

Government of Western Australia Department of Water and Environmental Regulation

Phosphorus reduction in a large agricultural drain

Hydrotalcite clay trial at Punrak Drain, Peel Harvey Catchment (October 2017)



Securing Western Australia's water future

Department of Water and Environmental Regulation Water Science Technical series Report no. 85 January 2020 Department of Water and Environmental Regulation Prime House, 8 Davidson Terrace Joondalup, Western Australia 6027 Telephone +61 8 6364 7000 Facsimile +61 8 6364 7001

National Relay Service 13 36 77 www.dwer.wa.gov.au

© Government of Western Australia

November 2019

This work is copyright. You may download, display, print and reproduce this material in unaltered form only (retaining this notice) for your personal, non-commercial use or use within your organisation. Apart from any use as permitted under the *Copyright Act 1968*, all other rights are reserved. Requests and inquiries concerning reproduction and rights should be addressed to the Department of Water and Environmental Regulation.

The recommended reference for this publication is: Tulipani, S, Degens, B, Shackleton, M & Grant, B 2019, Water Science Technical Series 85, Phosphorus-reduction in a large agricultural drain: Hydrotalcite clay trial at Punrak Drain, Peel Harvey Catchment (Oct 2017), Department of Water and Environmental Regulation, Western Australia

FIRST 115799

Acknowledgements

The Department of Water and Environmental Regulation would like to thank the following for their contribution to this publication. Team of authors: Svenja Tulipani, Brad Degens, Mark Shackleton, Bronte Grant. Review of this document: Cassie Paxman, Malcolm Robb, Sarah Larsen. Contribution of photographs: Peter Collins, Ashley Ramsay, Mark Shackleton, Brad Degens. Planning and executing trial and baseline sampling: Svenja Tulipani, Brad Degens, Mark Shackleton, Bronte Grant, Michael Kendrick, Andrew Sayce, Emma Christie, Ryan Kam, Ashley Ramsay, Andrew Weatherburn, Stephen Keen, Judith Le Gresley.

For more information about this report, contact Malcolm Robb, Branch Manager Aquatic Science Branch.

Cover photograph: Setup at the trial location taken by Ashleigh Ramsey

Disclaimer

This document has been published by the Department of Water and Environmental Regulation. Any representation, statement, opinion or advice expressed or implied in this publication is made in good faith and on the basis that the Department of Water and Environmental Regulation and its employees are not liable for any damage or loss whatsoever which may occur as a result of action taken or not taken, as the case may be in respect of any representation, statement, opinion or advice referred to herein. Professional advice should be obtained before applying the information contained in this document to particular circumstances.

This publication is available at our website <u>www.dwer.wa.gov.au</u> or for those with special needs it can be made available in alternative formats such as audio, large print, or Braille.

Contents

С	ontents iii							
Sı	ummary vii							
1	Purpose and background1							
	1.1 1.2 1.3 1.4	Why is it important to reduce nutrient loads delivered to our estuaries? What product was tested? Trial location Aims	1 1 2 4					
2	Meth	od	5					
	2.1 2.2 2.3	Trial set up and design Drain conditions and operational details Water quality monitoring Monitored variables Sampling regime and locations	5 7 9 9 11					
3	Resu	Its and interpretation	14					
	3.13.23.33.4	Did the clay reduce phosphorus? Phosphorus concentrations along the drain section Tracing clay and dosed water downstream Following clay movement in the field with in-situ tracers Other HT-clay tracers Did the clay reach Lake Amarillo? How much clay settled out in the drain? Limitations of clay tracers Side effects of clay application — potential environmental implications Significant increase in suspended solid content and turbidity Small increase in pH and alkalinity Reduction of dissolved organic carbon (DOC) Other effects Considerations for future in-drain clay application Estimation of drain discharge Clay dosing system design Mixing of the clay slurry in the dosing tank	14 15 17 17 19 21 21 26 26 26 26 26 26 21 31 31 31 32 33 33					
4	Outlo	bok and implications	35					
	4.1 4.2	Next stages of HT-clay development Dosing plant and monitoring considerations for potential future trials	35 35					
Re	eferer	nces	36					
Ap	pend	lices	37					
Sł	ortened forms61							
_								

Figures

Figure 1: Production of the first larger HT-clay batch.	2
Figure 2: A pipe culvert 20 m downstream of the clav dosing site	2
Figure 3: Trial location and sampling sites	3
Figure 4: Clay storage tank and dosing pumps at the treatment site on Punrak	-
Drain	5

Figure 5: Delivery of clay to the storage tank5
Figure 6: Clay dosing plant layout. The hoses (50 mm inner diameter) were rigid and
connected with Camlock fittings6
Figure 7: Clay application to the drain
Figure 8: Locations within the delta of Punrak Drain immediately upstream of Lake
Amarillo that were sampled once towards the end of the trial
Figure 9: Phosphorus concentrations at the sampling sites along Punrak Drain during
clay dosing. Coloured labels indicate when the clay was present at a particular
site, based on visual tracking of the clay and other tracers (see Section 3.2). 'DS'
stands for downstream of the clay dosing site14
Figure 10: Filterable reactive phosphorus (FRP), total phosphorus and dissolved
oxygen concentrations along the monitored section of Punrak Drain (HNCCULV,
PD-Fenceline, PD-delta) and further downstream at Lake Amarillo (AMRLOUT)
and the Serpentine River (AMAR) during clay dosing and 'before' and 'after'
monitoring. Note: Phosphorus in the drain was spiked during clay dosing but not
during sampling on the day before or after the trial
Figure 11: Visually tracking clay movement through Punrak Drain with a drone17
Figure 12: Specific conductivity and turbidity as clay tracers. Coloured labels indicate
when the clay was present at a particular sampling site, 'DS' stands for
downstream of the clay dosing site18
Figure 13: Magnesium and aluminium concentrations and their ratio as clay tracers.
Coloured labels indicate when the clay was present at a particular sampling site,
'DS' stands for downstream of the clay dosing site
Figure 14: Concentrations of total suspended solids and the bromide tracer during
the trial. Coloured labels indicate when the clay was present at a particular
sampling site, 'DS' stands for downstream of the clay dosing site
Figure 15: HT-clay tracers during clay dosing at the sampling sites along Punrak
Drain (average values) and at two locations within the delta immediately upstream
of Lake Amarillo that were sampled once only22
Figure 16: Clay tracers recorded during the trial (orange lines) and average seasonal
baseline conditions at the same sites recorded during October and November
2016 and 2017 as part of the regular REI monitoring program (yellow bars) and
during before and after monitoring of the clay dosing trial (blue and grey bars,
respectively)25
Figure 17: Water quality variables of environmental significance that may be
influenced by clay application: (a) during clay dosing (orange line), (b) during
before and after monitoring of the clay trial (blue and grey bars, respectively),
and (c) during spring 2016 and 17 (average seasonal conditions recorded during
October and November 2016 and 2017 as part of the regular REI monitoring
program; yellow bars)
Figure 18: Concentrations of dissolved organic carbon (DOC), dissolved organic
nitrogen (DON) and total nitrogen (TN) measured during clay dosing. DON was
only monitored at the first two sites. Coloured labels indicate when the clay was
present at a particular sampling site, 'DS' stands for downstream of the clay
Consing site
rigure 19. Concentrations of dissolved oxygen at the different sample locations
outing the dosing that. Coloured labels indicate when the clay was present at a
particular sampling site, US stands for downstream of the clay dosing site31

