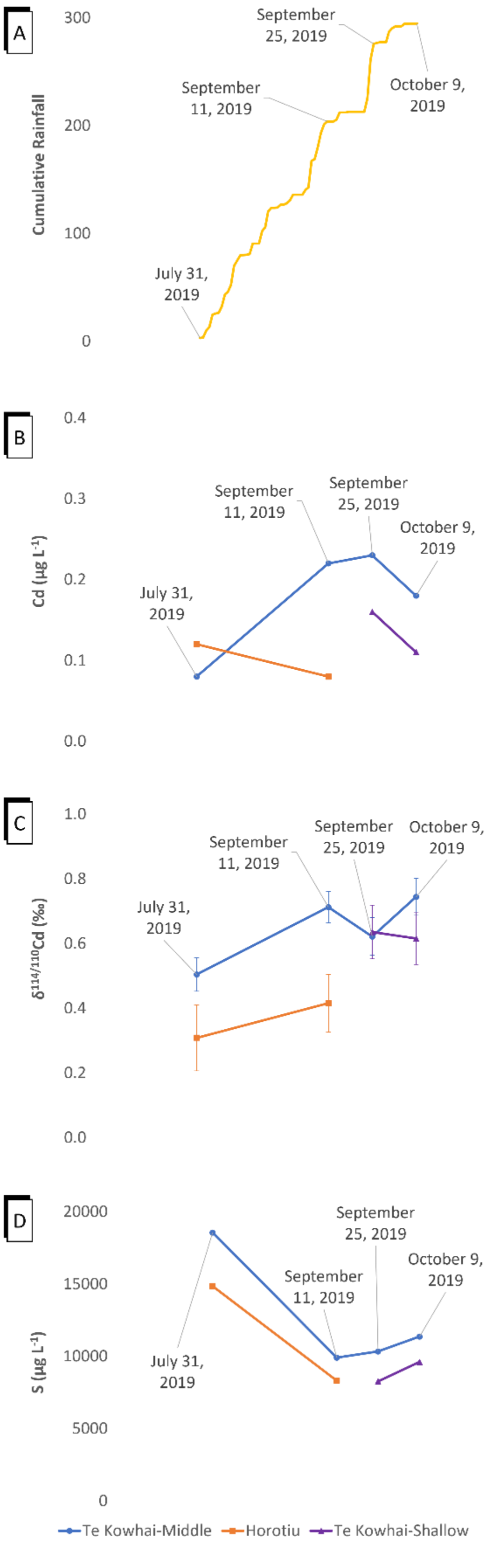


Figure 5.4: Groundwater' properties seasonal change, A: cumulative precipitation (mm) during the study (31 July 2019 – 9 Oct 2019), B: cadmium concentrations (µg L^{-1}), C: cadmium isotopic composition (‰), D: sulphur concentrations (µg L^{-1}).

Dynamics of Cd, Mn, S, Fe, and Cd-Isotopes in Soil−Solution Incubation

Cd batch incubations of Te Kowhai and Horotiu topsoils and the chemical compositions the filtered supernatant from each incubation period are shown in Figure 5.5. Results showed significantly ($p < 0.05$) higher Cd concentration in the soil−solution of Te Kowhai than Horotiu (Figure 5.5A). Over the first two days, Cd concentrations in Te Kowhai soil−solution increased by 85% (from 0.0048 to 0.0089 µmol L^{-1}), then declined significantly by 86% (from 0.0089 to 0.0012 µmol L^{-1}). Similarly, Cd concentrations in Horotiu soil−solution increased by 27% (from 0.0027 to 0.0034 µmol L^{-1}) in the first day, followed by a decline by 85% (from 0.0034 to 0.0007 µmol L^{-1}).

Reactions involving dissolution and precipitation of solids to Cd desorption and mobilisation was also investigated. During the incubation period, both soils showed similar trends in Zn, Mn, Fe and S, as they transitioned through dissimilatory reduction of Fe and Mn oxides to dissimilatory SO_4^{2-} reduction. Figure 5.5B shows that Zn concentration increased in the first day(s), followed by a decline. Figure 5.5C−E also showed that Fe and Mn concentrations in soil−solution increased during the incubation, while S concentrations significantly decreased after the second day of incubation. The concentrations of Zn ($p < 0.05$), Mn, Fe, and S in Te Kowhai were higher than in Horotiu, except at 56 days, when the Mn concentration of Horotiu was higher than Te Kowhai. Figure 5.5F shows that the Te Kowhai soil−solution was initially enriched with heavier Cd isotopes (from 0.11 ± 0.05 ‰ in soil to 0.58 ± 0.06 ‰ in soil−solution at 6 hr), followed by a plateau between 6 and 24 hours, leading to a shift to isotopically lighter values (from 0.58 ± 0.05 ‰ at 24 hr to 0.27 ± 0.06 ‰ at 8 d). There was no statistically significant difference in Horotiu soil−solution isotopic compositions during incubation (~ 0.21 ‰).

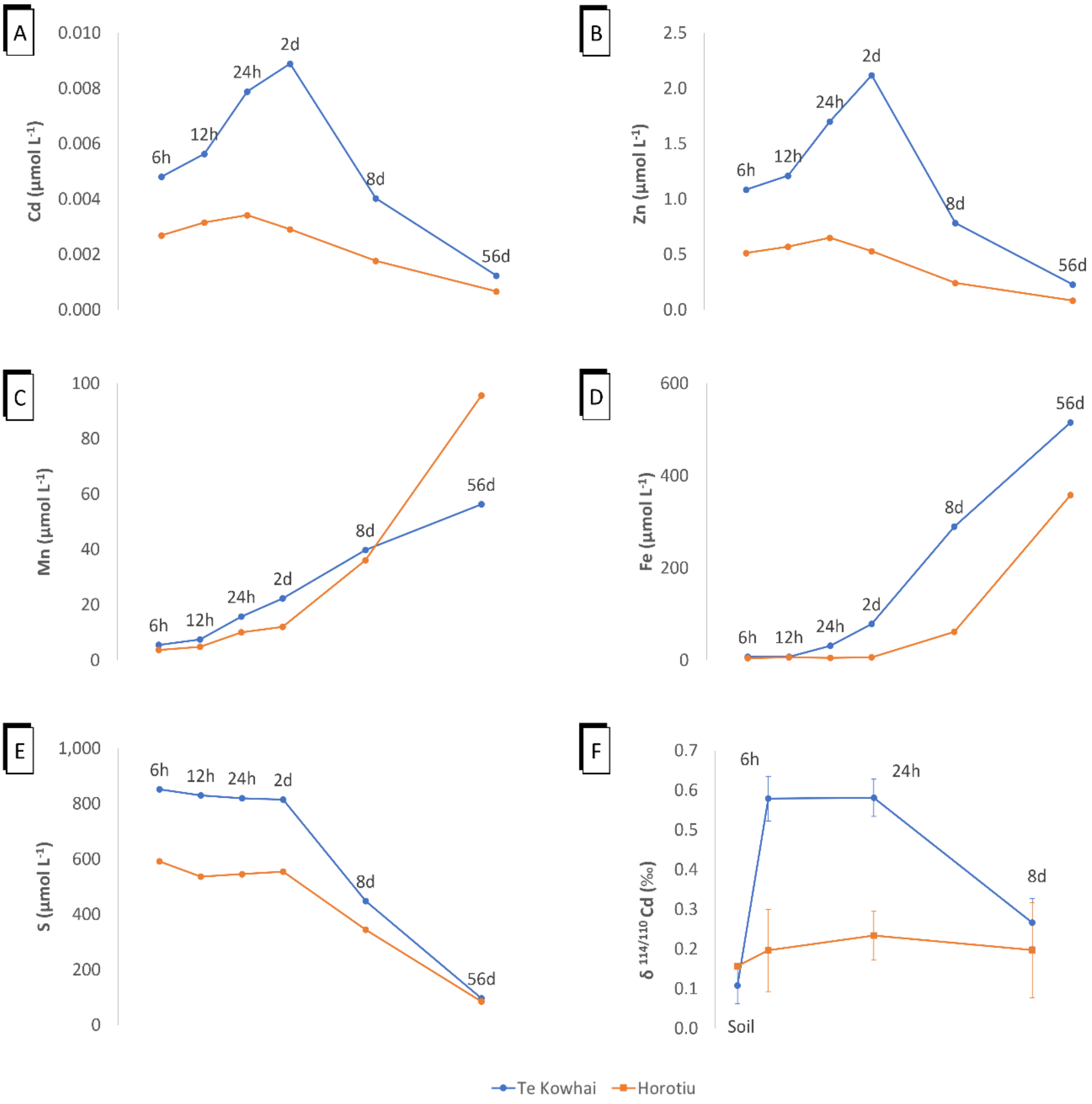


Figure 5.5: Dynamics of total Cd, Zn, Mn, Fe, S, and Cd isotope ratios under incubation experiments in fertilised Te Kowhai and Horotiu topsoils.

5.4. Discussion

Cadmium in Soil−Groundwater−Pasture Systems

The concentrations of Cd in the soils studied here were within the range of typical concentrations for agricultural farms across New Zealand (0−2.5 mg kg^{-1}) (Cavanagh, 2014; McDowell et al., 2013; Salmanzadeh et al., 2017; Stafford et al., 2018; Taylor et al., 2007). Soil types and land management history clearly influenced Cd concentrations in soil, groundwater and pasture. The significant difference between total Cd in the 1st and 2nd depths of fertilised and unfertilised soils indicates the influence of P fertiliser applications in farming on the accumulation of Cd in soil. Roberts et al. (1994) reported a similar mean concentration of Cd in the native/non-agricultural (0.13−0.31 mg kg^{-1}) and pastoral (0.12−0.75 mg kg^{-1}) soils. They reported that Cd concentrations in pastoral soils varied with soil types; and the concentration of Cd in topsoils of allophanic soils was higher than in those of non-allophanic soils. Our results showed similar trends for Horotiu (an allophanic soil) compared to Te kowhai (a gley soil).

Similar to our results, Stafford et al. (2018) observed significant linear correlation (Spearman's rho = 0.923) for total soil Cd and total P for the top 15 cm of Waikato farms. They also reported a stronger correlation between Cd and total P ($p < 0.001$) than Olsen P ($p = 0.953$). Numerous soil variables, such as mineral and organic matter content, and pH, are likely to affect the correlation between Cd and Olsen P (Edmeades et al., 2006). Hence, total soil P is a better indicator of the effect of P fertiliser applications for the amount of Cd in soil.

Cadmium concentrations were also monitored in four piezometers located in fertilised sites: Te Kowhai (screen 2.0−3.4 m), Te Kowhai−Shallow (screen 1.1−1.9 m), Te

Kowhai−Deep (screen 5.1−6.0 m), and Horotiu (screen 4.6−7.6 m). Cd concentrations in these sites ranged between 0.08−0.23 μg L^{-1}. Seasonal fluctuations in groundwater concentrations appear to have been associated with the duration and intensity of rainfall events and subsequent water-logging. Cadmium typically occurs up to 1 μg L^{-1} in groundwater, based on the international literature (Kubier et al., 2019). During this study, Cd concentrations in Te Kowhai groundwater exceeded the trigger Cd values (0.2 μg L^{-1}) for the 95% level of species protection (95%) in slightly to moderately disturbed ecosystems (ANZECC, 2018). However, Cd concentrations in Horotiu groundwater remained below the trigger value throughout this study. While our results showed that seasonal changes can affect groundwater quality, longer-duration monitoring is needed for groundwater protection and monitoring practices.

In this study, the mean concentration of Cd in pastures varied between soil types. Horotiu pasture Cd concentrations were slightly higher than that in Te Kowhai and Te Kowhai−unfertilised soil, but there was no significant difference between Cd concentrations in pasture of Te Kowhai and Te Kowhai−unfertilised. Similarly, Roberts et al. (1994) found no significant difference in Cd concentration between the pastures of pastoral (0.10 mg kg^{-1}) and native (0.08 mg kg^{-1}) sites. The degree of phytoavailability of Cd is affected by a wide range of soil and pasture variables, with soil pH being the major factor regulating uptake of Cd (Gray et al., 1999). As soil pH increases, sorption of Cd onto soil components (i.e., organic matter and soil oxides) increases, resulting in a reduction in the phytoavailability of Cd. In this study, the soil pH in the 1st depth (rooting depth) was within a narrow range (5.7−6.0) across all sites. However, the significant difference in pasture Cd concentrations between Te Kowhai and Horotiu, suggests that other factors, such as drainage-induced redox transformations, may affect the phytoavailability and leaching potential of Cd (Wan et al., 2018; G. Wang et al., 2020).

Cadmium Isotope Fractionation in Soil−Groundwater−Pasture Systems

Figure 5.6 illustrates the fractionation of Cd isotopes between soil, groundwater and pasture in this study compared to a comparable study on soil−wheat systems by Wiggenhauser et al. (2016). Our results showed that the Cd fractionation (Δ) between $Ca(NO_3)_2^-$ extractable and pasture in the Te Kowhai−unfertilised soil (Δ = 0.38) was higher than the fertilised Te Kowhai (Δ = 0.16) and Horotiu (Δ = 0.23) soils. In Oen (silt loam, Δ = 0.04) and Wied (sandy loam, Δ = 0.03) soils, the fractionation between these two phases were small by comparison.

Cadmium leaching within the Horotiu soil column was associated with higher Cd fractionation. The cumulative processes operating in Horotiu lead to a ^{114}Cd depletion in deeper horizons (Δ = - 0.21). While a similar magnitude and direction of fractionation was observed in Wied soil (Δ = - 0.12), other sites studied by Wiggenhauser et al. (2016) did not show significant fractionation with depth (Δ ~ 0). The mobilisation of Cd from the 5th depth interval to groundwater (1.0 (Te Kowhai) and 5.6 (Horotiu) m vertical distance) was associated with enrichment in $\delta^{114/111}$Cd in the aqueous phase, with associated fractionations of +0.48 and +0.15 in Te Kowhai and Horotiu groundwater, respectively.

Overall, Cd mobilsation from soil to pastures was associated with high Cd fractionation, where the receiving phase (pasture) was enriched with ^{114}Cd. The fractionation in the Te Kowhai−unfertilised soil (Δ = 0.59) was higher than that observed in the fertilised Te Kowhai (Δ = 0.43) and Horotiu (Δ = 0.45) soils. Wiggenhauser et al. (2016)

reported similar fractionation in Oen soil (Δ = 0.39) and Wied soil (Δ = 0.13) between topsoil (A horizon) and wheat. The broadly consistent fractionation of Cd between topsoil and pasture supports the inference that mechanisms of accumulation into grasses were consistent in both Te Kowhai and Horotiu, in the generally aerobic upper few centimeters of the soil profile (i.e., to rooting depth).

In general, Cd mobilisation from soil to groundwater was associated with enrichment of ^{114}Cd between soil and groundwater (i.e., retention of lighter Cd isotopes in the soil column). However, the fractionation varied with soil type, with Te Kowhai fractionation (Δ = 0.40) being significantly higher than Horotiu (Δ = 0.34).

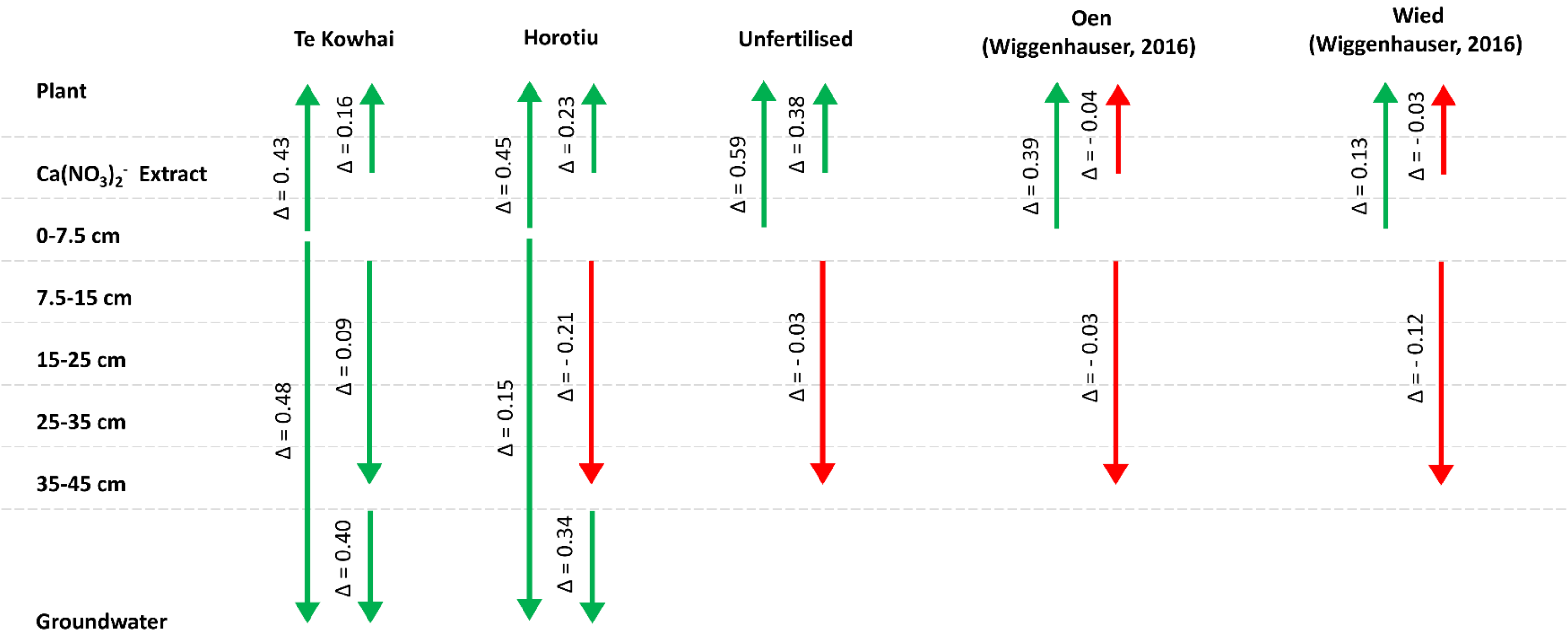


Figure 5.8: Cd isotope fractionation between soil, groundwater and pasture on Te Kowhai, Horotiu, and Te Kowhai–unfertilised soils. We also compare the fractionations to Oen and Wied soils. Supplementary data from Wiggenhauser et al. (2016).