Figure 20: Method used to dose sodium bromide to the clay. Inner diameter of hoses was 50 mm
Figure 21: Comparison of discharge estimates from fortnightly flow velocity measurements at Punrak Drain with Hydstra discharge records from a gauging station 3 4km upstream of the clay dosing site (PD1)
Figure 22: Total alkalinity and pH at the different sample locations along Punrak Drain during HT-clay dosing. Coloured labels indicate when the clay was present at a particular sampling site. 'DS' stands for downstream of the clay dosing site44
Figure 23: Total solid content (TSS) vs. Turbidity during clay application along the treated drain section

Tables

Table 1: Drain conditions and operational trial details. The target clay dosing rate was
1 g dry-weight clay/mg filterable reactive phosphorus (FRP)
Table 2: Variables that were monitored before, during and after the trial
Table 3: Sampling locations monitored as part of the clay trial
Table 4: Average values of recorded clay tracers and estimated percentage loss of
clay between the first sampling location after clay dosing and sites further
downstream according to the different tracers23
Table 5: Average changes in water quality indicators (± standard deviation) as a
result of HT-clay dosing between the upstream baseline site and the first sample
location downstream of the dosing site
Table 6: Differences between targeted and actual concentrations of bromide tracer
and spiked filterable reactive phosphorus (FRP) in the drain water
Table 7: Variations between different methods of drain discharge determination at the
clay dosing site on the trial day
Table 8: Results from quality control sampling. A duplicate and a replicate sample of
a regular sample at PD-fenceline were collected during clay dosing. The field
blank sampling was conducted with Milli-Q water
Table 9: Water quality data in water samples collected during the clay dosing trial on
25/10/2017. A coloured cell background indicates that the clay plume was present
at the site (based on in-situ clay tracers and visual observations). These samples
were used to calculate average values during clay dosing. n.d. = not determined 45
Table 10: Water quality data in water samples collected during 'before' and 'after'
monitoring of the clay dosing trial and average water quality data during clay
dosing (± standard deviation)
Table 11: Water quality data measured in-situ during the clay dosing trial on
25/10/2017. A coloured cell background indicates that the clay plume was present
at the site (based on in-situ clay tracers and visual observations). These samples
were used to calculate average values during clay dosing
Table 12: Water quality data measured in-situ during 'before' and 'after' monitoring of
the clay dosing trial and average data during clay dosing (± standard deviation)60

Summary

The Department of Water and Environmental Regulation (the department) trialled an innovative phosphorus-binding clay product in a large agricultural drain in the Peel-Harvey Catchment as part of the Regional Estuaries Initiative (REI). During the field experiment, over 10,000 L of slurry containing more than half a tonne of clay was applied to the drain over a duration of five hours, treating about three million L of water. The water quality at the dosing site and at locations further downstream was closely monitored before, during and after the trial to evaluate the treatment efficiency.

Increased nutrient inputs from agricultural and urban sources can fuel extensive algal blooms in estuaries and other water bodies, which often have severe ecological and economic impacts. The new clay product, currently referred to as hydrotalcite (HT)-clay is intended as an immediate, highly effective action to reduce phosphorus loads and limit algal growth while other long-term measures to manage nutrient input, such as amendment of agricultural practices, can take effect.

HT-clay works by locking up the nutrient phosphorus, making it unavailable to fuel algal growth. It is applied as a slurry and can be dosed directly to flowing streams, where it immediately adsorbs dissolved phosphorus as it mixes with the water. In addition, the clay removes algae by flocculation. If low flows allow settling of the clay, it forms a protective layer on top of the sediments, reducing phosphorus release in the longer-term. The current trial is the largest field application of HT-clay to date and it was the first time that this clay or any similar product was applied to a large drain.

The trial location was at Punrak Drain, an agricultural drain that delivers large phosphorus loads to the Peel Harvey Estuary via Lake Amarillo and the Serpentine River. Seasonal algal blooms occur regularly in the lower stretch of the Serpentine River and in the estuary itself. The clay dosing site was at an easily accessible location of Punrak Drain, about 1.8 km upstream of Lake Amarillo.

Improved water quality

- The clay treatment reduced the concentration of filterable reactive phosphorus (FRP) from 0.05-0.08 mg P/L to an average of 0.02 mg P/L, which is well below the recommended target threshold of 0.04 mg P/L. FRP is the soluble form of phosphorus immediately available to algae, which is targeted by the clay.
- The clay travelled well through the drain with a similar speed as the treated water. Some of the clay was retained in the drainage channel, but at least half of it reached the lake.
- The clay could be dosed using a simple pump and tank mixing system at a constriction point of the drain achieving efficient mixing with the drain water.

HT-clay tracers

We identified several methods to track the clay (and treated water) movement in the field, which were:

- visual tracking of the clay plume with a drone
- in-situ measurements of turbidity indicating suspended clay
- in-situ measurements of specific conductivity and relative bromide (spiked to the clay slurry), tracing treated water.

We also identified tracers that can be analysed in water samples to reconstruct the clay movement after the trial:

- magnesium and aluminium concentrations and the magnesium/aluminium ratio (both are abundant elements in the hydrotalcite coating)
- total suspended solids
- bromide concentrations, allowing estimation of groundwater input and verification of dosing rates and drain flow.

Overall, bromide added to the clay slurry was the most suitable tracer to follow movement of the treated water with little interferences under more saline conditions or in places with enhanced natural sediment disturbance.

Potential environmental implications

- The HT-clay application increased turbidity and suspended solid content in the water during the trial. This may cause problems for invertebrate organisms such as filter feeders and might influence fish, if applied continuously. However, the peak values reached during clay dosing are within the typical range that occurs in the drain after heavy rainfall. Once the clay plume had moved past a sampling site, baseline conditions returned within minutes.
- The clay treatment also reduced the dissolved organic carbon content (DOC) by up to 38 per cent, which may potentially have some ecological effects. These may be beneficial, benign or detrimental depending on the respective environment.
- To further investigate these issues, specifically designed tests with invertebrate organisms will be needed.

Where to next?

HT-clay is a new product and still requires further development and test work before large-scale field applications may become possible. This includes additional experiments to inform a detailed environmental risk assessment and appropriate dosing rates for clay application in different environments as well as optimisation of the clay production process to enable economic large-scale manufacturing and transport.

To further investigate the clay efficiency in more saline environments, the department will conduct a large field trial in the lower stretch of the Serpentine River in 2020. In

this case the increase in turbidity and TSS is of less concern because it is only temporary. Preliminary tests in the Lower Vasse River have found no adverse effect for macroinvertebrates in that environment.

1 Purpose and background

1.1 Why is it important to reduce nutrient loads delivered to our estuaries?

Estuaries are complex ecosystems that provide habitat to diverse flora and fauna. They are also an important asset for recreational use and of high economic value for the tourism industry, regional development and fisheries. Extensive nutrient loads that largely come from a mix of agricultural and urban sources present a threat to most of Western Australia's estuaries (Kilminster, 2010).

Elevated concentrations of nutrients such as phosphorus accelerate algal growth in rivers, streams and estuaries, potentially resulting in large algal blooms that contribute to the build-up of black, organic matter-rich sediments. The degradation of the organic material often consumes most of the oxygen in the sediments and the water layer above it, causing effects such as the production of malodorous toxic gases, eutrophication and potentially fish kills. Sediment build-up may also impact hydrology and block transport channels.

The Department of Water and Environmental Regulation (the department) is testing novel and innovative products that reduce phosphorus concentrations in waterways as part of the State Government's Regional Estuaries Initiative (REI). These products have been designed as an immediate action to reduce soluble phosphorus in waterways and estuaries while long-term nutrient-management options, such as the amendment of agricultural practices, can take effect.

1.2 What product was tested?

The department is trialling a recently developed clay product for the reduction of soluble phosphorus loads and the treatment or prevention of algal blooms. It consists of a naturally occurring bentonite clay that is modified with a phosphorus-binding hydrotalcite mineral coating and is currently referred to as hydrotalcite (HT)-clay.

HT-clay is sprayed on to the water as a slurry. It works by locking up the soluble form of phosphorus (phosphate), making it unavailable to fuel algal growth. When it is applied to drains it is carried with the flow of water, adsorbing the phosphate as it mixes. Where flows slow, such as in lakes, the clay treatment has a longer-term benefit by forming a thin protective layer on top of nutrient-rich sediments, which reduces phosphorus release to the overlying water.

HT-clay can be made in a relatively simple process from economic and easily accessible raw materials. Small pilot field trials and laboratory testing have shown promising results. However, HT-clay is a new, experimental product and further testing needs to be completed successfully before wide-scale application may become possible.



Figure 1: Production of the first larger HT-clay batch.

HT-clay works similar to Phoslock®, which is currently the only commercially available phosphorus-binding clay. Phoslock[®] was developed by CSIRO and the Water and Rivers Commission in the 1990s and is now being used worldwide. However, the limited efficiency and potential environmental concern for Phoslock® application in marine environments make it unsuitable for the treatment of estuaries. Furthermore, Phoslock® has to be applied before the onset of an algal bloom (unless combined with algal flocculants). The new HT-clay is intended to overcome some of these limitations.

1.3 Trial location

The trial was conducted in the lower reach of Punrak Drain, an agricultural drain in the Peel-Harvey catchment that delivers high loads of soluble phosphorus to the Serpentine River and Peel-Harvey Estuary (Kelsey et al, 2011). The lower Serpentine River as well as the estuary are subject to seasonal algal blooms, enhanced eutrophication and occasional fish kills.

As part of the Regional Estuaries Initiative, the department is investigating options to reduce soluble phosphorus loads that fuel algal blooms in the lower Serpentine River by in-stream dosing of the new phosphorus-binding clay product to surface drains within the catchment, or alternatively by direct clay applications to the lower Serpentine River.

Clay was dosed directly into the lower reach of Punrak Drain at an easily accessible location 1.8 km upstream of Lake Amarillo (see Figure 3). The clay dosing site was located at a narrow point where flow entered a small meander before passing through a pipe culvert into a pool (Figure 2). This site was chosen to enable maximum mixing of the clay with the water within a short distance after dosing. The

section downstream of the culvert was a meandering channel set between straight banks that contained flood flows. The channel contained a few pools and minor riffles. At the delta of Punrak Drain, the main channel branches out into a number of smaller channels that drain into Lake Amarillo.

As part of the REI project, we have monitored the water quality in Punrak Drain, Lake Amarillo and the lower



Figure 2: A pipe culvert 20 m downstream of the clay dosing site.

Serpentine River over several years before the trial and also investigated bathymetry and sediment quality in Lake Amarillo and the lower Serpentine River. This was to:

- a. determine seasonal phosphorus loads (total and soluble)
- b. identify suitable locations for clay application
- c. assess fate and potential environmental impacts of the clay in the drain and at potential settling locations further downstream



Figure 3: Trial location and sampling sites.

1.4 Aims

The trial represented the largest field application of HT-clay at that time. It was also the first time that a phosphorus-binding clay had been applied to a high-flowing agricultural drain.

The trial was designed to:

- test if HT-clay treatment can efficiently reduce dissolved phosphorus loads when applied directly to a large drain
- test transport and settling behaviour of HT-clay in a drain
- find suitable HT-clay tracers to follow the clay movement with the flow
- inform dosing design and logistics for potential longer-term in-drain clay application
- inform an environmental risk assessment of in-drain clay application

2 Method

During the trial 10,780 L of slurry containing more than half a tonne of dry-weight HT-clay was continuously dosed into Punrak Drain over five hours, treating a total water volume of about three-million L. In order to evaluate the treatment efficiency, phosphorus concentrations and other water quality indicators were monitored before, during and after the trial at four locations along Punrak Drain, including a baseline site immediately upstream of the dosing location.



Figure 4: Clay storage tank and dosing pumps at the treatment site on Punrak Drain.

2.1 Trial set up and design

The clay was dosed from a 32,000 L poly storage tank installed on the bank of the drain (Figure 4). It was produced in bulk and delivered to the site as low-density slurry that was thickened slightly by settling on-site (see Appendix A).

Clay slurry was dosed using a simple tank and pumping system (Figure 6). Dosing was carried out with a petrol-motor driven centrifugal pump with a tap at the hose outlet to regulate the flow rate. In order to ensure the clay was well-mixed within the tank, the slurry was simultaneously



Figure 5: Delivery of clay to the storage tank.

recirculated with a second centrifugal pump to keep it in suspension. Recirculation pumping was started one hour before the trial (achieving at least 3 x volume recirculation) and maintained throughout the clay application. On the day before the

trial, both pumps were used together to mix and recirculate the clay for several hours. Analysis of the solid content in three clay slurry samples collected from different depths within the tank indicated that the clay was well-mixed after this treatment. The measured solid content was also used to calculate the appropriate flow rate for clay dosing.

The flow rate at the hose outlet to the drain was adjusted based on manual flow measurements using a graded 30-L container and a stopwatch. The flow rate was checked immediately before the trial and twice during the trial.



Figure 6: Clay dosing plant layout. The hoses (50 mm inner diameter) were rigid and connected with Camlock fittings.

To enable better mixing of the clay with the drain water, the outlet hose was fixed to star pickets and the slurry was sprayed into the drain against the direction of flow (Figure 7). Furthermore, the dosing site was set up about 20 m upstream of a pipe culvert to ensure complete mixing in the turbulent flow created by this structure.

Sodium bromide (75 kg) was added to the clay as a tracer to follow the downstream movement of the



Figure 7: Clay application to the drain.

treated water with a bromide probe during the trial (see Appendix A). In addition, a drone equipped with a camera was used to track the clay.

2.2 Drain conditions and operational details

The trial was conducted in spring 2017 (25 October) under moderate flow conditions. Phosphorus concentrations in the drain water were lower than expected, with only 0.03 mg/L of filterable reactive phosphorus (soluble phosphorus fraction targeted by the clay). In order to effectively test the clay treatment under these conditions, we had to spike the drain with a small volume of sodium phosphate solution, which was added at a consistent rate by a peristaltic pump upstream of the dosing site (see Appendix A).

The environmental impact of this intervention was minimal because:

- 1. the added phosphate amount was very low in comparison to typical daily loads in Punrak Drain
- most of this phosphate was expected to be taken up by the clay. The dissolved organic carbon (DOC) concentration was less than 20 mg/L and was therefore not expected to influence the treatment efficiency. (Higher DOC concentrations about 50 mg/L can reduce the clay's phosphorus uptake capacity by up to 30 per cent.)