Controlling Factors of Cadmium Mobilisation

In this study, the effect of water-logging on Cd mobility was explored through soil−solution incubations. The results showed the significant role of water-logging duration on the availability and mobility of Cd in soil−solution. Our results showed marked increases in the dissolved Cd concentration during the first days of incubation, followed by a significant decrease after the second day. Wan et al. (2018) showed that flooding decreases Cd concentrations in soil−solution and rice plants, however in their experiments the first water sample was extracted after the second day of incubation. Therefore, the dynamics of Cd in soil−solution in the aforementioned study is unknown. Similarly, Wang et al. (2020) reported a decreasing trend in aqueous Cd concentrations after flooding, which could be attributed to organic complexation of Cd, or alternatively, adsorption and precipitation/co-precipitation of CdS and FeS_2. They concluded that redox cycles in sulphur (SO_4^{2-}/HS^-), induced by anerobic organic carbon metabolism, could drive Cd dynamics in water-logged paddy fields. Alternative reaction pathways can be considered, including Cd binding to iron and manganese (hydr)oxide phases (Wasylenki et al., 2014; Yan et al., 2021). In this study, the decline in Cd and Zn concentrations following 2 d of incubation, coincided with a marked decline in S concentration. The change in SO_4^{2-} between 2 d and 8 d amounts to a loss of 366 µM, whereas Cd and Zn reduced in concentration by 1.3 µM. Since ΔS was >270 times greater than Δ(Cd + Zn), the loss of these metals is consistent with formation of metal sulfide precipitates. However, Cd and Zn are not responsible for the drop in S, with the residual difference in S likely due to formation of FeS/FeS_2. Indeed, this coheres with the expected reaction sequence observed in the incubation data, i.e., O_2 -> MnO_x, FeO_x -> SO_4^{2-} (Figure 5.5). Wiggenhauser et al. (2021) reported a slight enrichment of soil−solution with heavier Cd isotopes (Δ = - 0.04) after flooding. This is consistent with our results from the Te Kowhai incubation, in which we observed no fractionation (Δ within error of soil values) during the first day of soil incubation, followed by a negative fractionation (Δ = - 0.31) after around eight days. We can interpret these isotope effects as reflecting Cd dissociation (day one), followed by scavenging of ^{114}Cd into CdS_2 (s) after sulfate reduction had initiated.

We observed similar trends following the major rainfall event between the 11th and 25th of September 2019. After this time, the Cd isotope ratio of Te Kowhai groundwater decreased (Δ = - 0.09), while the Cd concentration in Te Kowhai groundwater slightly increased. During this period, metal-sulfide precipitates were seen in the UDMS flowcells (supplementary information, Figure 5.S3), suggesting that water-logging due to heavy rainfall affects Cd mobilisation to groundwater. As previously noted, the consistent, positive fractionation from soil-to-pasture in both soil types, is consistent with aerobic conditions in the topsoil.

The evidence compiled here, suggests that Cd can be translocated within the soil column through adsorption and desorption cycles, and wetting/drying cycles which promote the cycling of Fe, Mn and S. Our results demonstrate that Cd cycling, particularly due to redox transitions, can cause contrasting fractionation effects in different soils. In principle, these processes could obscure the isotopic characteristics of Cd as it moves between soil, pasture and groundwater. However, Cd tracing and source attribution are still possible if appropriate fractionation factors are used to correct isotope ratios, e.g., the negative overprint of inferred CdS_2 formation on groundwater values. Our results reinforce the emerging understanding that Cd is dynamically-cycled in soil, which is certainly not a permanent sink for Cd, but rather a temporary reservoir for Cd. Groundwater and pasture concentrations and $\delta^{114/111}$Cd ratios may fluctuate seasonally in response to wet/dry cycles and a seasonally-resolved study would certainly assist in confirming this hypothesis. We also suggest that Cd isotope ratios could prove particularly useful in constraining Cd mass-transfer into biomass, but that groundwater $\delta^{114/111}$Cd must be corrected when attempting to discriminate inputs (e.g., fertiliser-derived vs non-anthropogenic sources).

5.5. Conclusion

Stable metal isotope ratios are a novel tool that can improve our understanding of biogeochemical processes in shallow soil−groundwater−pasture systems. This study used $\delta^{114/111}$Cd measurements to assess Cd uptake and transport from soil to groundwater, and from soil to pasture on two contrasting agricultural soils, with uniform fertilisation histories, alongside an unfertilised soil. Our results demonstrate that Cd isotopes are significantly and systematically fractionated in groundwater−soil−pasture systems, and the fractionation patterns provide information on the biogeochemical processes in operation. In particular, the results illustrate that water-logging in poorly-drained soils can affect Cd mobilisation and its isotopic composition. The novel combination of isotope tracing and diffusive gradients in thin films (DGT) may therefore offer the potential to better understand Cd dispersion in aquifers, and to Cd in the wider environment.

Funding

This study was funded by The University of Waikato, DairyNZ, and the Ministry of Business, Innovation, and Employment (MBIE, Smart Ideas Contract UOWX1804). AH was also supported by a Rutherford Discovery Fellowship [RDF-UOW1601]. The views expressed in this paper are those of the authors and do not necessarily reflect the views or policies of The University of Waikato, Waikato Regional Council, DairyNZ, and MBIE.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Supplementary Information Content

The Supporting Information is available free of charge via the internet at http://pubs.acs.org. Table 5.S1 – 5.S3, Figure 5.S1 – 5.S3.

Acknowledgments

We would like to acknowledge John Hadfield at Waikato Regional Council for installing the piezometers, DairyNZ for providing access to the Scott Farm site, Amanda French for sample preparation and ICP-MS analysis, and Mehdi Ghorashi Nezhad for graphical design.

References

Abouchami, W., Galer, S. J. G., Horner, T. J., Rehkämper, M., Wombacher, F., Xue, Z., Lambelet, M., Gault-Ringold, M., Stirling, C. H., Schönbächler, M., & others. (2013). A common reference material for cadmium isotope studies--NIST SRM 3108. Geostandards and Geoanalytical Research, 37(1), 5–17.

Alloway, B. J. (2012). Heavy metals in soils: trace metals and metalloids in soils and their bioavailability (Vol. 22). Springer Science \& Business Media.

ANZECC. (2018). Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

Arcega-Cabrera, F., Sickman, J. O., Fargher, L., Herrera-Silveira, J., Lucero, D., Oceguera-Vargas, I., Lamas-Cosío, E., & Robledo-Ardila, P. A. (2021). Groundwater Quality in the Yucatan Peninsula: Insights from Stable Isotope and Metals Analysis. Groundwater, 59(6), 878–891. https://doi.org/10.1111/gwat.13109

Baily, A., Rock, L., Watson, C. J., & Fenton, O. (2011). Spatial and temporal variations in groundwater nitrate at an intensive dairy farm in South-East Ireland: Insights from stable isotope data. Agriculture, Ecosystems and Environment, 144(1), 308–318. https://doi.org/10.1016/j.agee.2011.09.007

Blakemore, L. C. (1987). Methods for chemicalanalysis of soils. NZ Soil Bureau Sci. Rep., 80, 72–76.

Bolan, N. S., Khan, M. A. R., Tillman, R. W., Naidu, R., & Syers, J. K. (1999). The effects of anion sorption on sorption and leaching of cadmium. Soil Research, 37(3), 445–460.

Brümmer, G. W. (1986). Heavy metal species, mobility and availability in soils. In The importance of chemical “speciation” in environmental processes (pp. 169–192). Springer.

Caporale, A. G., & Violante, A. (2016). Chemical Processes Affecting the Mobility of Heavy Metals and Metalloids in Soil Environments. Current Pollution Reports, 2(1), 15–27. https://doi.org/10.1007/s40726-015-0024-y

Carrillo-González, R., Šim\uunek, J., Sauve, S., & Adriano, D. (2006). Mechanisms and pathways of trace element mobility in soils. Advances in Agronomy, 91, 111–178.

Cavanagh, J. (2014). Status of cadmium in New Zealand soils: 2014. Landcare Research.

Christensen, J. B., & Christensen, T. H. (2000). The effect of pH on the complexation of Cd, Ni and Zn by dissolved organic carbon from leachate-polluted groundwater. Water Research, 34(15), 3743–3754. https://doi.org/10.1016/S0043-1354(00)00127-5

CliFlo NIWA. (2022). New Zealand's National Climate Database. National Institute of Water and Atmospheric Research New Zealand (NIWA).

Davison, W. (2016). Diffusive gradients in thin-films for environmental measurements. Cambridge University Press.

Davison, W., & Zhang, H. (1994). In situ speciation measurements of trace components in natural waters using thin-film gels. Nature, 367(6463), 546–548.

Edmeades, D. C., Metherell, A. K., Waller, J. E., Roberts, A. H. C., & Morton, J. D. (2006). Defining the relationships between pasture production and soil P and the development of a dynamic P model for New Zealand pastures: a review of recent developments. New Zealand Journal of Agricultural Research, 49(2), 207–222.

Garmo, Ø. A., Naqvi, K. R., Røyset, O., & Steinnes, E. (2006). Estimation of diffusive boundary layer thickness in studies involving diffusive gradients in thin films (DGT). Analytical and Bioanalytical Chemistry, 386(7), 2233–2237.

Gault-Ringold, M., & Stirling, C. H. (2012). Anomalous isotopic shifts associated with organic resin residues during cadmium isotopic analysis by double spike MC-ICPMS. Journal of Analytical Atomic Spectrometry, 27(3), 449–459.

Gray, C. W., McLaren, R. G., Roberts, A. H. C., & Condron, L. M. (1999). Effect of soil pH on cadmium phytoavailability in some New Zealand soils. New Zealand Journal of Crop and Horticultural Science, 27(2), 169–179. https://doi.org/10.1080/01140671.1999.9514093

Jeng, A. S., & Singh, B. R. (1995). Cadmium status of soils and plants from a long-term fertility experiment in southeast Norway. Plant and Soil, 175(1), 67–74. https://doi.org/10.1007/BF02413011

Kelliher, F. M., Gray, C. W., & Noble, A. D. L. (2017). Superphosphate fertiliser application and cadmium accumulation in a pastoral soil. New Zealand Journal of Agricultural Research, 60(4), 404–422. https://doi.org/10.1080/00288233.2017.1363058

Kubier, A., Wilkin, R. T., & Pichler, T. (2019). Cadmium in soils and groundwater: A review. Applied Geochemistry, 108(February). https://doi.org/10.1016/j.apgeochem.2019.104388

Liu, Z., Ji, X., Guan, D., Xie, Y., Zhu, J., Peng, J., & others. (2017). Effects of timing and duration of waterlogging on Cd absorption and accumulation by rice under cadmium stress. Journal of Ecology and Rural Environment, 33(12), 1125–1131.

Loganathan, P., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2012). Cadmium sorption and desorption in soils: a review. Critical Reviews in Environmental Science and Technology, 42(5), 489–533.

Lyons, W. B., & Fitzgerald, W. F. (1983). Trace metals speciation in nearshore anoxic and suboxic pore waters. In Trace Metals in Sea Water (pp. 621–641). Springer.

Mann, S. S., Rate, A. W., & Gilkes, R. J. (2002). Cadmium accumulation in agricultural soils in Western Australia. Water, Air, and Soil Pollution, 141(1), 281–297.

McDowell, R. W. (2012). The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. New Zealand Journal of Agricultural Research, 55(2), 133–146.

McDowell, R. W., Taylor, M. D., & Stevenson, B. A. (2013). Natural background and anthropogenic contributions of cadmium to New Zealand soils. Agriculture, Ecosystems and Environment, 165, 80–87. https://doi.org/10.1016/j.agee.2012.12.011

Mohammadi, A., Corbett, T., French, A., J. Lehto, N., Hadfield, J., Jarman, P., Sandwell, D., Shokri, A., Schipper, L., & Hartland, A. (2022). Application of Diffusive Gradients in Thin Films for Monitoring Groundwater Quality. ACS ES&T Water, 0(0). https://doi.org/10.1021/acsestwater.1c00279

Nokes, C., & Weaver, L. (2014). Cadmium in Groundwater : review of regional council data. Ministry of Health, Wellington, May.

Olsen, S. R. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate (Issue 939). US Department of Agriculture.

Ratié, G., Chrastný, V., Guinoiseau, D., Marsac, R., Vaňková, Z., & Komárek, M. (2021). Cadmium Isotope Fractionation during Complexation with Humic Acid. Environmental Science and Technology, 55(11), 7430–7444. https://doi.org/10.1021/acs.est.1c00646

Roberts, A. H. C., Longhurst, R. D., & Brown, M. W. (1994). Cadmium status of soils, plants, and grazing animals in New Zealand. New Zealand Journal of Agricultural Research, 37(1), 119–129. https://doi.org/10.1080/00288233.1994.9513048

Salmanzadeh, M., Hartland, A., Stirling, C. H., Balks, M. R., Schipper, L. A., Joshi, C., & George, E. (2017). Isotope Tracing of Long-Term Cadmium Fluxes in an Agricultural Soil. https://doi.org/10.1021/acs.est.7b00858

Soil Survery Staff. (2014). Keys to soil taxonomy. United States Department of Agriculture: Washington, DC, USA.

Stafford, A. D., Palmer, A. S., Jeyakumar, P., Hedley, M. J., & Anderson, C. W. N. (2018). Soil cadmium and New Zealand dairy farms: Impact of whole-farm contaminant variability on environmental management. Agriculture, Ecosystems and Environment, 254(August 2017), 282–291. https://doi.org/10.1016/j.agee.2017.11.033

Stumm, W., & Morgan, J. J. (2012). Aquatic chemistry: chemical equilibria and rates in natural waters (Vol. 126). John Wiley \& Sons.

Taylor, M. D. (1997). Accumulation of cadmium derived from fertilisers in New Zealand soils. Science of the Total Environment, 208(1–2), 123–126. https://doi.org/10.1016/S0048-9697(97)00273-8

Taylor, M., Gibb, R., Willoughby, J., Hewitt, A., & Arnold, G. (2007). Soil Maps of Cadmium in New Zealand. June.

Wan, Y., Camara, A. Y., Yu, Y., Wang, Q., Guo, T., Zhu, L., & Li, H. (2018). Cadmium dynamics in soil pore water and uptake by rice: Influences of soil-applied selenite with different water managements. Environmental Pollution, 240, 523–533. https://doi.org/10.1016/j.envpol.2018.04.044

Wang, G., Hu, Z., Li, S., Wang, Y., Sun, X., Zhang, X., & Li, M. (2020). Sulfur controlled cadmium dissolution in pore water of cadmium-contaminated soil as affected by DOC under waterlogging. Chemosphere, 240, 124846. https://doi.org/10.1016/j.chemosphere.2019.124846

Wang, L., Jin, Y., Weiss, D. J., Schleicher, N. J., Wilcke, W., Wu, L., Guo, Q., Chen, J., O’Connor, D., & Hou, D. (2021). Possible application of stable isotope compositions for the identification of metal sources in soil. Journal of Hazardous Materials, 407(November 2020), 124812. https://doi.org/10.1016/j.jhazmat.2020.124812

Warnken, K. W., Zhang, H., & Davison, W. (2006). Accuracy of the Diffusive Gradients in Thin-Films Technique : Diffusive Boundary Layer and Effective Sampling Area Considerations. 78(11), 3780–3787. https://doi.org/10.1021/ac060139d

Wasylenki, L. E., Swihart, J. W., & Romaniello, S. J. (2014). Cadmium isotope fractionation during adsorption to Mn oxyhydroxide at low and high ionic strength. Geochimica et Cosmochimica Acta, 140, 212–226.

Welikala, D., Robinson, B. H., Moltchanova, E., Hartland, A., & Lehto, N. J. (2021). Soil cadmium mobilisation by dissolved organic matter from soil amendments. Chemosphere, 271, 129536. https://doi.org/10.1016/j.chemosphere.2021.129536

Wiggenhauser, M., Aucour, A. M., Bureau, S., Campillo, S., Telouk, P., Romani, M., Ma, J. F., Landrot, G., & Sarret, G. (2021). Cadmium transfer in contaminated soil-rice systems: Insights from solid-state speciation analysis and stable isotope fractionation. Environmental Pollution, 269. https://doi.org/10.1016/j.envpol.2020.115934

Wiggenhauser, M., Bigalke, M., Imseng, M., Keller, A., Rehkämper, M., Wilcke, W., & Frossard, E. (2019). Using isotopes to trace freshly applied cadmium through mineral phosphorus fertilization in soil-fertilizer-plant systems. Science of the Total Environment, 648, 779–786. https://doi.org/10.1016/j.scitotenv.2018.08.127

Wiggenhauser, M., Bigalke, M., Imseng, M., Müller, M., Keller, A., Murphy, K., Kreissig, K., Rehkämper, M., Wilcke, W., & Frossard, E. (2016). Cadmium isotope fractionation in soil-wheat systems. Environmental Science and Technology, 50(17), 9223–9231. https://doi.org/10.1021/acs.est.6b01568

Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., & Boeckx, P. (2009). Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Research, 43(5), 1159–1170. https://doi.org/10.1016/j.watres.2008.12.048

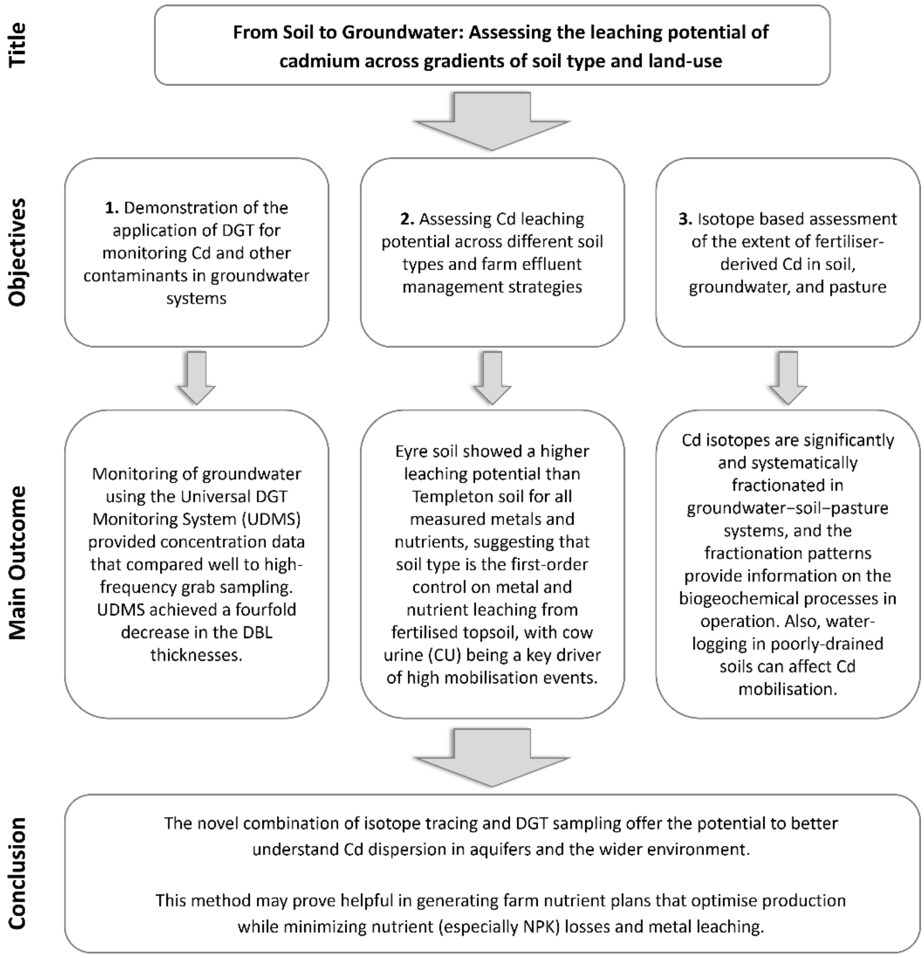
Yan, X., Zhu, M., Li, W., Peacock, C. L., Ma, J., Wen, H., Liu, F., Zhou, Z., Zhu, C., & Yin, H. (2021). Cadmium Isotope Fractionation during Adsorption and Substitution with

Iron (Oxyhydr)oxides. Environmental Science and Technology, 55(17), 11601–11611. https://doi.org/10.1021/acs.est.0c06927.