On the day before clay application the drain discharge was estimated with a portable flowmeter at two locations near the dosing site. Filterable reactive phosphorus (FRP) concentrations at the trial site were measured with a portable field photometer (Hanna Instruments) and also analysed overnight by an external laboratory.

The estimated discharge and the measured FRP concentrations were used to calculate:

- 1. the required pumping rates for the clay slurry
- 2. the required pumping rate for the phosphate solution used to spike the drain
- 3. the required sodium bromide amount.

We also collected two clay samples from the dosing outlet at different times during the trial to analyse bromide concentrations.

This was done to:

- 1. ensure the slurry was well mixed
- 2. back-calculate drain flow and clay dosing rates for the evaluation of the trial.

For a summary of drain conditions and operational trial parameters see Table 1. For more method details see Appendix A.

Table 1: Drain conditions and operational trial details.	The target clay dosing rate was
1 g dry-weight clay/mg filterable reactive phosphorus	(FRP).

Drain conditions	
Estimated discharge at trial site	0.169 m³/s
Non-modified FRP concentration at trial site	0.03 mg P/L
Dissolved inorganic carbon (DOC) concentration	14-19 mg/L
Clay dosing	
Amount of HT-clay slurry	10,780 L
Solid content in clay slurry	54.2 g/L
Mass of dry-weight HT-clay	580 kg
Target HT-clay dosing rate	121 kg/h (or 1g clay /mg FRP)
Clay slurry pumping rate	0.6 L/s
Pumps	5.5 HP centrifugal petrol engine driven pumps capable of delivering >8.5 L/s. Inlet and delivery: 50 mm
Trial duration	ca. 5h
Approximate volume of treated water	3000 m ³
Phosphate-spiking	
Target spiked phosphate concentration	0.2mg P/L
Pumping rate of 0.5M NaH ₂ PO ₄ solution	1.86 mL/s
Bromide tracer	
Target bromide concentration in drain water	20mg Br ⁻ /L
Amount of NaBr added to the tank	ca. 75 kg
Target bromide concentration in slurry	5.42 g Br ⁻ /L

2.3 Water quality monitoring

Monitored variables

To evaluate the trial we monitored the water quality variables listed in Table 2 at the clay dosing site and at selected downstream locations on:

- a. the day before the trial ('before' monitoring)
- b. during the trial
- c. one day after the trial ('after' monitoring).

Instrument-measured water quality variables such as pH, turbidity and specific conductivity were measured in-situ with YSI-proDSS and EXO probes. The remaining variables were analysed externally by ALS according to standard APHA laboratory methods for surface-water analysis. Water samples were collected and handled according to the quality standards outlined in the department's standard sampling procedures. For more information see Appendix A.

Variable	Why was this analysed?							
арН	 Will impact clay efficiency in extremely low and high ranges May increase as a result of clay application (significant for environmental risk assessment) 							
^a Specific conductivity	Potential in-situ tracer for clay transport							
^a Salinity	 Higher salinity impacts clay efficiency Lake Amarillo and the lower stretch of the Serpentine River have varying seasonal salinities ranging from freshwater to hypersaline 							
^a Dissolved Oxygen (DO)	• May indicate the presence of algae (which effects oxygen concentrations via photosynthesis and respiration) or groundwater input and influences nutrient release from sediments							
^a Turbidity	 Suspected to increase as a result of clay application (significant for environmental risk assessment) Potential in-situ tracer for clay transport 							
^b Filterable reactive phosphorus (FRP)	Monitor treatment efficiency							
^b Alkalinity (HCO3 ⁻ , CO3 ²⁻ and total)	May increase as a result of HT-clay applicationMay interfere with clay efficiency							
^b Total phosphorus (TP)	Monitor treatment efficiency							
^b Dissolved organic carbon (DOC)	 May influence clay efficiency DOC removal by HT-clay could potentially impact ecology of the receiving environment 							
^b Total Nitrogen (TN)	Nutrient for algaePotentially adsorbed by clay							
^b Reactive silica	Nutrient for algae							
^{b,c} Dissolved organic nitrogen (DON)	May have some affinity to the HT-clay and might be partly removedOnly monitored at selected sites							

Table 2: Variables that were monitored before, during and after the trial.

^{b,c} Ammonia (NH ₃), Total oxidised nitrogen (NO _x)	Nutrient for algaeOnly monitored at selected sites
^b Total suspended solids (TSS)	 Suspected to increase as a result of clay application (significant for environmental risk assessment)
^b Total magnesium (Mg) and aluminium (Al)	Potential tracers for clay transport
^b Bromide	 Added to clay slurry and used as tracer to follow transport of treated water (relative concentration differences measured in-situ, absolute concentrations analysed externally) May be used to calculate any groundwater inflow or to monitor consistency of clay dosing rates

^a Analysed in-situ

^b Analysed externally by ALS

° Only analysed at locations 10 m upstream and 30 m downstream of clay dosing site

Sampling regime and locations

Sampling during clay dosing

Four locations along Punrak Drain were monitored during the trial:

- 1. 10 m upstream of the clay dosing site (baseline)
- 2. 30 m downstream of the dosing site (about 10 m below the culvert)
- 3. ca. 1.2 km downstream of the clay dosing site (PD-fenceline)

4. ca. 1.8 km downstream of the clay dosing site immediately upstream of the Punrak Drain delta (see Figure 3 and Table 3).

In-situ variables were logged in 10-minute intervals, water samples were collected every 50 minutes.

The sampling was started at each site once the clay plume had reached the location. This was judged by monitoring bromide concentrations and turbidity as well as by visual tracking with a drone. Sampling was continued until the clay plume had moved past (or until the end of the day for the last site). Two sites within the delta immediately upstream of Lake Amarillo were also sampled once to check whether the clay would reach the lake without settling out completely within the delta (see Figure 8).



Figure 8: Locations within the delta of Punrak Drain immediately upstream of Lake Amarillo that were sampled once towards the end of the trial.

WRC Site Code WIN Site No.		Description	Latitude	Longitude	
^a PD-10m Upstr		10 m upstream of clay dosing site (baseline)	-32.4204	115.8381	
^a PD-30m Downstr		30 m downstream of clay dosing site (30m DS)	-32.4204	115.8375	
♭HNCCULV	6141444	Regular REI sampling site at Keralup Culvert	-32.42041	115.8377	
^{a,b} PD-Fenceline		ca. 1.2 km downstream of dosing site (1.2 km DS)	-32.4207	115.8251	
^{a,b} PD-Delta		ca. 1.8 km downstream of dosing site, near Punrak Drain delta (1.8 km DS, near delta)	-32.4228	115.8193	
▶AMRLOUT	6141447	Lake Amarillo Outlet	-32.4304	115.8203	
♭AMAR	6140665	Serpentine River Downstream of Lake Amarillo	-32.4474	115.8135	

Table 3: Sampling I	locations	monitored as	part of t	he cla	v trial
					,

^a Monitored during clay dosing

^b Monitored on the day before the trial and on the day after the trial ('before' and 'after' monitoring)

Before and after monitoring

Monitoring on the day before and after clay dosing, ('before and 'after' monitoring) was conducted at the same locations Table 3). However, we sampled the regular REI sampling site HNCCULV (located immediately upstream of the culvert), instead of the sites 10 m upstream and 30 m downstream of the clay dosing site.

Two additional sites further downstream were also sampled (AMROUT and AMAR, see Figure 3). Both sites are part of the regular REI monitoring program. AMROUT is located at the outlet of Lake Amarillo and AMAR is located in the Serpentine River.

Quality control sampling

Quality control (QC) sampling was performed on the trial day according to the department's standard operating procedures. A field duplicate and a field replicate of a randomly selected field sample from 'PD-fenceline' were collected along with blank samples of MilliQ water and sent to ALS for analysis to ensure consistent sampling practices and accurate laboratory analyses (for more detail and results of QC-sampling see Appendix B).

3 Results and interpretation

3.1 Did the clay reduce phosphorus?

The HT-clay treatment effectively reduced dissolved and total phosphorus in the drain water (see Figure 9). Once the clay plume had moved past a location, phosphorus concentrations returned to the baseline level.



Figure 9: Phosphorus concentrations at the sampling sites along Punrak Drain during clay dosing. Coloured labels indicate when the clay was present at a particular site, based on visual tracking of the clay and other tracers (see Section 3.2). 'DS' stands for downstream of the clay dosing site.

The filterable reactive phosphorus (FRP) concentration, which represents the phosphorus fraction readily available to algae, was reduced to values well below the recommended ANZECC target threshold of 0.04 mg P/L (ANZECC & ARMCANZ, 2000). The FRP reduction between the upstream baseline site and the first downstream sampling site was 65 per cent on average, with a maximum of 75 per cent (Table 5). The spiked FRP concentrations at the baseline site varied between 0.05 and 0.08 mg P/L (average: 0.06 mg P/L), presumably because of incomplete mixing of the phosphate solution within the drain water or inconsistencies in the

dosing rate. In contrast, the treated FRP concentrations recorded during the clay dosing at the other sampling sites remained stable at 0.01-0.02 mg P/L.

The achieved FRP reduction was as expected for low initial FRP concentrations. At higher FRP concentrations above 0.5 mg/L, the clay is generally more efficient and can achieve reduction rates of more than 90 per cent at a dosing rate of 0.5 g clay/mg P (unpublished results from our laboratory experiments).

The clay treatment also reduced total phosphorus (TP) concentrations by an average of 45 per cent between the baseline site and the first sampling location downstream (0.18 to 0.10 mg/L). HT-clay is an algal flocculant that directly removes algae and the organic phosphorus stored within them. It presumably also binds other dissolved and particulate forms of organic phosphorus and potentially even particulate inorganic phosphorus.

The significant TP reduction recorded in the trial shows that the clay efficiently removed algae (or other forms of organic or inorganic phosphorus) in addition to the dissolved phosphate (FRP), which only accounted for a small fraction of the TP on the trial day. The results also indicate that a fraction of the clay (containing the bound phosphorus), either settled out in the drain or was caught by vegetation. If the clay was still suspended, the phosphorus bound within it would be picked up by the TP-analysis. Alternatively, it is also possible – although unlikely – that some phosphorus bound within the clay was missed during laboratory analyses, for example because the clay was not fully dissolved by the digestion method or because of insufficient sample homogenisation. Field duplicates and replicates collected as quality control showed less than 25 per cent variation in TP results.

Measured phosphorus reductions (FRP and TP) indicate that the dosing method and location (upstream of the culvert) enabled good mixing of the clay within the drain water, providing sufficient contact time between suspended clay particles and dissolved phosphorus. The FRP-reduction was in the same range as in laboratory trials, where complete mixing of the clay with the water was achieved by agitation on a sample roller for at least one hour. It remains to be tested whether mixing of clay with water is as efficient at higher flows or without structures such as the culvert, but the results are promising and suggest that the HT-clay can be applied to large agricultural drains.

Phosphorus concentrations along the drain section

There was a general trend of decreasing FRP concentrations along the monitored drain section, which was found during the clay treatment as well as in the 'before' and 'after' monitoring (Figure 10). This suggests transformation of the available P in the drain with no effect on total phosphorus, for example through phosphorus uptake by algae along the drain, with increasing algal growth towards the lake. This is also supported by the higher dissolved oxygen concentrations at the sample locations further downstream (Figure 10). TP concentrations stayed similar along the monitored drain section, but decreased in Lake Amarillo (Figure 10).



Figure 10: Filterable reactive phosphorus (FRP), total phosphorus and dissolved oxygen concentrations along the monitored section of Punrak Drain (HNCCULV, PD-Fenceline, PD-delta) and further downstream at Lake Amarillo (AMRLOUT) and the Serpentine River (AMAR) during clay dosing and 'before' and 'after' monitoring. **Note:** Phosphorus in the drain was spiked during clay dosing but not during sampling on the day before or after the trial.

3.2 Tracing clay and dosed water downstream

Following clay movement in the field with in-situ tracers

1. Visual clay tracing

We were able to follow the downstream clay movement by tracking the visual appearance of the light-grey coloured clay in the brown-stained (but translucent) water of Punrak Drain with a drone. This helped guide timing of sampling to correspond with arrival of the clay at each sampling site during dosing. However, visual observation of the plume may not be possible at other locations and in darker conditions, so it was important to explore other options to trace the clay in the field. In addition, visual tracking cannot be used to quantify how much of the clay actually travelled downstream and how much clay was lost in the drainage channel because of processes such as settling.



Figure 11: Visually tracking clay movement through Punrak Drain with a drone.

2. Turbidity

The increase in turbidity because of clay application was also an excellent nonspecific but quantifiable clay tracer. Profiles of turbidity over time clearly indicate when the clay reached each site and also when the clay plume had moved past after dosing stopped (Figure 12). There are small dips in the profiles in the middle and towards the end of the trial, which are consistent with:

- a drop in the clay pumping rate that was discovered and rectified at 1.20pm
- a drop in the clay pumping rate towards the end of the trial when the tank started to run empty.

The peak turbidity values recorded at the last sampling location upstream of the delta were slightly lower compared with the other sites, indicating some settling of the clay within the drain.

3. Specific conductivity

Specific conductivity is a measure of the ion content in water and can be analysed in-situ with a probe. It slightly increased as a result of clay application, presumably largely because of residual ions of dissolved sulfate and sodium (and the added sodium bromide tracer) in the clay slurry, although some suspended particles may also influence conductivity. Specific conductivity is therefore mostly a tracer for the clay-treated water (containing the dissolved ions) rather than a tracer for the suspended clay, which may travel slower or settle out.

The specific conductivity profiles over time were similar to the turbidity profiles, which indicates that the suspended clay moved at a similar speed as the treated water (Figure 12). During the trial, the peak conductivity reached similar values at each site irrespective of any clay settling (see later sections).

Laboratory trials can be used to confirm whether suspended clay particles have any effect on conductivity or whether the rise is solely caused by the dissolved ions in the clay slurry. This would involve measuring the specific conductivity in filtered and non-filtered clay-treated water (with and without clay particles, respectively).



Figure 12: Specific conductivity and turbidity as clay tracers. Coloured labels indicate when the clay was present at a particular sampling site, 'DS' stands for downstream of the clay dosing site.