Chapter 6 - Summary, Conclusions and Recommendations

6.1. Summary and Conclusions

The following section summarises the findings of the three chapters and links them back to this research's objectives. Each of these studies, individually and collectively, improves our understanding of Cd mobilisation in soil−groundwater−pasture systems and resolves experimental challenges that hinder monitoring the fate of Cd and other fertiliser-derived contaminants in agricultural systems (Figure 6.1).



From Soil to Groundwater: Assessing the leaching potential of cadmium across gradients of soil type and land-use

1. Demonstration of the application of DGT for monitoring Cd and other contaminants in groundwater systems

2. Assessing Cd leaching potential across different soil types and farm effluent management strategies

3. Isotope based assessment of the extent of fertiliser-derived Cd in soil, groundwater, and pasture

Monitoring of groundwater using the Universal DGT Monitoring System (UDMS) provided concentration data that compared well to high-frequency grab sampling. UDMS achieved a fourfold decrease in the DBL thicknesses.

Eyre soil showed a higher leaching potential than Templeton soil for all measured metals and nutrients, suggesting that soil type is the first-order control on metal and nutrient leaching from fertilised topsoil, with cow urine (CU) being a key driver of high mobilisation events.

Cd isotopes are significantly and systematically fractionated in groundwater−soil−pasture systems, and the fractionation patterns provide information on the biogeochemical processes in operation. Also, water-logging in poorly-drained soils can affect Cd mobilisation.

The novel combination of isotope tracing and DGT sampling offer the potential to better understand Cd dispersion in aquifers and the wider environment.

This method may prove helpful in generating farm nutrient plans that optimise production while minimizing nutrient (especially NPK) losses and metal leaching.

Figure 6.1: PhD Thesis Overview

6.1.1. Demonstration of the application of DGT for monitoring Cd and other contaminants in groundwater systems

The first study of this thesis focused on the application of diffusive gradients in thin-films (DGTs) to groundwater quality monitoring. Results are published in the article entitled “Application of diffusive gradients in thin films (DGT) for monitoring groundwater quality”.

In groundwater, ambient Cd concentrations are typically below the detection limit of analytical instruments, making it difficult to estimate the rate of accumulation and Cd translocation from soil to groundwater (Gray & Cavanagh, 2022). Moreover, groundwater quality can fluctuate rapidly, sometimes over just a few hours. Therefore, conventional grab sampling cannot provide accurate information on the quality of groundwater with respect to low-level contaminants. DGT is an established passive sampling method to measure contaminants in solution (Davison, 2016). With the additional advantage that DGTs can accumulate analytes to levels that exceed instrumental quantification limits. However, there are some limitations associated with the deployment of DGTs in stagnant solutions, where the increased length of the diffusive boundary layer (DBL) must be accounted for (Uher et al., 2013).

Three different approaches were tested using NO_3^- to estimate the DBL thickness: (1) static DGT suspension arranged on nylon line, (2) motorised ‘DGT-shaker’ designed to steadily move the DGTs up and down within bores and piezometers, and (3) the ‘universal DGT monitoring system (UDMS)’ which was programmed to pump groundwater through opaque flowcells loaded with DGTs. The main conclusions of this study were:

- The static DGT suspension can be deployed quickly, but is unreliable for stagnant solutions because thicker DBLs reduce accuracy. It is also difficult to deploy DGTs in small diameter piezometers using this method, as DGTs can rest against the piezometer walls, which increases the stagnancy of water at the DGT interface, increasing the DBL thickness.
- The 'DGT-shaker' is easy to transport to sampling sites and reduces the physical DBL of the DGT. However, the nylon line in the DGT shaker method was prone to getting tangled, or would sometimes adhere to the walls of piezometers. This method can be used for large diameter boreholes with minor modifications to the pulley (by increasing the pulley groove width and depth), however, it is not recommended for small diameter piezometers ($x < 100$ mm).
- Monitoring of groundwater using the UDMS provided concentration data that compared well to high-frequency grab sampling. The UDMS overcomes the limitations associated with stagnancy by pumping groundwater through DGT flowcells. UDMS decreased the DBL thicknesses by fourfold compared with the static suspension.
- NO_3^- can be used as a conservative (fully labile) tracer alongside measurements of metals with DGT, allowing the effect of the physical DBL to be measured independently. Using the NO_3^- DBL:metal ADBL ratio as an indicator can help determine metal bioavailability and potential toxicity, e.g., to freshwater organisms.
- It was observed that complexes of Cd and Zn dissociate quickly, while complexes of other metals (e.g., Cu and Al) are relatively inert.

- UDMS is particularly suitable to monitoring of low-level contaminants, such as Cd, and in settings where higher frequency changes in solute concentration are expected, such as in alluvial groundwater systems, or denitrifying bioreactors.

6.1.2. Assessing Cd leaching potential across different soil types and farm effluent management strategies

The second study sought to assesses the individual and combined effects of farm dairy effluent (FDE) and cow urine (CU) on the leaching of metals and nutrients in Eyre (excessively-drained) and Templeton (well-drained) soils. Results will be published in an article entitled “Effects of dairy farm effluent management on metal, nutrient and organic matter leaching: A lysimeter trial on two contrasting soils”.

New Zealand is now one of the largest dairy exporters in the world. Inevitably, NZ's soil and groundwater have become polluted with contaminants originating from fertilisers used in intensive dairy farming. There are several factors that affect the mobilisation of fertiliser-derived contaminants, including soil hydrology, the amount of generated effluent (farm dairy effluent and cow urine), and farm effluent management strategies (Gray et al., 2021; Silva et al., 2005). Therefore, the purpose of this study was to test whether adding FDE and cow urine to soil would synergistically increase the leaching of metals and nutrients; and whether different soil types have different intrinsic contaminant leaching potentials.

A total of 77 leachate samples were collected from sixty lysimeters across the Lincoln University Dairy Farm (LUDF). To reduce skewness in the distributions, a non-linear transformation was used (Box and Cox, 1964). The modified Z-score method (Iglewicz and

Hoaglin, 1993) was also used as a complementary method to detect high mobilisation events in the datasets. The main conclusions of this study were:

- Different soil types exhibit different levels of metal and nutrient leaching, which can be enhanced or reduced by land treatments.
- The data points with high concentrations were particularly important for overall mass-transfer. 88% of high values were related to urine applications, with a higher proportion occurring in the excessively drained Eyre soil. Despite the fact that the cases of greatest mobilisation occured less frequently (less than 14%), they accounted for 63% of the total mass transferred by leachates.
- Our results suggest that applying urine to FDE-treated soil enhances the leaching of metals, nutrients, and fDOM, while adding FDE to urine-treated soil causes antagonistic effects on leaching. It appears that the order in which treatments are given also matters. Overall, urine caused greater leaching ($p < 0.05$) than FDE.
- The application of different treatments indicated significantly greater mass transfer in the Eyre soil compared to Templeton soil for all measured chemical components (Cd, Zn, Ni, Pb, U, As), nutrients (Mg, P, K, S, Cl^-, NO_3^-), and fDOM components (C1, C2, C3). Eyre soil is extremely drained and has a lower water retention capacity than Templeton soil, which may be an important contributing factor to its higher level of metal and nutrient mobilisation.
- It was concluded that soil type is likely a more powerful factor than farm management strategies for metal and nutrients leaching, when significant differences between soils and treatments are compared.

- Farm nutrient plans based on this information may optimise production while minimising nutrient losses (especially for NPK).

6.1.3. Isotope based assessment of the extent of fertiliser-derived Cd in soil, groundwater, and pasture

The third part of this thesis reports Cd isotope ratios ($\delta^{114/111}$Cd) from two contrasting but uniformly fertilised soils (Te Kowhai and Horotiu), along with pasture and in-situ groundwater $\delta^{114/111}$Cd measurements. Results will be published in an article entitled "Tracing fertiliser-derived cadmium in soil−pasture-groundwater systems: Coupling stable isotope ratio analysis and diffusive gradients in thin films".

Three decades of research have revealed contradictory results concerning the accumulation and mobilisation of Cd in NZ agricultural systems. Researchers reported both accumulation (Kelliher et al., 2017; Taylor, 1997) and declining (McDowell, 2012) conditions in soil Cd mass balances. Conflicting observations of topsoil Cd concentrations within this context (i.e., an annual application of millions tons of P-fertiliser on NZ farms) suggest either variable rates of bioaccumulation, or variable degrees of leaching to groundwater, or both.

A number of hydrochemical and biogeochemical processes can affect Cd transport in the subsurface including complexation by organic and inorganic ligands, pH variations in soil−solution, and redox variations caused by waterlogging (Brümmer, 1986; Caporale & Violante, 2016; Z. Liu et al., 2017). Recently, researchers have employed stable isotope ratio analysis as a means of probing contaminant cycling in agricultural systems. However, this method cannot directly be applied in these systems due to analytic and experimental challenges, i.e., soil heterogeneity and low groundwater' contaminant concentrations.

The UDMS developed in the first part of this thesis was used to measure [Cd] and $\delta^{114/111}$Cd in groundwater. To ensure homogeneity of soil samples, soil and plant samples were collected from three different sides of the study paddocks. Two paddocks with contrasting soils (Te Kowhai and Horotiu) and the same fertilisation history were sampled. Te Kowhai soil is poorly drained with slowly-permeable subsoil layers, which become water-logged and chemically reduced in winter and spring. Horotiu, on the other hand, is well-drained and has freely-draining subsoils, leading to oxic conditions in the shallow groundwater. A series of incubation experiments were conducted to investigate the effect of water-logging on Cd isotope ratios in soil−solution. The main conclusions of this study were:

- Results suggest a significant fractionation of Cd isotopes in groundwater−soil−pasture systems. The distribution patterns indicate hydrogeochemical processes in action. Fractionation of δ^{114}Cd occurred during solubilisation from soil, leading to enrichment in receiving phases (pastures and groundwater).
- Cd isotope ratios of fertilised− and unfertilised−Te Kowhai soils were within standard errors of each other in the 3rd to 5th depths. The difference in Cd isotope ratio of the 1st and 2nd depths of these two sites can be attributed to fertiliser application (0.11 ‰ difference).
- The Cd concentrations and isotopic compositions of soils, groundwater, and pastures differed between sites, but they trended similarly across all sites. All soil

types showed a decrease in Cd concentration with depth. Horotiu had higher Cd concentrations than Te Kowhai, except in groundwater.

- Results indicated that water-logging duration has a significant effect on the mobility and availability of Cd in soil−solution. The dissolved Cd concentration increased during the first days of incubation, followed by a significant decrease after the second day. Therefore, wet/dry cycles which promote fluxes of Fe, Mn, and S may facilitate Cd translocation within the soil column.
- It was concluded that soil is certainly not a permanent sink for Cd, but rather a temporary reservoir. Hydrogeochemical processes can redistribute Cd within the soil column through dissolution/precipitation and adsorption/desorption processes.
- The novel combination of stable isotope ratios analysis and DGT improved our understanding of biogeochemical processes in soil−groundwater−pasture systems.

6.1.4. Revisiting the aims of this research

The aims of this thesis were to illustrate the effects of soil type and land-use on the mobilisation of fertiliser-derived Cd in the agricultural systems. This thesis addresses each of these objectives in separate research chapters. These chapters address some of the experimental and analytical challenges associated with the assessment of fertiliser-derived contaminants in the wider environment. The UDMS overcame the limitations associated with the direct application of DGTs in groundwater, and it enabled us to monitor low level contaminants, i.e., Cd, in groundwater. Using lysimeter leachate samples in a controlled environment allowed us to understand the effects of farm management strategies on metal, nutrient, and organic matter leaching in different soil types. Different data analysis methods were used to capture information about mobilisation mechanisms and how these contribute to net translocations from soil to groundwater. Coupling stable isotope ratio analysis and diffusive gradients in thin films improved our understanding of the dispersion of Cd in soil−pasture-groundwater systems. Groundwater sampling and sample preparation for stable isotope analysis were made easier with the UDMS. This new toolkit proved to be useful for monitoring the environment and could be used for regulatory monitoring of agricultural practices, where appropriate.

6.1.5. Recommendations and Future Research

Although several aspects have been addressed in this study, questions remain about Cd dispersion in agricultural systems.

Since soil type is the first-order control for metal and nutrient leaching from fertilised topsoil, I suggest that further research be conducted on a wide range of agricultural soils in New Zealand. Researchers and regulatory agencies can use this information to revise policies. With the recent improvements in environmental assessment and monitoring methods, a review and update of the Tiered Fertiliser Management System (TFMS) is recommended.

Our research suggests that soil does not necessarily serve as a permanent repository for Cd. Rather, it is a temporary one, since hydrogeochemical processes can transfer Cd to groundwater and pastures. Combining stable isotope ratio analysis with long-term lysimeter trials will provide a deeper understanding of the effects of land management strategies on metal translocation in the subsurface.

A switch to organic farming could have a significant impact on the stabilisation of Cd in soils and could slow groundwater degradation. Long-term studies will be necessary to detect the effects of this transition. However, the continued reliance on P-fertilisers means that removal of Cd and other contaminants during feedstock processing is the best solution for environmental outcomes.

The UDMS can be redesigned to improve set up and transport time. Also, with minor modifications to the pulley (by increasing the width and depth of the groove), the DGT shaker method can be used in large diameter boreholes.

This study compared metal and nutrient leaching from soils with different land treatments using leachate samples from Lincoln University Dairy Farm (LUDF) lysimeters. However, it was impossible to determine the intrinsic degree of leaching without control trials. Consequently, further research is needed to determine and confirm the magnitude of differences between amended and unamended soils, so that we can determine what drives high mobilisation events.

Our results showed that cow urine is a key driver of high mobilisation events. Additional research is needed to examine how the diet of dairy cows, including forage type and grazing cycle, affect cow urine volume and composition. This information may be useful for reducing metal and nutrient leaching associated with cow urine infiltration.

In waterlogged soil, dissolved Cd is controlled by redox conditions, indicating that drainage is a key determinant of Cd mobilisation in soil. However, the impact of continuous wet/dry cycles remains unknown. Therefore, further studies are needed to investigate how sulphur, iron, and manganese interact with Cd mobilisation in soil under a range of hydroclimatic conditions.

References

Brümmer, G. W. (1986). Heavy metal species, mobility and availability in soils. In The importance of chemical "speciation" in environmental processes (pp. 169–192). Springer.

Caporale, A. G., & Violante, A. (2016). Chemical Processes Affecting the Mobility of Heavy Metals and Metalloids in Soil Environments. Current Pollution Reports, 2(1), 15–27. https://doi.org/10.1007/s40726-015-0024-y

Davison, W. (2016). Diffusive gradients in thin-films for environmental measurements. Cambridge University Press.

Gray, C. W., & Cavanagh, J.-A. E. (2022). The state of knowledge of cadmium in New Zealand agricultural systems: 2021. New Zealand Journal of Agricultural Research, 1–51.

Gray, C. W., Lucci, G. M., Cavanagh, J., & Gray, C. W. (2021). Can the application of farm dairy effluent enhance cadmium leaching from soil ? 50919–50929.

Kelliher, F. M., Gray, C. W., & Noble, A. D. L. (2017). Superphosphate fertiliser application and cadmium accumulation in a pastoral soil. New Zealand Journal of Agricultural Research, 60(4), 404–422. https://doi.org/10.1080/00288233.2017.1363058

Liu, Z., Ji, X., Guan, D., Xie, Y., Zhu, J., Peng, J., & others. (2017). Effects of timing and duration of waterlogging on Cd absorption and accumulation by rice under cadmium stress. Journal of Ecology and Rural Environment, 33(12), 1125–1131.

McDowell, R. W. (2012). The rate of accumulation of cadmium and uranium in a long-term grazed pasture: implications for soil quality. New Zealand Journal of Agricultural Research, 55(2), 133–146.

Silva, R. G., Cameron, K. C., Di, H. J., & Jorgensen, E. E. (2005). A lysimeter study to investigate the effect of dairy effluent and urea on cattle urine N losses, plant uptake and soil retention. Water, Air, and Soil Pollution, 164(1–4), 57–78. https://doi.org/10.1007/s11270-005-2249-7

Taylor, M. D. (1997). Accumulation of cadmium derived from fertilisers in New Zealand soils. Science of the Total Environment, 208(1–2), 123–126. https://doi.org/10.1016/S0048-9697(97)00273-8

Uher, E., Tusseau-Vuillemin, M. H., & Gourlay-France, C. (2013). DGT measurement in low flow conditions: Diffusive boundary layer and lability considerations. Environmental Sciences: Processes and Impacts, 15(7), 1351–1358. https://doi.org/10.1039/c3em00151b

Appendices

Appendix A – Supplementary Information for Chapter 3: Application of diffusive gradients in thin films (DGT) for monitoring groundwater quality

[1]Amir Mohammadi, [1]Thomas Corbett, [1]Amanda French, [2]Niklas J. Lehto, [3]John Hadfield, [1]Peter Jarman, [1]Dean Sandwell, [4]Ali Shokri, [1]Louis Schipper, [1]Adam Hartland*

1. Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand
2. Faculty of Agriculture and Life Science, Lincoln University, Lincoln 7647, New Zealand
3. Waikato Regional Council, Hamilton 3204, New Zealand
4. School of Engineering, University of Waikato, Hamilton 3216, New Zealand

*. Corresponding author: adam.hartland@waikato.ac.nz

Uptake and elution efficiency and binding capacity tests

To ensure that DGT binding layers accumulate the analyte of interest in field deployments, the binding discs' uptake and elution efficiencies were determined. Uptake efficiency is the percentage of the analyte mass accumulated into the binding disk from a small solution of known mass. Elution efficiency is the percentage of the analyte mass eluted from the binding disk. The uptake and elution efficiencies of the binding discs were measured in the lab by immersing them in 10 mL of 0.01 mol L^{-1} NaCl solutions with a range of analyte concentrations. ICP multi-element standard (0.4–40.0 µg L^{-1}) and KH_2PO_4 (10–1000 µg P L^{-1}) were used as emersion solutions for Chelex and ferrihydrite discs, respectively. Solution samples were taken before uptake tests and upon DGT retrieval. The discs were agitated on a shaker for 24 h before being removed, rinsed thoroughly, and then eluted using 1 mL of 1 mol L^{-1} HNO_3 and 10 mL of 0.25 mol L^{-1} H_2SO_4 for Chelex and ferrihydrite for 24 h, respectively. Uptake and elution efficiencies were calculated as described by Davison (2016). The uptake and elution efficiencies of NO_3^- for A520E were 98.8% and 93.4%, respectively (Corbett et al., 2020).

To ensure the long-term deployment capability of DGT devices, the binding capacity of binding disks was measured. The capacity was determined by exposing binding disks or DGT devices to a high concentration of the analyte(s) until saturation was reached. The intrinsic binding capacity is the binding layer' capacity, in the absence of any competition effects. The effective binding capacity is the capacity of binding disks where competition is likely to be an issue, for example, in field deployments or when the binding gel can accumulate multiple analytes. The binding capacity of Chelex disks was measured using 8 mg L^{-1} of ICP multi-element standard. Ferrihydrite discs were measured using 100 mg P L^{-1}

solutions. A520E was measured using 1000 mg N L^{-1} solution as per Corbett et al. (2020). All efficiencies and capacity tests were carried out in triplicate for each binding gel at each analyte concentration.

The background masses of Al, Ni, Cu, and Zn per blank Chelex disk were all below the quantification limit, and the background masses of Cd, Co, and Pb were below the detection limits. The P background mass per ferrihydrite disk was also below detection. The NO_3^- background mass per A520E disk was 7.42E-02 ± 12.6% mg NO_3^- per binding disk (Corbett et al., 2020).

The uptake and elution efficiencies, and the binding capacities for Chelex, ferrihydrite, and A520E DGTs were measured and are shown in Table S 1. The efficiencies and capacities of Purolite DGTs were obtained from Corbett et al. (2020).

Table 3.S1: Uptake efficiency, elution efficiency, and the binding capacity of different binding disks for the analytes of interest

Analyte/ Binding Disk	Uptake efficiency (%)	Elution efficiency (%)	Binding capacity (per disk)
Nitrate/ A520E	98.8% (Corbett et al., 2020)	93.4% (Corbett et al., 2020)	3.5 mg ± 0.98% $_a$ (Corbett et al., 2020)
Cadmium/ Chelex	88.5 ± 4.50% $_b$	83.0 ± 5.45% $_b$	1.6 µg ± 7.50% $_{b,c}$
Phosphorous/ Ferrihydrite	92.3 ± 6.51%	82.9 ± 5.96%	29.6 µg ± 1.66% $_a$

a: intrinsic binding capacity, b: In competition with 19 other elements at the same concentrations, c: effective binding capacity

Study area

Table 3.S2: Site locations, applications, dimensions, screen details, land-uses, and soil types

No.	Site Location	Site ID[1]	Type	Application	Diameter (mm)	Depth (m)	Screen (m)	Water table[2] range (m)	Land-use	Soil type
1	Newstead	72-10024	Piezometer	Monitoring	50	1.8	1.0-1.8	N/A - 0.5	Dairy	Te Kowhai
2	Newstead	72-10023	Piezometer	Monitoring	50	3.3	1.9-3.3	0.7 - 2.4	Dairy	Te Kowhai
3	Newstead	72-10022	Piezometer	Monitoring	50	5.9	5.0-5.9	2.0 - 3.0	Dairy	Te Kowhai
4	Newstead	72-10020	Piezometer	Monitoring	50	4.8	2.8-4.8	3.1 - 4.0	Dairy	Bruntwood
5	Newstead	72-10021	Piezometer	Monitoring	50	7.5	5.5-7.5	3.9 - 4.4	Dairy	Bruntwood
6	Newstead	72-10019	Piezometer	Monitoring	50	7.6	4.6-7.6	6.0 - 6.2	Dairy	Horotiu
7	Newstead	69-163	Bore	Monitoring	900	3.35	3-3.35	2.7 – 2.8	Dairy	
8	Gordonton	69-173	Bore	Pumping	900	6	4-6	2.8	Dairy	
9	Newstead	69-248	Bore	Monitoring	900	2.75		2.0	Orchard	
10	Leamington	70-47	Bore	Pumping	900	4.5	2.5-4.5	3.2	Dairy	
11	Matangi	69-295	Bore	Pumping	900	6.35		4.0 – 4.1	Berry Farm	
12	Matangi	69-233	Piezometer	Monitoring	900	5.49		3.2	N/A	
13	Eureka	69-97	Bore	Pumping	900	4.71		3.1	Orchard	
14	Matangi	72-6169	Piezometer	Monitoring	100	10	7-10	5.0	Orchard	
15	Tamahere	72-801	Piezometer	Pumping	100	10		4.4	Horticulture	

Note: 1. Site ID is the reference number of the sites in the Environment Waikato database.

2. Water table range (m) is the groundwater depths during the UDMS deployments.

Table 3.S3: Groundwater properties for the study sites (average of parameters before DGT deployment and upon retrieval)

No.	Site Location	Site ID	Date	pH	Temperature °C	DO (mg L^{-1})	EC (µS cm^{-1})	Eh
1	Newstead	72-10024	Jun 2019 – Oct 2019	5.6	13.0	10.5	232	195
2	Newstead	72-10023	Jun 2019 – Oct 2019	5.6	13.6	4.6	271	150
3	Newstead	72-10022	Jun 2019 – Oct 2019	6.1	14.9	2.7	320	42
4	Newstead	72-10020	Jun 2019 – Oct 2019	6.1	15.0	9.7	342	206
5	Newstead	72-10021	Jun 2019 – Oct 2019	6.0	15.7	2.2	334	29
6	Newstead	72-10019	Jun 2019 – Oct 2019	5.9	15.6	4.8	316	206
7	Newstead	69-163	Jan 2020 – Feb 2020	5.7	17.7	5.2	276	N/A
8	Gordonton	69-173	Jan 2020 – Feb 2020	5.9	16.9	8.5	263	N/A
9	Newstead	69-248	Jan 2020 – Feb 2020	5.7	17.4	5.8	99	N/A
10	Leamington	70-47	Feb 2020	5.5	19.1	6.5	200	N/A
11	Matangi	69-295	Feb 2020	5.9	17.0	7.0	335	155
12	Matangi	69-233	Feb 2020	5.9	17.0	6.1	271	87
13	Eureka	69-97	Mar 2020	5.6	16.9	N/A	N/A	179
14	Matangi	72-6169	Mar 2020	6.2	16.0	N/A	N/A	164
15	Tamahere	72-801	Mar 2020	6.6	16.5	N/A	N/A	139

DGT deployment methods' catalogue

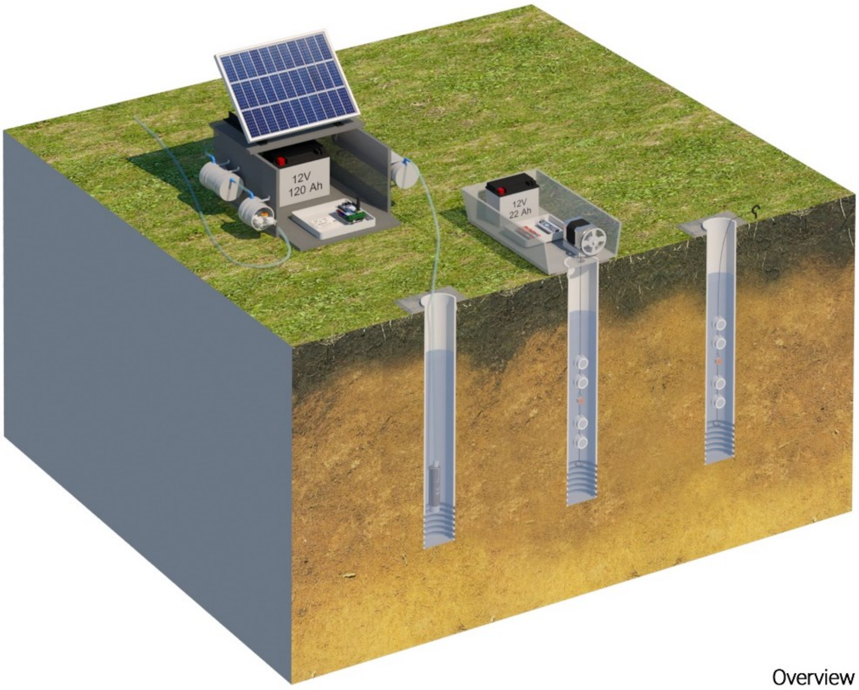


Figure 3.S1: Overview of three DGT deployment approaches for groundwater monitoring

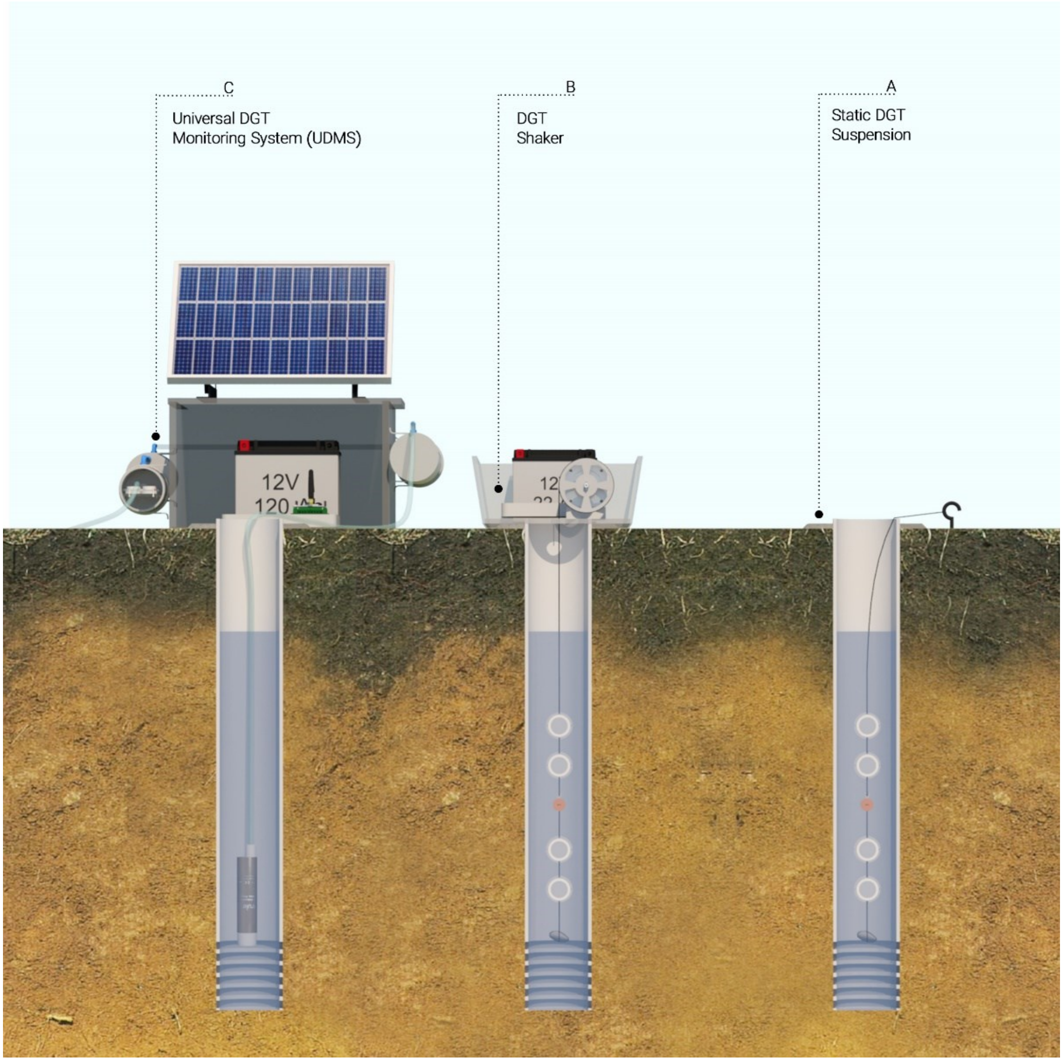


Figure 3.S2: The cross-section of the three DGT deployment approaches for groundwater monitoring, A: static DGT suspension, B: DGT Shaker, C: Universal DGT Monitoring System (UDMS)

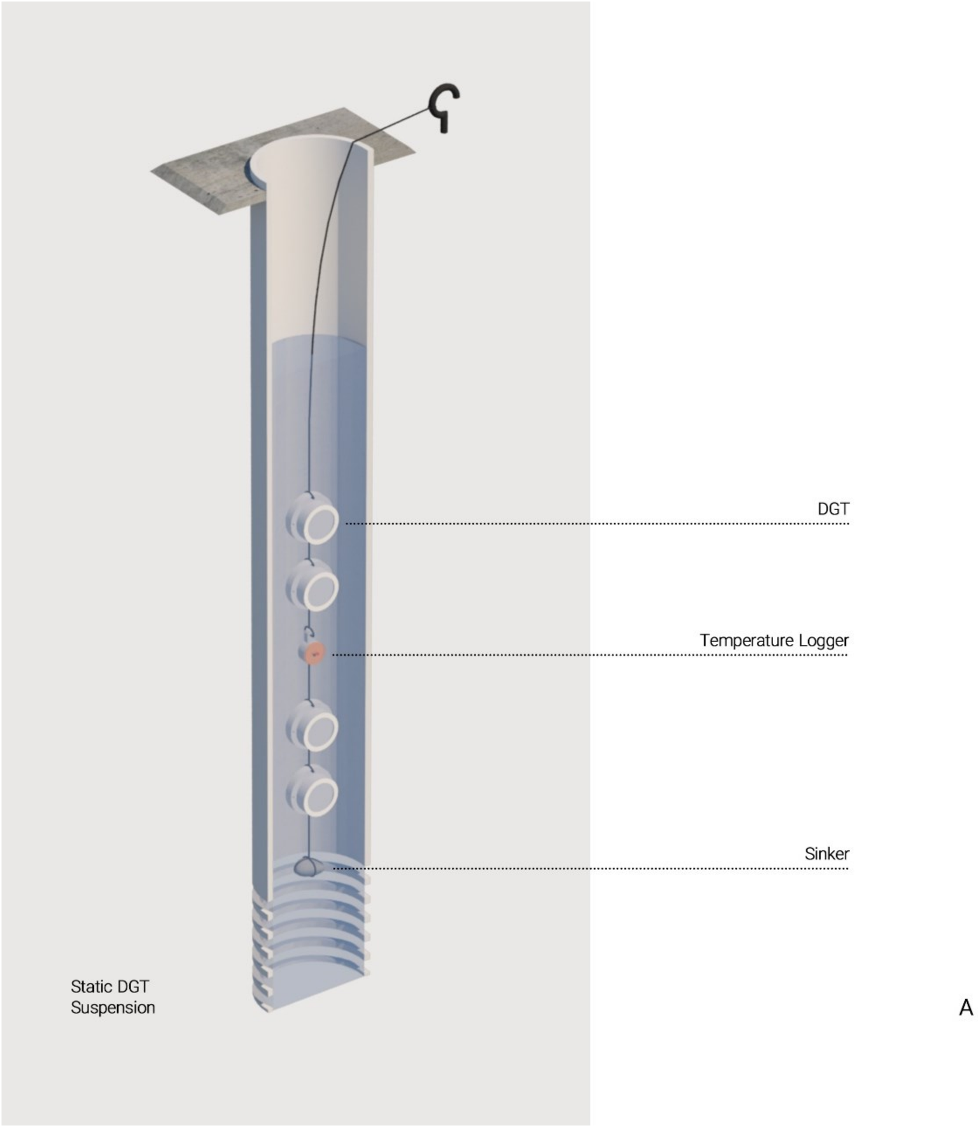


Figure 3.S3: Static DGT Suspension (arranged on a fishing line) in a piezometer/ borehole,

Components: Temperature Logger, Sinker, and Fishing Line

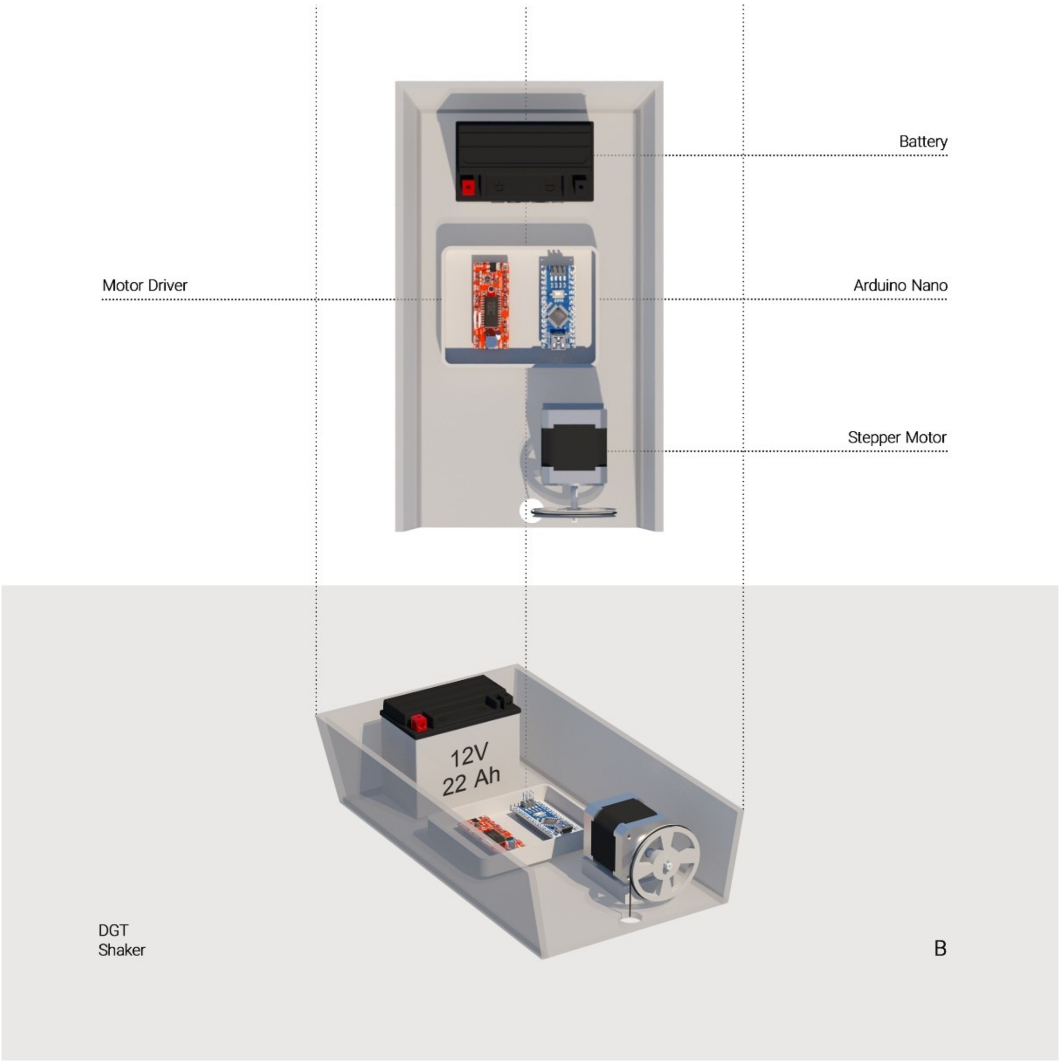


Figure 3.S4: Design of DGT Shaker, Components: Stepper Motor and Pulley, Arduino Nano, Motor Driver, and Battery