4. Bromide tracking in the field

The water-soluble bromide salt, which we added to the slurry as a tracer, indicates the movement of the treated water (similar to specific conductivity). We used a probe to trace increasing bromide concentrations in the field, which correlated well with the visual clay tracking from the drone and with turbidity or specific conductivity measurements. The probe was a useful asset to trace the clay in the field; however, it was not calibrated to record absolute concentrations or log data. Absolute bromide concentrations were subsequently analysed in collected water samples.

Other HT-clay tracers

1. Magnesium and aluminium

Magnesium and aluminium are major elements in the hydrotalcite mineral of the clay coating. The increase in their concentrations as well as the increase of the aluminium to magnesium ratio were all good HT-clay tracers. The profiles recorded during the trial were similar to the in-situ clay tracers discussed above (see Figure 13). However, the inconsistencies in the clay pumping rates were not picked up because of the larger 50-minute sampling intervals. Peak concentrations of magnesium and aluminium declined as the clay moved down the drain, indicating some clay loss.

2. Bromide concentration in water samples

Peak Bromide concentrations in the collected water samples were in a similar range at all sampling sites, indicating no major loss or dilution of the drain water. Although bromide is a tracer for the treated water, the similar downstream travelling speed of clay particles in a high-flowing drain (such as Punrak Drain) make bromide suitable for tracking the clay movement in such settings.

3. Total suspended solid content

The clay application increased the content of suspended solids (TSS) in the drain water by two orders of magnitude (Figure 14). The peak TSS concentrations during clay dosing were up to 55 per cent lower at the sampling sites further downstream, indicating significant settling or retention of the clay while travelling.



Figure 13: Magnesium and aluminium concentrations and their ratio as clay tracers. Coloured labels indicate when the clay was present at a particular sampling site, 'DS' stands for downstream of the clay dosing site.



Figure 14: Concentrations of total suspended solids and the bromide tracer during the trial. Coloured labels indicate when the clay was present at a particular sampling site, 'DS' stands for downstream of the clay dosing site.

Did the clay reach Lake Amarillo?

The clay travelled well through the drain and was detected at all sampling sites that were monitored during the trial. These included the two locations within the delta just upstream of Lake Amarillo, which were sampled once only (see Figure 15). All tracers measured within the delta were generally similar to the values recorded at the site immediately upstream of the delta (1.8 km downstream from the dosing point), indicating that significant clay amounts entered Lake Amarillo. Nevertheless, the clay amount dosed in this trial was very small relative to the total water volume in the lake. Therefore the lake itself was not monitored during the trial.

The clay travelled at a similar velocity as the drain water based on comparison of tracers of the treated water (bromide and specific conductivity) and that of the suspended clay itself (visual, turbidity, total suspended solids, magnesium and aluminium). The clay reached the sampling site 1.2 km downstream within three hours and the sampling site 1.8 km downstream within four hours.



Figure 15: HT-clay tracers during clay dosing at the sampling sites along Punrak Drain (average values) and at two locations within the delta immediately upstream of Lake Amarillo that were sampled once only.

How much clay settled out in the drain?

Although the clay travelled well within the moving water, a decline in peak tracer concentrations/intensities at locations further downstream indicates up to 55 per cent clay loss within the monitored drain section because of settling in smaller pools or adhering to vegetation. The extent of clay loss differed between tracers. TSS measurements indicated up to 54.8 per cent loss whereas turbidity measurements indicated 17.4 per cent loss (Table 4). Similarly, the reduction in magnesium and aluminium concentrations indicate a clay loss of 19.8 per cent and 42.7 per cent, respectively. TSS may have also been reduced because of the removal of algae in addition to settling of the clay, which may lead to an overestimation of the clay loss.

Overall these results indicate in the order of 17-20 per cent retention of clay in the drain; however, this is likely to be flushed out during high flows, and therefore insignificant in the long-term.

Site	Specific conductivity ^a		Bromideª		Total suspended solids (TSS) ^b		Turbidity ^b		Magnesium ^b		Aluminium ^b		Al/Mg ratio ^b	
	avg. (mS/cm)	% change	avg. (mg/L)	% change	avg. (mg/L)	% loss	average (NTU)	% Ioss	average (mg/L)	% Ioss	average (mg/L)	% Ioss	average	% Ioss
30m downstr.	0.53	0.00	14.2	0.0	108	0.0	27.7	0.0	21.50	0.0	5.76	0.0	0.27	0.0
1.2km downstr.	0.52	0.58	13.2	-7.1	68.5	-36.8	29.8	7.7	18.75	-12.8	4.06	-29.5	0.22	-19.1
near delta	0.53	0.81	13.0	-8.5	49	-54.8	22.9	-17.4	17.25	-19.8	3.30	-42.7	0.19	-28.7
In delta Site 1	0.53	1.29	12.8	-10.1	19	-82.5	18.9	-31.7	17	-20.9	3.44	-40.3	0.20	-24.4
In delta Site 2	0.53	1.29	13	-8.7	56	-48.3	19.8	-28.6	17	-20.9	3.5	-39.2	0.21	-23.1

Table 4: Average values of recorded clay tracers and estimated percentage loss of clay between the first sampling location after clay dosing and sites further downstream according to the different tracers

^a Tracer for treated water

^bTracer for clay

Limitations of clay tracers

While the tracers discussed above were useful in the drain environment, different environmental conditions – such as higher salinities or different hydrological conditions - may reduce their effectiveness in detecting the clay or treated water movement. This may become relevant when trying to trace the clay further downstream in Lake Amarillo and the lower Serpentine River in trials over longer dosing periods or during clay application directly to the Serpentine River. Lake Amarillo and the lower Serpentine River both have a tidal influence and widely fluctuating salinities, ranging from freshwater conditions during high winter and spring flows, to potentially hypersaline conditions during summer. Lake Amarillo is very shallow, with average depths of less than 0.5 m in summer, leading to frequent sediment disturbance by wind.

To assess the suitability of the clay tracers at these locations, we plotted the average values reached during the clay dosing in Punrak Drain and compared them with the natural range of values typically occurring at Lake Amarillo, Punrak Drain and the Serpentine River during spring (see Figure 16).

Although specific conductivity was an accurate indicator of clay-treated water under the freshwater conditions in Punrak Drain, the profiles in Figure 16 indicate that it may be less suitable in more saline environments such as Lake Amarillo and the Serpentine River (salinities in spring 2016 and 2017 ranged from 0.4-2.6 ppt). The increase in specific conductivity because of mixing with more saline water is greater than the original increase because of clay addition making it difficult to reliably determine where the treated water has travelled.

Similarly, the increase in magnesium concentrations in clay dosed water was very small compared with the higher magnesium concentrations that arise as the drain water mixes with more saline downstream locations.

While aluminium concentrations show less salinity-dependant variations, they may be significantly influenced by wind or current resuspension of sediments. This was particularly evident in the follow-up monitoring of the trial in Lake Amarillo, which was conducted on a windy day (Figure 16). Although absolute magnesium and aluminium concentrations may not be suitable clay tracers under these conditions, the profile of the aluminium to magnesium ratio looks more promising (Figure 16).

Turbidity was also an excellent HT-clay tracer in the drain; however, in shallow-water environments such as Lake Amarillo the turbidity values reached during clay dosing may easily be exceeded significantly by wind resuspension of the sediments (Figure 16).