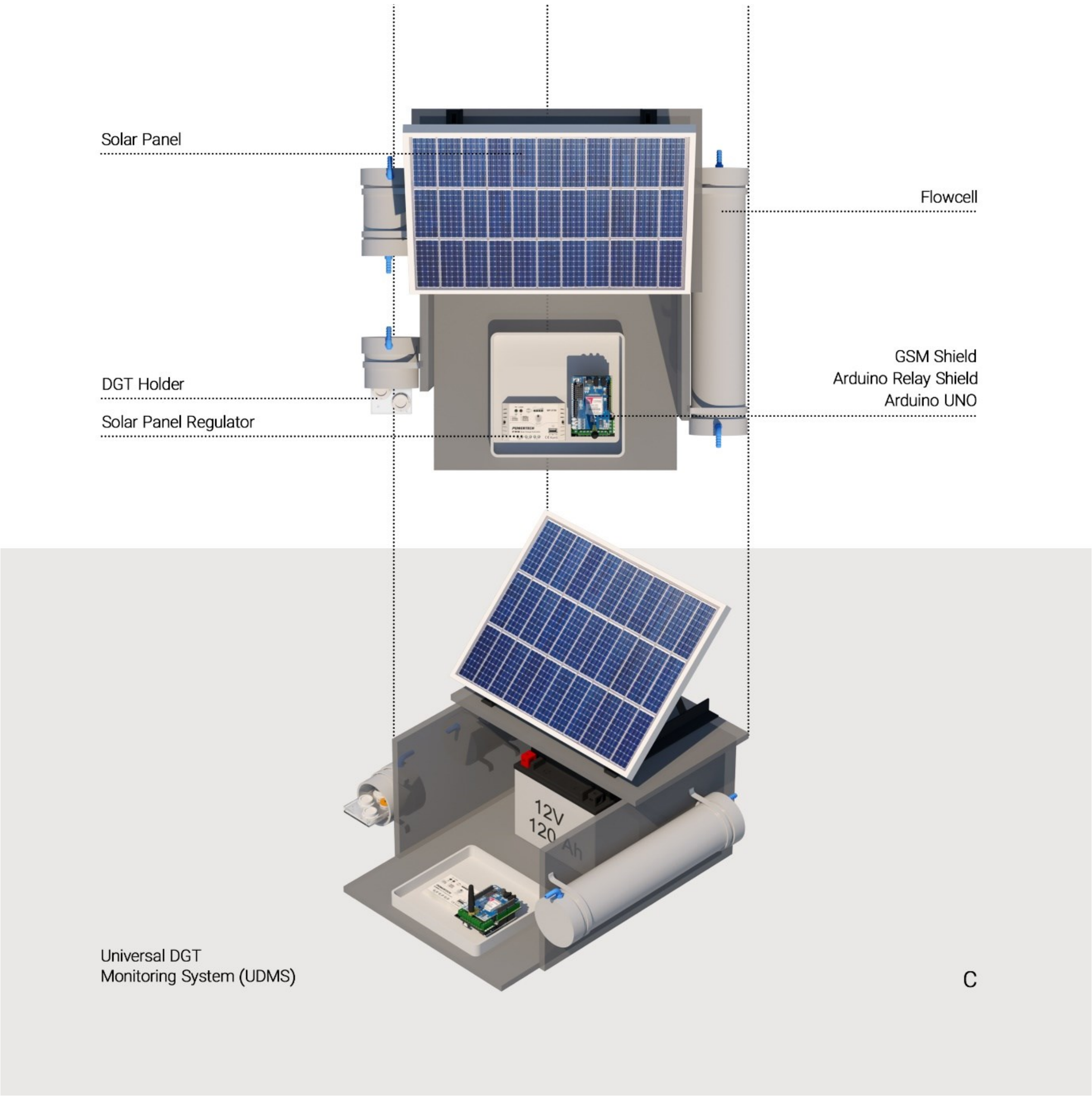


Figure 3.S5: Design of Universal DGT Monitoring System (UDMS), Components: Flowcell, DGT Holder, Solar Panel, Battery, Pump, Solar Panel Charge Controller, Arduino Uno, Arduino Relay Shield, and GSM/GPRS Shield

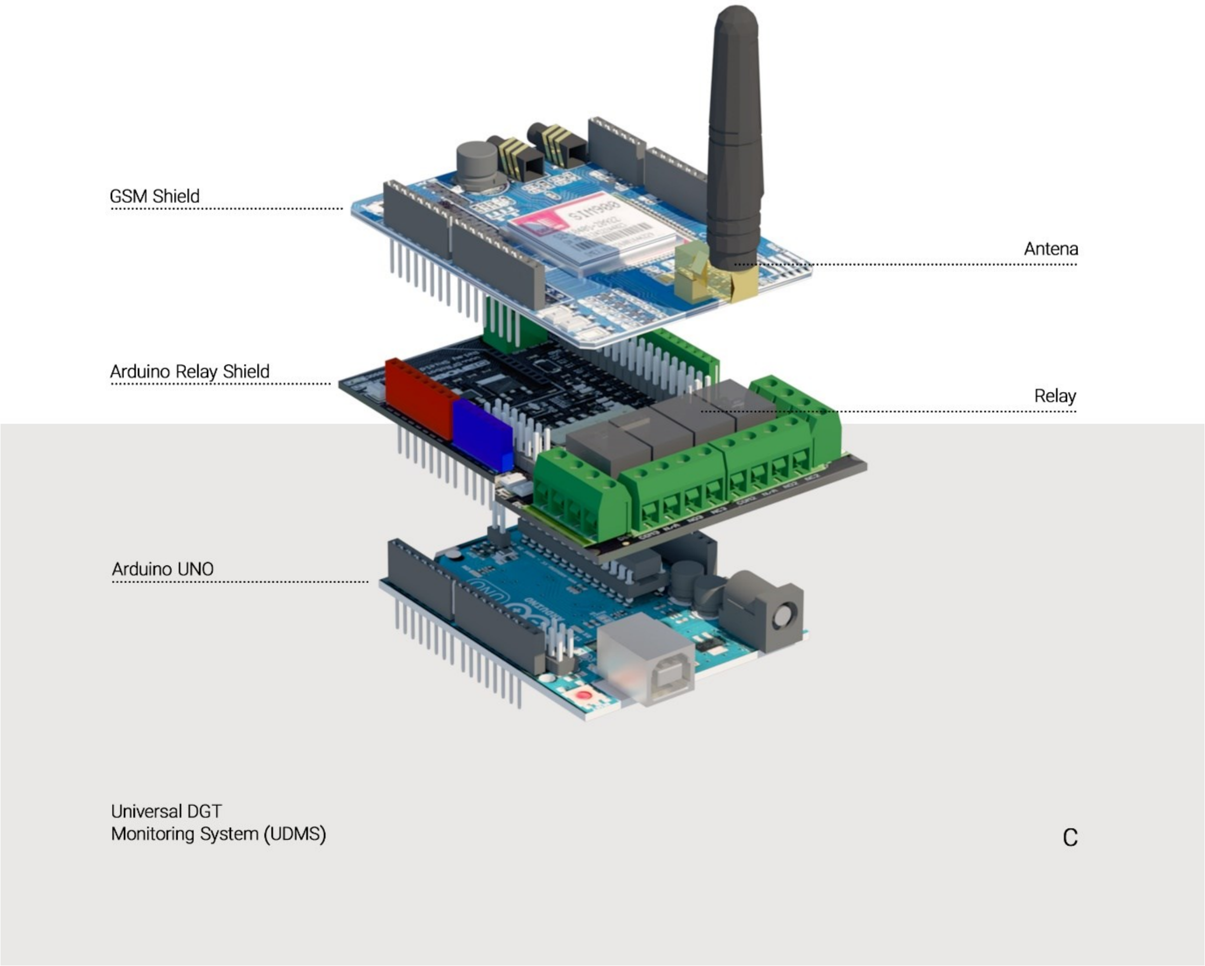


Figure 3.S6: The arrangement of Arduino Compatible electronic boards of UDMS,

Components: Arduino Uno, Relay Shield, and GSM/GPRS Shield

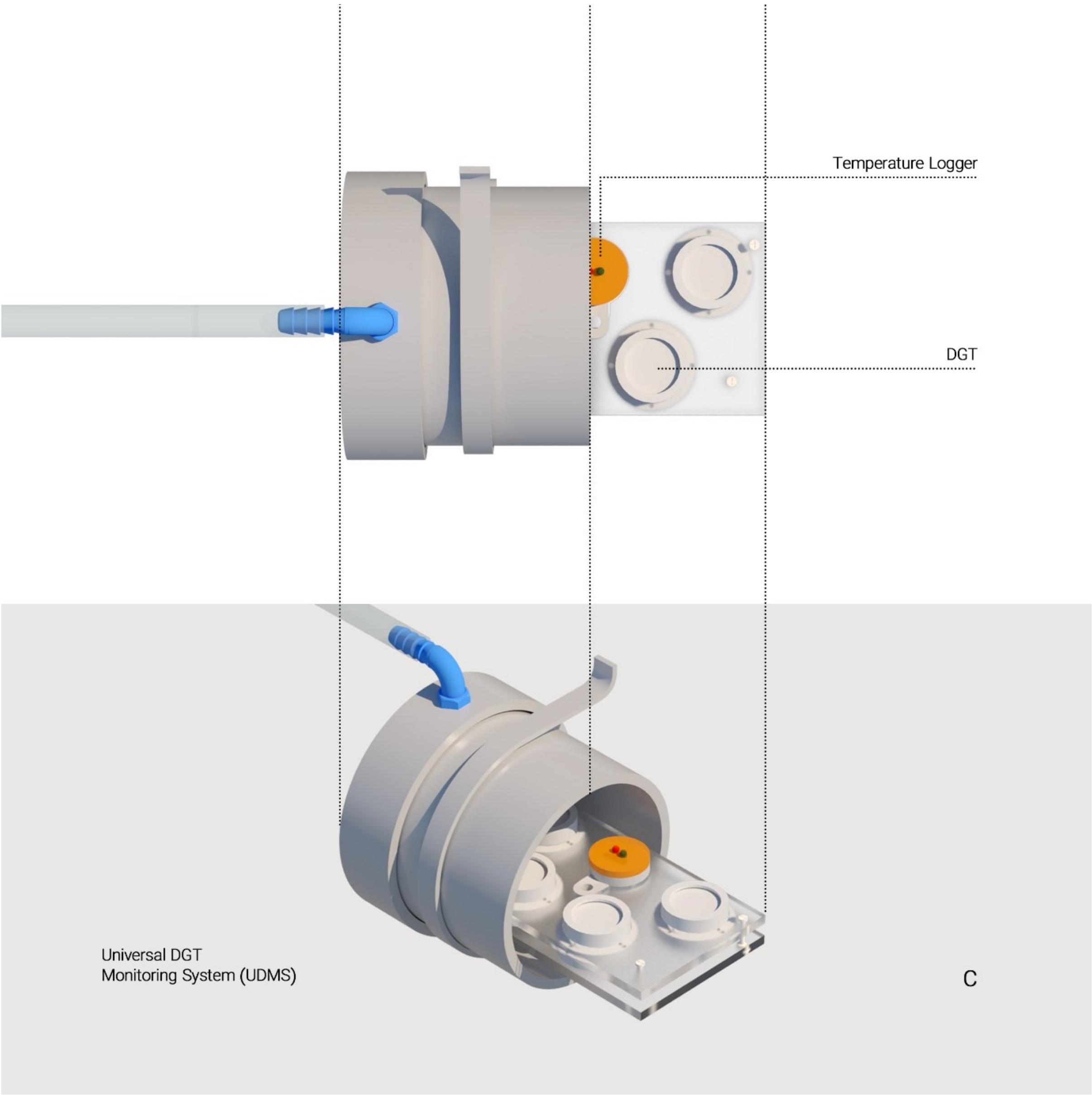


Figure 3.S7: The cross-section of a flowcell containing the DGT Holder

Universal DGT Monitoring System components and specifications

a) Schematic Diagram of UDMS Electronic Board

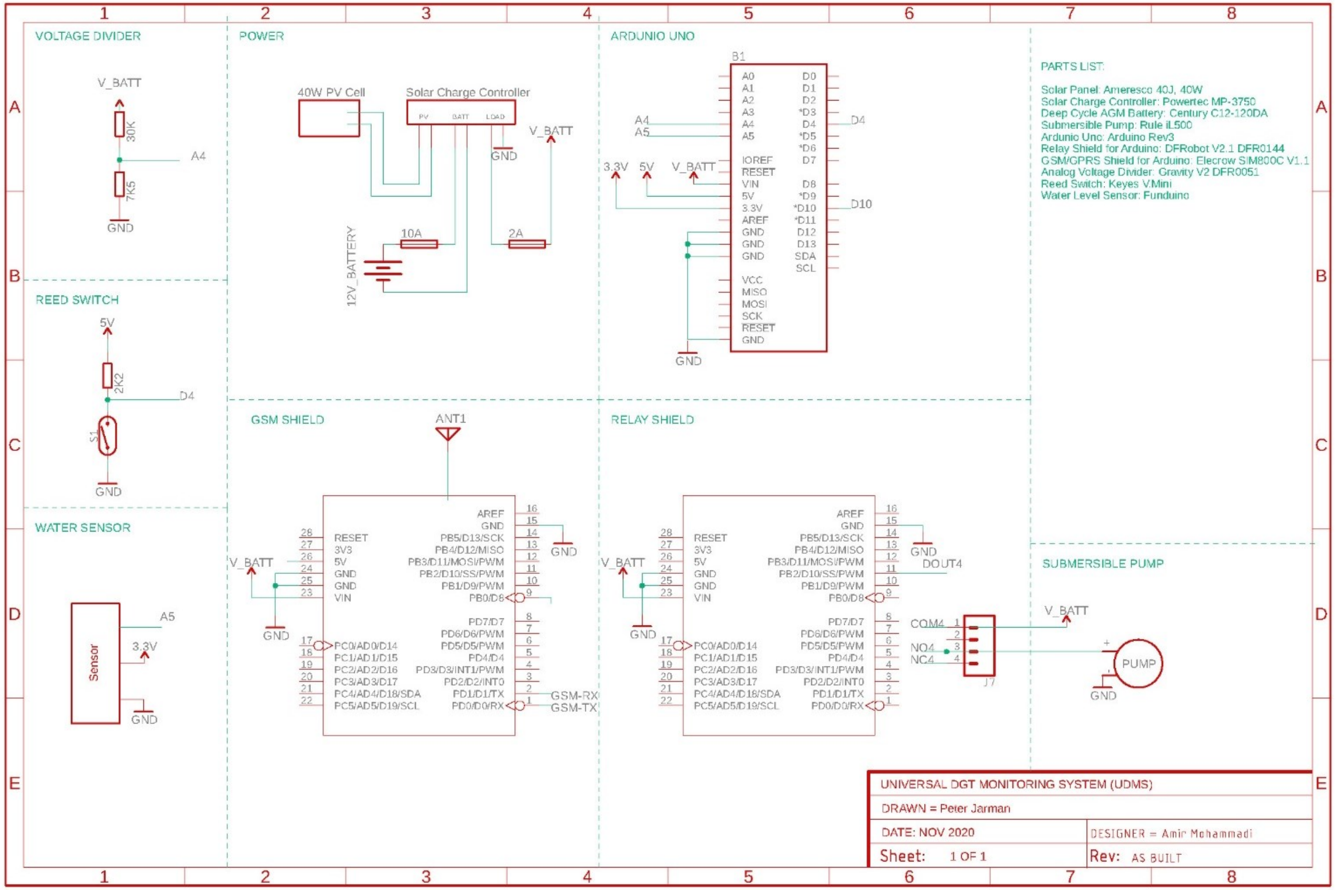


Figure 3.S8: Universal DGT Monitoring System Schematic Diagram and Parts List

DGT Holder Technical Drawing

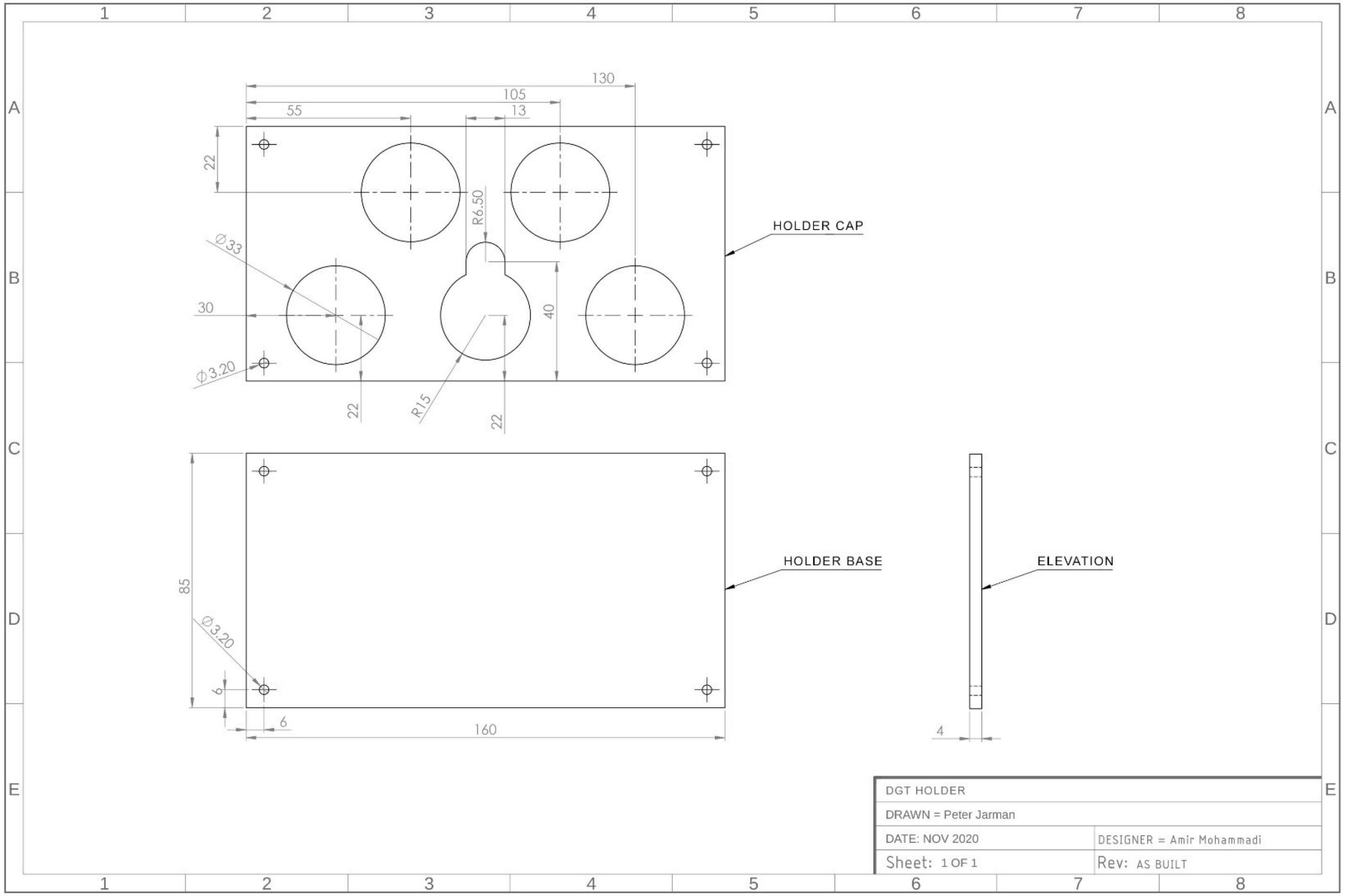


Figure 3.S9: DGT Holder Design

UDMS Submersible Pump and Solar Panel Performance

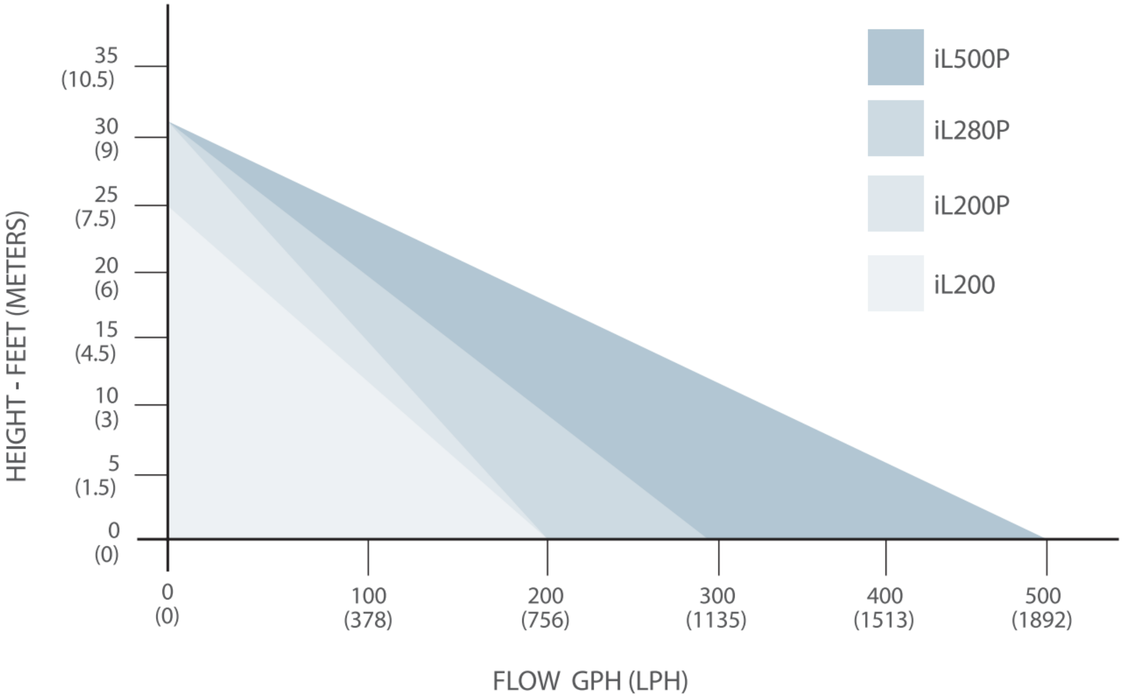


Figure 3.S10: Relationship between the pump's flow rate and the pumping height in an ideal system. The graph was adapted from Xylem industrial pumps catalog (Xylem, 2021). The submersible pump used in this research was a 12 V 14 psi Direct Coupling Water Pump. The pump was capable of pumping 6–9 L min-1 depending on the position of the pump in bores/ piezometers, and groundwater quality

Battery and Solar Panel capacity were calculated using a free and robust calculator available online: https://www.batterystuff.com/. Solar panel capacity varies throughout the days and seasons. Days are longer in summer and shorter in winter. Hence, the amount of solar power generated through the same solar system and in the same location, changes with the seasons. Adjusting the angle of solar panels can increase the power production.

Arduino Uno Code of UDMS:

```
#include <SoftwareSerial.h>

SoftwareSerial mySerial(7,8);

int Magnet; // Magnetic Reed Switch Sensor variable to store the value read

int VoltageRead1; // Voltage Sensor variable to store the value read

int VoltageRead2; // Voltage Sensor variable to store the value read

float Voltage1; // Voltage Sensor variable to store the value read

float Voltage2; // Voltage Sensor variable to store the value read

float V1; // Voltage Sensor variable to store the value read

float V2; // Voltage Sensor variable to store the value read

int SMSnumberBattery=0; // SMS counter variable to store the value read

int SMSnumberMagnet=0;  // SMS counter variable to store the value read

int SMSnumberPump=0;  // SMS counter variable to store the value read

int SMSnumberWater=0; // SMS counter variable to store the value read

int x;  // Pump On cycle counter variable to store the value read

int y;  // Pump Off cycle counter variable to store the value read

int WS = 0; // Water Sensor variable to store the value read

int CycleOn = 0; // On Cycle variable to store the value read

int CycleOff = 0; // Off Cycle variable to store the value read
```

```
int CycleT = 0; // Total Cycle variable to store the value read
void setup()
{
  pinMode(9, OUTPUT); // Digital Pin for GSM module power On/Off
  digitalWrite(9,HIGH);  // Turning GSM module On
  delay(60000); // wait for GSM module to start
  pinMode(10, OUTPUT);  // Digital Pin for Pump relay power On/Off
  pinMode(4, INPUT);  // Digital Pin for Magnet Reed Switch
  pinMode(A4, INPUT);  // Analog Pin for Voltage reading
  pinMode(A5, INPUT);  // Analog Pin for Water Sensor reading
  //Serial.begin(9600); //Debugging
}
void SMS()
{
  mySerial.begin(19200);  //Default serial port setting for the GPRS modem is 19200bps 8-N-1
  mySerial.print("\r");
  delay(1000);                    //Wait for a second while the modem sends an "OK"
  mySerial.print("AT+CMGF=1\r");    //Because we want to send the SMS in text mode
```

```
  delay(1000);
  mySerial.print("AT+CSCA=\"+6421600600\"\r");  //Setting for the SMS Message center
number,
  delay(1000);                              //Replace with the message center number obtained
from your GSM service provider or put // to deactivate it. Note that when specifying a
tring of characters " is entered as \"
  mySerial.print("AT+CMGS=\"+64YOURNUMBER\"\r");    //Start accepting the text for
the message to be sent to the number specified. Replace this number with the target
mobile number.
  delay(1000);
}
void SendSMSWater()
{
  pinMode(A5, INPUT);  // Analog Pin for Water Sensor reading
  WS = analogRead(A5); // read the Analog Pin for water sensor
  if (WS>200 && SMSnumberWater==0) //200 for 3V and 500 for 5V pin
  {
    //Serial.println("Water inside the UDMS");
    digitalWrite(10, LOW); // sets the digital pin 10 off (or low so 12V goes to the relay and
turns bilge pump off via NC)
```

```
    SMS();

    mySerial.print("Box#1: Water inside the UDMS");   //The text for the message

    delay(1000);

    mySerial.write(0x1A);  //Equivalent to sending Ctrl+Z

    delay (60000);

    SMSnumberWater++; // SMS counter variable to avoid spamming

  }

}

void SendSMSDoor()

{

  pinMode(4, INPUT);  // Digital Pin for Magnet Reed Switch

  Magnet=digitalRead(4); // Read the Digital Pin for Magnetic Reed Switch

  if(Magnet==1 && SMSnumberMagnet==0 && CycleT>5)  //Magnet=0: door is closed,
Magnet=1: door is open, CycleT>6 to avoid sending msg in the first hour

  {

    //Serial.println("The door is Open");

    SMS();

    mySerial.print("Box#1: The door is open");   //The text for the message

    delay(1000);
```

```
    mySerial.write(0x1A);  //Equivalent to sending Ctrl+Z

    delay (60000);

    SMSnumberMagnet++; // SMS counter variable to avoid spamming

  }

}

void SendSMSBattery()

{

  pinMode(A4, INPUT);  // Analog Pin for Voltage reading

  VoltageRead1=analogRead(A4);  // Read the Analog Pin for Voltage

  Voltage1=(VoltageRead1)/40.92;  // Voltage Calculation

  //Serial.println("Voltage");

  //Serial.println(Voltage1);

  //Serial.println("_____________________");

    if(Voltage1<11.4 && SMSnumberBattery==0 && CycleT>5)  //Voltage<11.4 means
battery is getting flat, CycleT>6 to avoid sending msg in the first hour

    {

      SMS();

      mySerial.print("Box#1: Battery is going flat (V=11.4)");   //The text for the message

      delay(1000);
```

```
      mySerial.write(0x1A);  //Equivalent to sending Ctrl+Z
      delay (60000);
      SMSnumberBattery++; // SMS counter variable to avoid spamming
    }
}
void SendSMSPump()
{
  pinMode(A4, INPUT);  // Analog Pin for Voltage reading
  VoltageRead1=analogRead(A4);  // Read the Analog Pin for Voltage
  Voltage1=(VoltageRead1)/40.92;  // Voltage Calculation
  //Serial.println("Voltage");
  //Serial.println(Voltage1);
  //Serial.println("_____________________");
  if((Voltage2)-(Voltage1)<0.3 && SMSnumberPump==0 && CycleT>5) //Monitoring Voltage drop to see if the pump is working, CycleT>6 to avoid sending msg in the first hour
  {
    SMS();
    mySerial.print("Box#1: Pump is not working");   //The text for the message
```

```
    delay(1000);

    mySerial.write(0x1A);  //Equivalent to sending Ctrl+Z

    delay (60000);

    SMSnumberPump++; // SMS counter variable to avoid spamming

  }

}

void SendSMSHeartBeat()

{

  if(CycleT%180==0) // Sending SMS every 24hr to say I am OK, SMS counter variable to

avoid spamming

  {

    SMSnumberBattery=0; // SMS counter variable to store the value read

    SMSnumberMagnet=0;  // SMS counter variable to store the value read

    SMSnumberPump=0;  // SMS counter variable to store the value read

    SMSnumberWater=0; // SMS counter variable to store the value read

    SMS();

    mySerial.print("Box#1: I am OK");   //The text for the message

    delay(1000);

    mySerial.write(0x1A);  //Equivalent to sending Ctrl+Z
```

```
    delay (60000);
  }
}
void SendSMSStart()
{
  if(CycleT==1) // Sending SMS after start
  {
    SMS();
    mySerial.print("Box#1: Start :)");   //The text for the message
    delay(1000);
    mySerial.write(0x1A);  //Equivalent to sending Ctrl+Z
    delay (60000);
  }
}
void BildgePumpOn()
{
  pinMode(A4, INPUT);  // Analog Pin for Voltage reading
  VoltageRead2=analogRead(A4);  // Read the Analog Pin for Voltage
  Voltage2=(VoltageRead2)/40.92;  // Voltage Calculation
```

```
  digitalWrite(10, HIGH); // sets the digital pin 10 on (or high so 12V goes to the relay and
turns bilge pump on via NO)
  //Serial.println("---=== PUMPING ===---");
  //Serial.println("Total Cycle=");
  //Serial.println(CycleT);
  delay(1000);
}
void BildgePumpOff()
{
  digitalWrite(10, LOW); // sets the digital pin 10 off (or low so 12V goes to the relay and
turns bilge pump off via NC)
  //Serial.println("---=== Resting ===---");
  //Serial.println("Total Cycle=");
  //Serial.println(CycleT);
  CycleT++; //One cycle of Pump On and Pump Off is done
  SendSMSHeartBeat();
  SendSMSStart();
  delay(1000);
}
```

```
void loop()
{
  BildgePumpOn();
  SendSMSPump();
  for(x= 1, CycleOn=1; x<61 && CycleOn<61; x++, CycleOn++)  //Monitoring the security of
the UDMS every second
  {
    SendSMSDoor();
    SendSMSWater();
    SendSMSBattery();
    delay (1000);
  }
  BildgePumpOff();
  for(y= 1, CycleOff=1; y<421 && CycleOff<421; x++, CycleOff++) //Monitoring the security
of the UDMS every second
  {
    SendSMSDoor();
    SendSMSWater();
    delay (1000);
```

```
 }

}
```

DGT Shaker components and specifications

a) Schematic Diagram of DGT Shaker Electronic Board

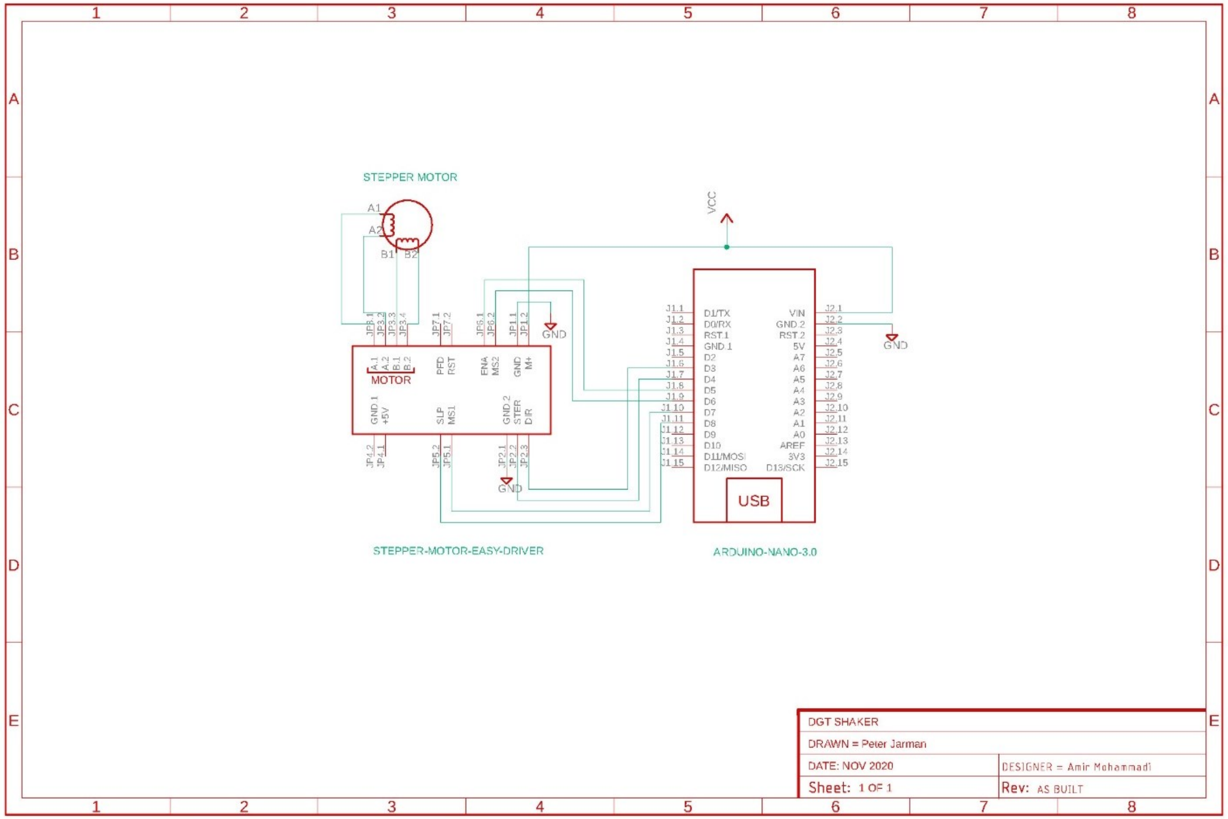


Figure 3.S11: DGT Shaker Schematic Diagram and Parts List

Arduino Nano Code with Sleep Mode (Lindqvist, 2015) **for DGT Shaker**

```
#include "Arduino.h"
#include <avr/sleep.h>
#include <avr/power.h>
#include <avr/wdt.h>


//Pin Functions on Easy Driver
#define dir 4
#define stp 5
#define EN  6
#define MS2 7
#define MS1 8


//Variables
char user_input;
int x;
int y;
int state;
```

```
int counter = 0;

int timeCount = 200;

int TotalRotationCounter = 0;



// SleepMode Definitions

#define LED_PIN (13)

volatile int f_wdt=1;



// Main Functions

void setup() {

  pinMode(stp, OUTPUT);

  pinMode(dir, OUTPUT);

  pinMode(MS1, OUTPUT);

  pinMode(MS2, OUTPUT);

  pinMode(EN, OUTPUT);

  resetEDPins();

  pinMode(LED_PIN, OUTPUT);

  WatchdogEnable(0b100001);

  TotalRotationCounter = 0;
```

```
}

//Main loop

void loop()

{

  // Watchdog Triggera wake up.

  if(f_wdt != 1)

  {

    return;

  }

  digitalWrite(LED_PIN, 1);

  delay(20);

  digitalWrite(LED_PIN, 0);

      digitalWrite(EN, LOW);

        ForwardBackwardStep();

        resetEDPins();

        f_wdt = 0;

        wdt_reset();

        enterSleep();

}
```

```
//Step Motors Rotation

void ForwardBackwardStep()

{

 TotalRotationCounter++;

 for(x= 1; x<20; x++)

 {

  state=digitalRead(dir);

  if(state == HIGH)

  {

   digitalWrite(dir, LOW);

  }

  else if(state ==LOW)

  {

   digitalWrite(dir,HIGH);

  }

  for(y=1; y<500; y++)

  {

   digitalWrite(stp,HIGH);

   delay(1);
```

```
      digitalWrite(stp,LOW);

      delay(1);

    }

  }


}

//Reset Easy Driver Pins

void resetEDPins()

{

  digitalWrite(stp, LOW);

  digitalWrite(dir, LOW);

  digitalWrite(MS1, LOW);

  digitalWrite(MS2, LOW);

  digitalWrite(EN, HIGH);

}

//Sleep Mode

int i;

ISR(WDT_vect)

{
```

```
  if(f_wdt == 0) {
    counter++;
    if(counter >= timeCount)
    {
      f_wdt=1;
      counter= 0 ;
      awakeFunc();
    }
    else
    {
    wdt_reset();
    }
  }
}
void awakeFunc(void)
{
  sleep_disable();
  power_all_enable();
}
```

```
void enterSleep(void)

{

  set_sleep_mode(SLEEP_MODE_PWR_DOWN);

  sleep_enable();

  sleep_mode();

}

void setupWatchDogTimer()

{

  MCUSR &= ~(1<<WDRF);

  WDTCSR |= (1<<WDCE) | (1<<WDE);

  WDTCSR  = (1<<WDP3) | (0<<WDP2) | (0<<WDP1) | (1<<WDP0); // 8 seconds

  WDTCSR |= _BV(WDIE);

}

void WatchdogEnable(const byte interval)

{

  MCUSR = 0;                          // reset various flags

  WDTCSR |= 0b00011000;               // see docs, set WDCE, WDE

  WDTCSR = 0b01000000 | interval;    // set WDIE, and appropriate delay

}
```

References

Corbett, Thomas D.W., Hannah Dougherty, Bryan Maxwell, Adam Hartland, William Henderson, Gerald J. Rys, and Louis A. Schipper. 2020. “Utility of ‘Diffusive Gradients in Thin-Films’ for the Measurement of Nitrate Removal Performance of Denitrifying Bioreactors.” Science of the Total Environment 718: 135267. https://doi.org/10.1016/j.scitotenv.2019.135267.