The most promising method for tracing the HT-clay movement under more saline conditions and in shallow standing water environments appears to be the addition of a bromide tracer to the clay slurry. However, the soluble bromide travels with the treated water and the actual clay movement may be slower under some conditions.



Figure 16: Clay tracers recorded during the trial (orange lines) and average seasonal baseline conditions at the same sites recorded during October and November 2016 and 2017 as part of the regular REI monitoring program (yellow bars) and during 'before' and 'after' monitoring of the clay dosing trial (blue and grey bars, respectively).

3.3 Side effects of clay application – potential environmental implications

Although HT-clay itself is not toxic, large-scale or continuous clay application may affect organisms and ecosystems and therefore requires detailed environmental risk assessment.

Significant increase in suspended solid content and turbidity

The main environmental risk with clay application is the substantial increase in turbidity and suspended solid content while the clay is suspended. This may impact organisms such as invertebrate filter feeders, or even fish when raised over the longer term. During this trial the total suspended solid (TSS) content increased by almost two orders of magnitudes from an average of 1.5 mg/L at the upstream baseline site to an average of 108 mg/L at the 30 m downstream location (Table 5). Turbidity of the water also increased significantly, from an average of 7.4 to 27.7 NTU (Table 5). However, when dosing ceased and the clay plume had moved past, the TSS content and turbidity immediately returned to the baseline values measured before clay dosing (Figures 12 and 14). When clay is dosed to standing water bodies, turbidity and TSS content also similarly return to baseline values within hours after application once the clay has settled (Tulipani 2019). Although the increase in TSS content recorded during this trial was significant, similarly high TSS concentrations have been previously measured in Punrak Drain after big rain events (in samples collected with rising stage samplers) or in Lake Amarillo as a result of sediment disturbance by wind (e.g. Figure 17).

Specifically designed toxicity tests with invertebrate organisms (from Punrak Drain and other habitats) are needed before any widespread or continuous clay application to further investigate the impact of raised suspended solids and turbidity by in-stream clay dosing over longer periods of time.

Small increase in pH and alkalinity

The HT-clay dosing also caused small temporary increases in pH (6.6 to 6.8) and alkalinity (29 to 40 mg CaCO₃/L; Table 5). The clay slurry itself is alkaline (pH 9 to 10), and clay application can significantly raise the pH value in waters with low buffering capacity and low initial pH values (unpublished laboratory trials). However, in Punrak Drain the pH increase was slight and the peak values reached during clay application were within the typical range measured at this location (e.g. Figure 17). A natural pH increase along the monitored drain section (from 6.6 to 6.9) occurred independent from the clay application and was presumably caused by enhanced algal growth along the open channel (Figure 16).

Although not considered a risk for dosing of Punrak Drain, potential changes to pH and alkalinity with clay application still need to be considered for environmental risk assessments at other locations. The department is currently testing modifications to the clay production process that may further reduce the pH in the clay slurry.
	Average difference	Average value 10m upstream	Average value 30m downstream
FRP	-64.9 ±8.2%	0.06 ±0.01 mg P/L	0.02 ±0.00 mg P/L
ТР	-45.2 ±7.8%	0.18 ±0.01 mg/L	0.10 ±0.01 mg/L
DOC	-38.2 ±12.4%	15.8 ±1.8 mg/L	9.7 ±1.5 mg/L
Sp Cond.	5.5 ±1.4%	0.5 ±0.00mS/cm	0.5 ±0.01 mS/cm
Turbidity	273.0 ±42.5%	7.4 ±0.05 NTU	27.7 ±3.16 NTU
Aluminium	1149 ± <i>135%</i>	0.5 ±0.0 mg/L	5.8 ±0.4 mg/L
Magnesium	123 ±18.1%	9.7 ±0.5mg/L	21.5 ±0.8 mg/L
Al/Mg ratio	461 ±56.2%	0.048 ±0.004	0.268 ±0.0
TSS	6270 ± <i>2045%</i>	1.5 ±0.8mg/L	108.3 ±6.3 mg/L
Reactive Si	-3.6 ±4.0%	2.3 ±0.1mg Si/L	2.2 ±0.1 mg Si/L
TN	-8.4 ±9.1%	0.7 ±0.0 mg/L	0.7 ±0.1 mg/L
DON	27.9 ±23.5%	0.5 ±0.2 mg/L	0.4 ±0.2 mg/L
Ammonia	35.9 ±69.8%	0.02 ±0.01 mg N/L	0.03 ±0.00 mg N/L
NOx	17.7 ±2.9%	0.1 ±0.0mg N/L	0.1 ±0.0 mg N/L
Alkalinity	47.9 ±13.9%	28.7 ±2.0mg CaCO₃/L	42.2 ±1.2 mg CaCO ₃ /L
рН	2.9 ±0.6%	6.6 ±0.01	6.8 ±0.04
DO	3.6 ±1.2%	87.2 ±3.27 % sat	90.3 ±2.42% sat

Table 5: Average changes in water quality indicators (\pm standard deviation) as a result of HT-clay dosing between the upstream baseline site and the first sample location downstream of the dosing site.

FRP: filterable reactive phosphorus; TP: Total Phosphorus; DOC: Dissolved organic carbon; Sp. Cond.: Specific conductivity; TSS: Total suspended solids; TN: Total nitrogen; DON: Dissolved organic nitrogen; NO_x: Total oxidised Nitrogen; DO: Dissolved oxygen



Figure 17: Water quality variables of environmental significance that may be influenced by clay application: (a) during clay dosing (orange line), (b) during 'before' and 'after' monitoring of the clay trial (blue and grey bars, respectively), and (c) during spring 2016 and 17 (average seasonal conditions recorded during October and November 2016 and 2017 as part of the regular REI monitoring program; yellow bars).

Reduction of dissolved organic carbon (DOC)

HT-clay removes significant amounts of dissolved organic carbon (DOC) from the treated water, which competes with the clay's phosphorus uptake. In Punrak Drain, the clay reduced DOC concentrations by an average of 38 per cent between the upstream baseline site and the first downstream sampling location (15.8-9.7 mg/L; Figure 18).

The clay dosing did not have a statistically significant effect on concentrations of dissolved organic nitrogen (DON) and total nitrogen (TN) (which was largely composed of DON); see Figure 18 and Table 5. This is somewhat surprising because it is contradictory to the DOC removal and suggests some selectivity of the clay towards binding organic matter low in nitrogen. Although DON concentrations have never been monitored in previous HT-clay field trials, we did observe some reduction in TN as a result of the clay treatment during clay application in the Lower Vasse River (Busselton) (Tulipani 2019), which reflected the removal of algae containing organic nitrogen and potentially some dissolved organic nitrogen.

DOC removal from environmental waters may have some impacts such as increased light permeability of the water (removal of coloured particles), which could potentially favour phytoplankton growth at greater depths. Furthermore, many microorganisms feed on organic carbon and might be affected if a fraction of it is removed.

The consequences of DOC removal are difficult to predict and may be beneficial, benign or detrimental for environmental health, and the outcomes are likely to vary between different locations. Further investigations of which fraction or type of organic matter is preferably adsorbed by the HT-clay may aid the assessment of potential environmental implications.

DOC content in the water also needs to be considered when selecting appropriate locations or seasons for HT-clay treatments and calculating clay dosing rates, because of its effect on clay efficiency. High DOC contents over 50 mg/L lead to a noticeable reduction in phosphorus removal, whereas DOC concentration below 10 mg/L typically do not have a measurable effect (unpublished laboratory experiments).