Davison, W. 2016. Diffusive Gradients in Thin-Films for Environmental Measurements. Cambridge University Press.

Lindqvist, S. 2015. “Arduino Sleep Mode.” GitHub. 2015. https://gist.github.com/stojg.

Xylem. 2021. “Xylem Industrial Pumps Catalog.” 2021. https://www.xylem.com/siteassets/brand/jabsco/resources/brochure/industrial-catalogue-flojet-jabsco-rule-en.pdf.

Appendix B – Supplementary Information for Chapter 4: Effects of dairy farm effluent management on metal, nutrient and organic matter leaching: A lysimeter trial on two contrasting soils

[1]Amir Mohammadi, [2]Niklas Lehto, [3]Ali Shokri, [1]Louis Schipper, [2]Richard McDowell, [1*]Adam Hartland

1. Environmental Research Institute, School of Science, University of Waikato, Hamilton 3240, New Zealand
2. Faculty of Agriculture and Life Science, Lincoln University, Lincoln 7647, New Zealand
3. School of Engineering, University of Waikato, Hamilton 3240, New Zealand

* Corresponding author: adam.hartland@waikato.ac.nz

Rainfall data was collected from New Zealand' National Climate Database (CliFlo) at Broadfield Ews weather station (CliFlo NIWA, 2022). The station is located at Lat: -43.62622 and Long: 172.4704 degree and Height: 18 m.

Table 4.S1: Soil chemical properties. Values in brackets represent the standard error of the mean (n = 3 unless otherwise indicated) (Knowles et al. 2011).

Parameter	**Templeton**
pH	5.6
CEC (cmol$_{(+)}$/kg)	12.4 (0.5)
C (%)	2.0 (0.1)
N (%)	0.18 (0.01)
P (mg/kg)	518 (25)
S (mg/kg)	193 (15)
Ca (mg/kg)	3005 (101)
Mg (mg/kg)	855 (11)
K (mg/kg)	1401 (119)
Na (mg/kg)	136 (4)
Cd (mg/kg)	0.4 (0.1)
Cr (mg/kg)	11.6 (0.4)
Cu (mg/kg)	4.5 (0.1)
Pb (mg/kg)	12.0 (0.1)
Zn (mg/kg)	43 (1)

Table 4.S2: Daily amount of rainfall during each rainfall events at Lincoln Broadfield Ews weather station (CliFlo NIWA, 2022)

Year 2005		**Year 2013-2014**	
April 2, 2005	0.2	**December 18, 2013**	1
April 3, 2005	0	**December 19, 2013**	5.4
April 4, 2005	0	**December 20, 2013**	0.4
April 5, 2005	0	**December 21, 2013**	0
April 6, 2005	0	**December 22, 2013**	3.8
April 7, 2005	0	**December 23, 2013**	0
April 8, 2005	0	**December 24, 2013**	0.2
April 9, 2005	6.6	**December 25, 2013**	0
April 10, 2005	2.8	**December 26, 2013**	21.2
April 11, 2005	0	**December 27, 2013**	1.2
April 12, 2005	0	**December 28, 2013**	5
April 13, 2005	0	**December 29, 2013**	7.8
April 14, 2005	0	**December 30, 2013**	3
April 15, 2005	0	**December 31, 2013**	0.4
April 16, 2005	0	**January 1, 2014**	0
April 17, 2005	0	**January 2, 2014**	0
April 18, 2005	0	**January 3, 2014**	0
April 19, 2005	0	**January 4, 2014**	0
April 20, 2005	0	**January 5, 2014**	0
April 21, 2005	2.8	**January 6, 2014**	1
April 22, 2005	0	**January 7, 2014**	0.6
April 23, 2005	0	**January 8, 2014**	0
April 24, 2005	7.8	**January 9, 2014**	0
April 25, 2005	27.4	**January 10, 2014**	0
April 26, 2005	1.8	**January 11, 2014**	0
___	___	**January 12, 2014**	0
___	___	**January 13, 2014**	0
___	___	**January 14, 2014**	0
___	___	**January 15, 2014**	0
___	___	**January 16, 2014**	0
___	___	**January 17, 2014**	0.2

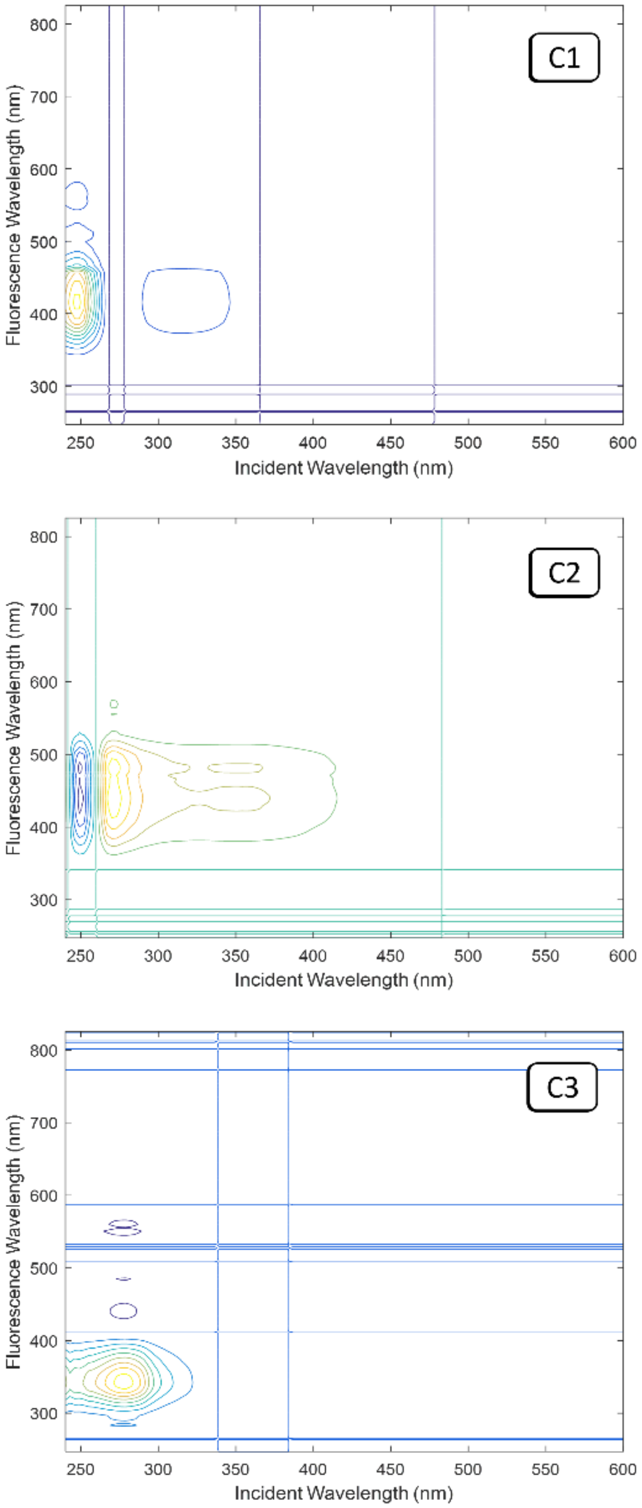


Figure 4.S1: 3D excitation-emission matrices of lysimeter leachate samples. C1 is typical of the humic-like peak A; C2 is composed of two non-separated humic-like peaks of A and C; and C3 matches protein-like Peak T (Coble, 1996).

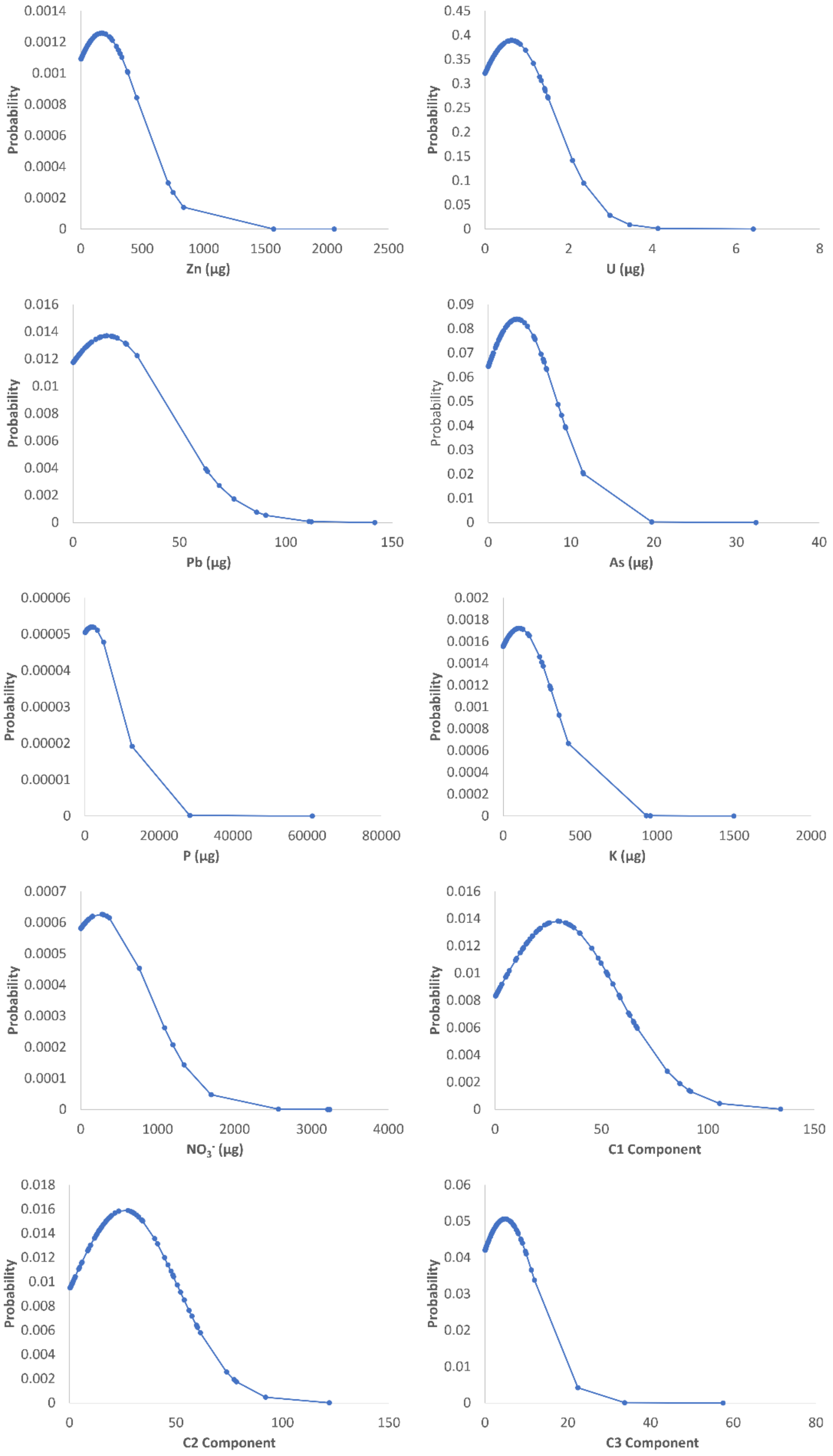


Figure 4.S2: Probability curves of uncorrected data of metals (Zn, U, Pb, As), nutrients (P, K, N), and fDOM component (C1, C2, C3) in leachate samples.

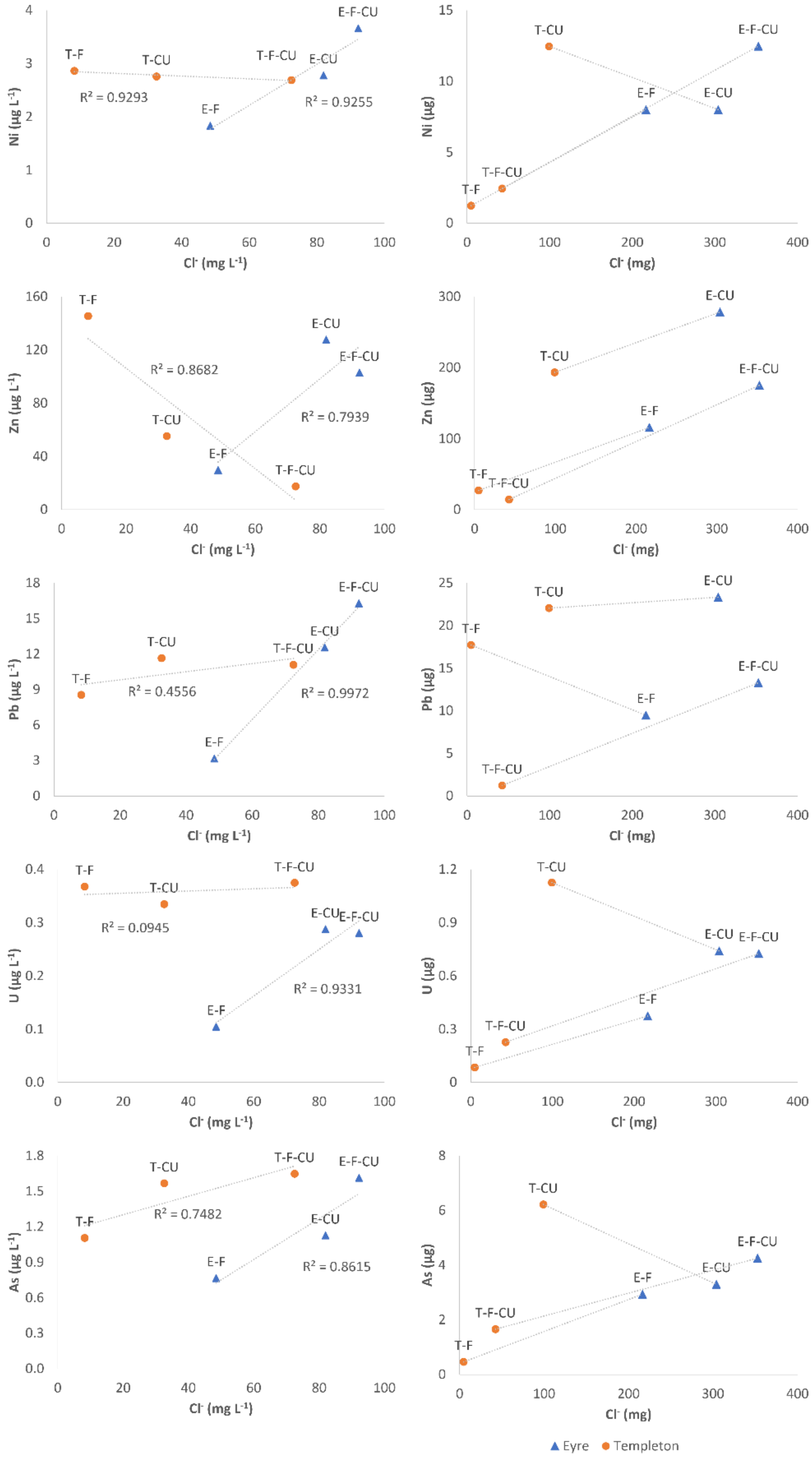


Figure 4.S3: Correlation between mean metals (Ni, Zn, Pb, U, As) and Cl⁻ concentrations and leached masses in soils under different farm effluent treatments. E: Eyre, T: Templeton, F: Farm Dairy Effluent, CU: Cow urine.

References

CliFlo NIWA. 2021. “New Zealand’s National Climate Database.” National Institute of Water and Atmospheric Research New Zealand (NIWA).

Coble, Paula G. 1996. “Characterization of Marine and Terrestrial DOM in Seawater Using Excitation-Emission Matrix Spectroscopy” 51: 325–46.

Knowles, O A, B H Robinson, A Contangelo, and L Clucas. 2011. “Biochar for the Mitigation of Nitrate Leaching from Soil Amended with Biosolids.” Science of the Total Environment 409 (17): 3206–10.

Appendix C – Supplementary Information for Chapter 5: Tracing fertiliser-derived cadmium in soil−pasture−groundwater systems: Coupling stable isotope ratio analysis and diffusive gradients in thin films

[1]Amir Mohammadi, [1]Mahdiyeh Salmanzadeh, [2]Claudine Stirling, [3]Ali Shokri, [4]Matt Taylor, [1]Adam Hartland*

1. Environmental Research Institute, School of Science, University of Waikato, Hamilton 3216, New Zealand
2. Centre for Trace Element Analysis and Department of Chemistry, University of Otago, Dunedin 9016, New Zealand
3. School of Engineering, University of Waikato, Hamilton 3216, New Zealand
4. Waikato Regional Council, Hamilton 3204, New Zealand

*. Corresponding author: adam.hartland@waikato.ac.nz

Study Area:

Table 5.S1: Site locations, applications, dimensions, screen details, land-uses, and soil types

No.	Site ID[1]	Site Location	Type	Application	Diameter (mm)	Depth (m)	Screen (m)	Water table[2] range (m)	Land-use/ Paddock	Soil type
1	72-10024	Newstead	Piezometer	Monitoring	50	1.8	1.06 – 1.86	0.5 – 1.8	Dairy/ C11	Te Kowhai
2	72-10023	Newstead	Piezometer	Monitoring	50	3.3	1.98 – 3.38	0.7 – 2.4	Dairy/ C11	Te Kowhai
3	72-10022	Newstead	Piezometer	Monitoring	50	5.9	5.06 – 5.96	2.0 – 3.0	Dairy/ C11	Te Kowhai
4	72-10019	Newstead	Piezometer	Monitoring	50	7.6	4.60 – 7.60	6.0 – 6.2	Dairy/ C24a	Horotiu

Note: 1. Site ID is the reference number of the sites in the Environment Waikato database.

2. Water table range (m) is the groundwater depths during this study (July 2019 – Oct 2019).

Table 5.S2: Metal concentrations of Horotiu, Te Kowhai–fertilised, and Te Kowhai–unfertilised soils

Soil Type	Depth Intervals	Mg (mg/kg)	P (mg/kg)	S (mg/kg)	K (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	U (mg/kg)
Horotiu	0-7.5 cm	536.62	1023.68	419.73	480.38	615.78	3.19	33.72	0.88	13.55	2.22
	7.5-15 cm	455.92	801.24	394.89	453.18	676.55	2.49	28.97	0.79	15.20	2.18
	15-25 cm	240.62	481.38	294.05	447.52	634.83	1.61	27.35	0.40	11.80	1.56
	25-35 cm	257.66	314.16	392.53	404.15	267.82	1.79	32.10	0.15	11.70	1.42
	35-45 cm	283.36	166.62	254.34	449.98	154.37	1.78	30.25	0.09	11.02	1.22
Te Kowhai–fertili	0-7.5 cm	527.65	1444.41	611.46	650.15	359.65	3.14	44.88	0.70	9.49	2.17
	7.5-15 cm	273.10	905.63	390.80	328.03	480.98	2.51	25.28	0.61	10.11	1.97

sed	15-25 cm	144.76	187.88	241.46	467.89	134.58	1.88	23.36	0.13	9.91	1.44
	25-35 cm	169.76	53.41	149.96	432.43	68.49	0.99	12.69	0.06	9.11	0.97
	35-45 cm	292.98	29.74	79.92	328.74	44.94	0.84	10.90	0.06	8.75	0.61
Te Kowhai–unfertilised	0-7.5 cm	475.15	247.66	222.39	575.13	123.05	1.35	38.36	0.20	7.65	0.76
	7.5-15 cm	399.97	189.01	179.79	298.44	132.28	1.38	24.40	0.21	9.47	0.91
	15-25 cm	189.56	125.35	125.46	196.35	94.13	1.18	10.40	0.13	7.88	0.87
	25-35 cm	159.09	54.34	54.27	266.45	34.98	0.83	8.53	0.06	7.81	0.83
	35-45 cm	234.12	17.98	11.52	304.69	11.02	1.09	8.95	0.03	8.51	0.63

Table 5.S3: Groundwater properties for the study sites (average of parameters during this study: July 2019 – Oct 2019)

No.	**Site ID**	**Date**	**pH**	**Temperature °C**	**DO (mg L^{-1})**	**EC (µS cm^{-1})**	**Eh**
1	72-10024	July 2019 – Oct 2019	5.6	13.0	10.5	232	195
2	72-10023	July 2019 – Oct 2019	5.6	13.6	4.6	271	150
3	72-10022	July 2019 – Oct 2019	6.1	14.9	2.7	320	42
4	72-10019	July 2019 – Oct 2019	5.9	15.6	4.8	316	206

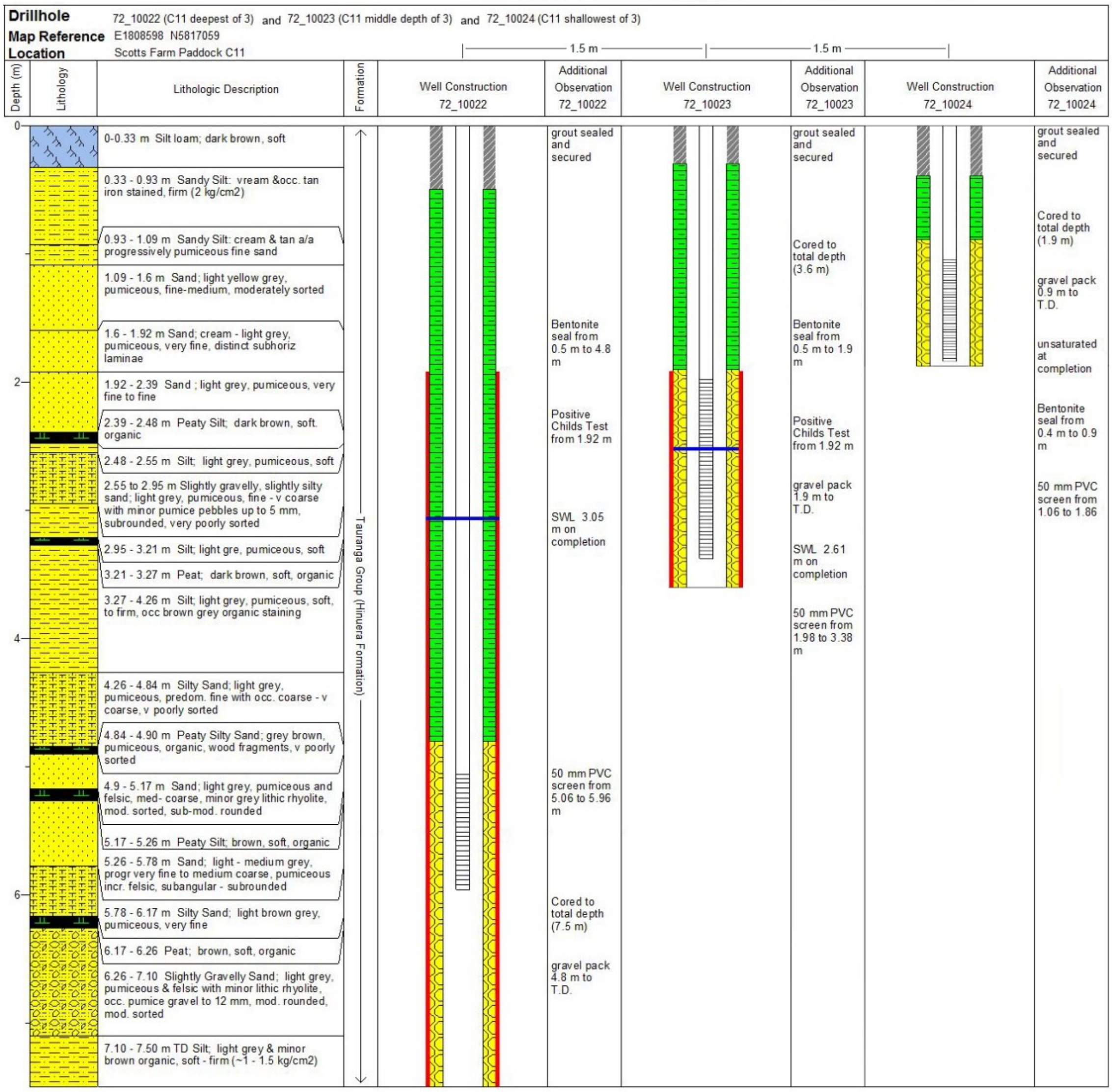
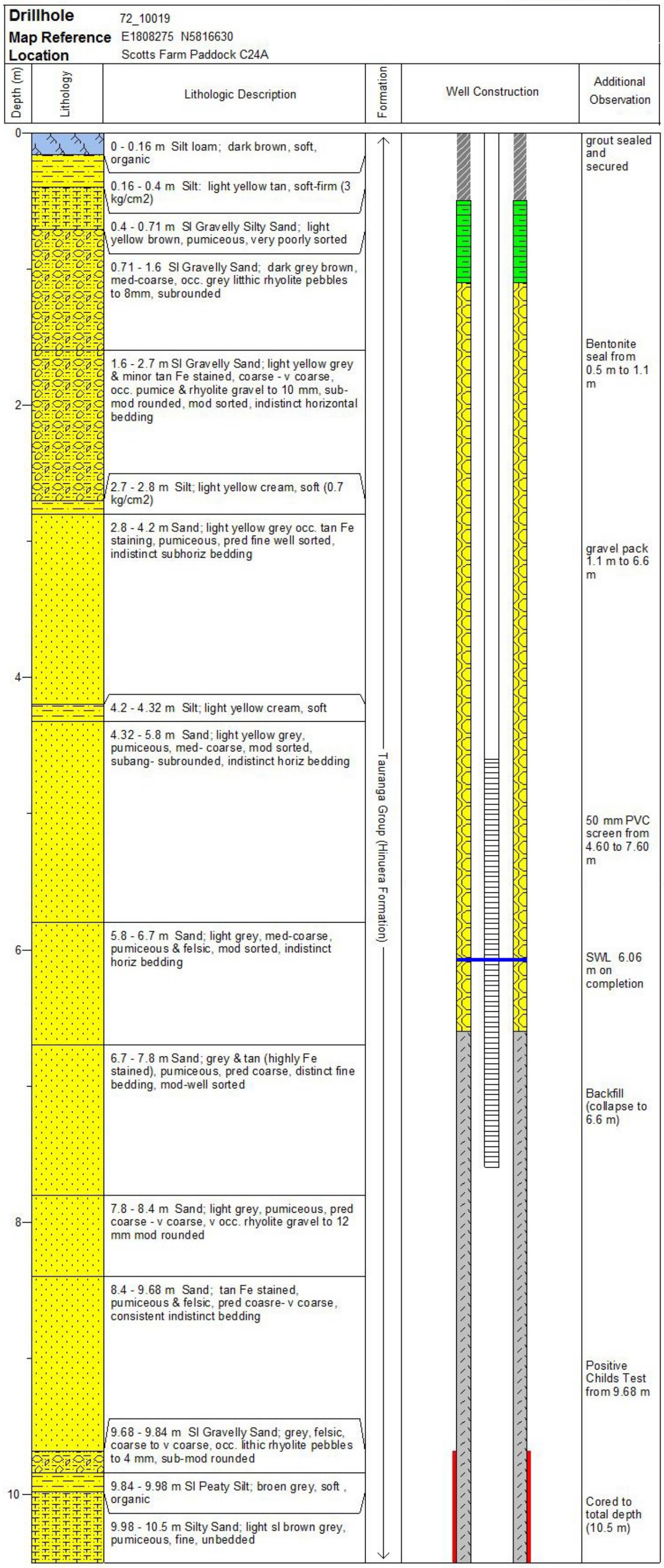


Figure 5.S4: Schematic description of the Te Kowhai piezometers, showing the lithological profile in depth.



Drillhole 72_10019
Map Reference E1808275 N5816630
Location Scotts Farm Paddock C24A

0 - 0.16 m Silt loam; dark brown, soft, organic

0.16 - 0.4 m Silt: light yellow tan, soft-firm (3 kg/cm2)

0.4 - 0.71 m Sl Gravelly Silty Sand; light yellow brown, pumiceous, very poorly sorted

0.71 - 1.6 Sl Gravelly Sand; dark grey brown, med-coarse, occ. grey litthic rhyolite pebbles to 8mm, subrounded

1.6 - 2.7 m Sl Gravelly Sand; light yellow grey & minor tan Fe stained, coarse - v coarse, occ. pumice & rhyolite gravel to 10 mm, sub-mod rounded, mod sorted, indistinct horizontal bedding

2.7 - 2.8 m Silt; light yellow cream, soft (0.7 kg/cm2)

2.8 - 4.2 m Sand; light yellow grey occ. tan Fe staining, pumiceous, pred fine well sorted, indistinct subhoriz bedding

4.2 - 4.32 m Silt; light yellow cream, soft

4.32 - 5.8 m Sand; light yellow grey, pumiceous, med- coarse, mod sorted, subang- subrounded, indistinct horiz bedding

5.8 - 6.7 m Sand; light grey, med-coarse, pumiceous & felsic, mod sorted, indistinct horiz bedding

6.7 - 7.8 m Sand; grey & tan (highly Fe stained), pumiceous, pred coarse, distinct fine bedding, mod-well sorted

7.8 - 8.4 m Sand; light grey, pumiceous, pred coarse - v coarse, v occ. rhyolite gravel to 12 mm mod rounded

8.4 - 9.68 m Sand; tan Fe stained, pumiceous & felsic, pred coasre- v coarse, consistent indistinct bedding

9.68 - 9.84 m Sl Gravelly Sand; grey, felsic, coarse to v coarse, occ. lithic rhyolite pebbles to 4 mm, sub-mod rounded

9.84 - 9.98 m Sl Peaty Silt; broen grey, soft , organic

9.98 - 10.5 m Silty Sand; light sl brown grey, pumiceous, fine, unbedded

grout sealed and secured

Bentonite seal from 0.5 m to 1.1 m

gravel pack 1.1 m to 6.6 m

50 mm PVC screen from 4.60 to 7.60 m

SWL 6.06 m on completion

Backfill (collapse to 6.6 m)

Positive Childs Test from 9.68 m

Cored to total depth (10.5 m)

Figure 5.S5: Schematic description of the Horotiu piezometer, showing the lithological profile in depth.

Table 5.S4: Cadmium fractionation through diffusion from immersion solution to the Chelex gels with varying material diffusive layer thicknesses

Material Diffusive Layer (MDL, cm)	Exposure Time (hr)	DGT $\delta^{114/110}$ Cd	DGT 2SD	Immersion Solution $\delta^{114/110}$ Cd	Immersion Solution 2SD	$\Delta^{114/110}$ Cd
0.093	12	-1.53	0.05	-1.44	0.05	-0.09
0.133	12	-1.42	0.05	-1.37	0.05	-0.05
0.213	12	-1.40	0.05	-1.30	0.05	-0.09
0.093	24	-1.46	0.05	-1.37	0.05	-0.09
0.133	24	-1.37	0.05	-1.43	0.05	0.06
0.213	24	-1.32	0.05	-1.28	0.04	-0.04
0.093	48	-1.33	0.05	-1.27	0.04	-0.05
0.133	48	-1.29	0.05	-1.32	0.05	0.02
0.213	48	-1.45	0.04	-1.40	0.05	-0.05

Figure 5.S6: Metal-sulfide precipitates in pump' tubing

THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

Co-Authorship Form

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +64 7 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Application of diffusive gradients in thin films (DGT) for monitoring groundwater quality

Nature of contribution by PhD candidate	Collaboration on project conception, design & development, data collection, analysis, interpretation, and manuscript writing
Extent of contribution by PhD candidate (%)	90

CO-AUTHORS

Name	Nature of Contribution
Adam Hartland	Collaboration on project conception, design, analysis, interpretation, and manuscript editing
Louis Schipper	Collaboration on project conception, analysis, interpretation, and manuscript editing
Ali Shokri	Collaboration on analysis, interpretation, and manuscript editing
Niklas Lehto/ Amanda French	Collaboration on analysis, interpretation, and manuscript editing
John Hadfield/ Thomas Corbett	Data collection and manuscript editing
Peter Jarman/ Dean Sandwell	Design and development

Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- that the candidate wrote all or the majority of the text.

Name	Signature	Date
Adam Hartland		5/10/22
Louis Schipper	L A Schipper.	31/5/22
Ali Shokri		02/062022
Niklas Lehto		30/05/2022
Amanda French	Amanda French	31/05/2022
John Hadfield		30/05/2022

THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

Co-Authorship Form

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +64 7 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work**. Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Application of diffusive gradients in thin films (DGT) for monitoring groundwater quality

Nature of contribution by PhD candidate	Collaboration on project conception, design & development, data collection, analysis, interpretation, and manuscript writing
Extent of contribution by PhD candidate (%)	90

CO-AUTHORS

Name	Nature of Contribution
Adam Hartland	Collaboration on project conception, design, analysis, interpretation, and manuscript editing
Louis Schipper	Collaboration on project conception, analysis, interpretation, and manuscript editing
Ali Shokri	Collaboration on analysis, interpretation, and manuscript editing
Niklas Lehto/ Amanda French	Collaboration on analysis, interpretation, and manuscript editing
John Hadfield/ Thomas Corbett	Data collection and manuscript editing
Peter Jarman/ Dean Sandwell	Design and development

Certification by Co-Authors

The undersigned hereby certify that:

- ❖ the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- ❖ that the candidate wrote all or the majority of the text.

Name	Signature	Date
Thomas Corbett		30/05/2022
Peter Jarman	PJarman.	1/June 2022
Dean Sandwell	DS	02/06/2022

THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

Co-Authorship Form

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +64 7 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Tracing fertiliser-derived cadmium in soil–pasture–groundwater systems: Coupling stable isotope ratio analysis and diffusive gradients in thin films

Nature of contribution by PhD candidate	Collaboration on project conception, data collection, sampling, analysis, interpretation, and manuscript writing
Extent of contribution by PhD candidate (%)	90

CO-AUTHORS

Name	**Nature of Contribution**
Adam Hartland	Collaboration on project conception, analysis, interpretation, and manuscript editing
Ali Shokri	Collaboration on project conception, interpretation, and manuscript editing
Mahdiyeh Salmanzadeh	Collaboration on project conception, sampling, analysis, interpretation, and manuscript editing
Matt Taylor	Collaboration on interpretation, sampling, and manuscript editing
Claudine Stirling	Collaboration on analysis, interpretation, and manuscript editing

Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- that the candidate wrote all or the majority of the text.

Name	**Signature**	**Date**
Adam Hartland		5/10/22
Ali Shokri		02/06/2022
Mahdiyeh Salmanzadeh	M. Zadeh	31/05/2022
Matt Taylor		30/5/2022
Claudine Stirling		07 June 2022

THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +64 7 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

Co-Authorship Form

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Effects of dairy farm effluent management on metal, nutrient and organic matter leaching: A lysimeter trial on two contrasting soils

Nature of contribution by PhD candidate	Collaboration on project conception, analysis, interpretation, and manuscript writing
Extent of contribution by PhD candidate (%)	90

CO-AUTHORS

Name	Nature of Contribution
Adam Hartland	Collaboration on project conception, analysis, interpretation, and manuscript editing
Louis Schipper	Collaboration on project conception, interpretation, and manuscript editing
Ali Shokri	Collaboration on project conception, interpretation, and manuscript editing
Niklas Lehto	Collaboration on analysis, interpretation, and manuscript editing
Richard McDowell	Collaboration on interpretation, and manuscript editing

Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- that the candidate wrote all or the majority of the text.

Name	Signature	Date
Adam Hartland		5/10/22
Louis Schipper	L A Schipper.	31/5/22
Ali Shokri		31/05/2022
Niklas Lehto		30/05/2022
Richard McDowell		02/06/2022