Figure 18: Concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and total nitrogen (TN) measured during clay dosing. DON was only monitored at the first two sites. Coloured labels indicate when the clay was present at a particular sampling site, 'DS' stands for downstream of the clay dosing site.

Other effects

It is possible that HT-clay application may influence dissolved oxygen (DO) concentrations by removing algae. This may cause lower DO concentrations during the day, but would presumably also reduce the extent of the drop in DO concentrations overnight that is associated with respiration activity of algae. Slight changes in the DO concentration do not have any effect in well-oxygenated waters such as the current location; however, they could be relevant elsewhere in waters that are already depleted in oxygen. The DO profiles recorded during this trial show trends of typical diurnal fluctuations as a result of algal activity, with increasing values in the morning, a maximum in the middle of the day and a decrease as light fades in the afternoon (Figure 19). At the locations further downstream, DO concentrations were higher, with more pronounced fluctuations, reflecting increased algal growth at these sites. The clay application may have enhanced the decrease of DO concentrations towards the late afternoon; however, to further investigate this, baseline DO concentrations would need to be monitored over several days around future clay trials with temporarily installed sensors.



Figure 19: Concentrations of dissolved oxygen at the different sample locations during the dosing trial. Coloured labels indicate when the clay was present at a particular sampling site, 'DS' stands for downstream of the clay dosing site.

3.4 Considerations for future in-drain clay application

This trial was the first time that a phosphorus-binding clay has been applied directly to a large agricultural drain. A critical review of the application design – what worked and what areas need improvement – is important to inform potential larger scale, in-drain clay applications at this or other locations, using HT-clay or potentially Phoslock®.

Estimation of drain discharge

The accurate estimation of drain discharge is critical for in-stream clay dosing because it is used to calculate phosphate loads and appropriate clay dosing rates. Errors in discharge estimation can result in under-dosing drain waters or applying unnecessarily high clay amounts.

In the current trial, lower than expected bromide tracer and spiked phosphate concentrations in the drain water (Table 6) indicate that we underestimated the drain discharge with the utilised method (local flow velocity measurements and estimation of cross-sectional drain areas; see Appendix A). Whereas this did not impact the trial outcome or treatment efficiency (in this case spiked phosphate concentrations and clay dosing rates were equally low), it does show the need for more reliable discharge measurements, such as purpose-built gauging stations, for continuous instream clay dosing systems. If future short-term clay dosing trials are conducted in the same drain section, calculating drain discharge from measurements by a gauging station 3.4 km upstream may be more accurate (Table 7). For a more detailed discussion see Appendix C.

Anglista	Targeted	Actual conce	entration
Analyte	concentration	Range	Average
Bromide concentration	20 mg/L	12.7-15.4 mg/L	14.2 mg/L
Spiked FRP concentration	0.2 mg P/L	0.05-0.08 mg P/L	0.06 mg P/L

Table 6: Differences between targeted and actual concentrations of bromide tracer and spiked filterable reactive phosphorus (FRP) in the drain water.

Table 7: Variations between different methods of drain discharge determination at the clay dosing site on the trial day.

Method used	Calculated discharge
Discharge estimate based on flow velocity measurements (used in this trial)	0.17 m3/s
Discharge subsequently calculated from measured bromide concentrations	0.27 m3/s
Discharge calculated from correlation with a gauging station 3.4 km upstream	0.22 m3/s

Clay dosing system design

Whereas continuous clay application would require a purpose-built dosing unit and a holding tank with in-built mixing capability, we found that a simple dosing set-up with a holding tank and pumps was suitable for this short-term trial. The use of two pumps – one for clay dosing and one to agitate the clay slurry within the tank – worked well. The application method of spraying the clay against the direction of drain flow combined with the chosen location just upstream of the culvert enabled excellent mixing of the clay in the drain water. However, we also observed some flaws, such as some drift in the clay pumping rate over the duration of the trial, which was identified and rectified in the field when checking the clay flow rate (see section 3.2 and Figure 12). The clay dosing rate dropped from the 0.6 L/s set initially to 0.3 L/s during the middle of the trial for about 30 minutes.

Potential reasons for this include:

- a blockage in the outlet hose
- problems with the performance of the pump
- delivery of a thicker clay slurry due to insufficient mixing within the tank.

There was another drop in the flow rate towards the end of the trial when the tank started to run empty.

A flow-meter at the outlet hose should be used in future trials to continuously monitor the clay dosing rate and enable prompt readjustments if required. More robust pumps designed to pump slurries of at least 50 g solids/L would be advisable to reduce the effects of varying tank levels on dosing rates.

Mixing of the clay slurry in the dosing tank

To achieve accurate and stable dosing rates for in-stream clay application, the slurry within the dosing tank needs to be well-mixed and have a known solids content.

The recirculation pumping system we used before and during this trial (Figure 6) efficiently homogenised the slurry. This was confirmed by:

- a. the similar solid contents (54.10, 54.25 and 54.15 g dry weight-clay /L) in clay samples collected from different depth within the tank on the day before the trial (after recirculation with two pumps for several hours)
- b. the consistent signal of clay tracers at the first sampling site over the duration of clay dosing (apart from the dip in the turbidity profile due to the short term drop in the clay pumping rate, see above).

Although the set-up worked well for a trial of this scale (the 30,000-L holding tank was less than half full), more efficient mixing options would be required to homogenise larger clay volumes or a thickened clay slurry. We are currently exploring options to optimise the clay manufacturing process, with the aim to produce a thicker slurry to save production and transport costs. If successful, it may become necessary to mix the slurry with drain water on site before application.

Mixing options that could be explored for such applications include using mixing tanks with an automated impeller or recirculating the clay in a tank with a herringbone type outlet in the base and a sprinkler system on the top. Also of benefit would be the use of densitometer instruments to check on-site whether the clay slurry is well mixed (as an alternative to determining the clay solid content which requires drying of samples overnight).

4 Outlook and implications

4.1 Next stages of HT-clay development

Before HT-clay can be applied on a large scale, extensive laboratory testing needs to be completed to inform a detailed environmental risk assessment. This will include the investigation of clay performance under different environmental conditions such as higher salinities or varying pH ranges as well as toxicity/exposure tests with aquatic organisms, particularly filter feeders, which may be affected by increased turbidity and solids content in water treated with clay.

River Health assessments have been carried out in the downstream reach of Punrak Drain in spring 2017 (shortly after the dosing trial) to assist with the risk assessment. However, macroinvertebrate organisms where not included in the River Health survey and should therefore be studied in Punrak Drain and immediate downstream environments, if considering longer-term clay dosing at this location.

The clay production method will also be reviewed with the aim to reduce manufacturing cost in the hope that more cost-effective production will enable a widespread application of this product in rivers and estuaries.

In the near future, we will further upscale HT-clay field trials and are currently planning to treat a large section of the lower Serpentine River. The clay will be applied from a moving barge with a spray boom.

The long-term goal is to design a treatment plan for phosphorus reduction in the estuarine stretch of the Serpentine River; either by in-stream clay application at Punrak Drain or by regular clay applications at the lower Serpentine River itself.

4.2 Dosing plant and monitoring considerations for potential future trials

- Install a flow-meter at the outlet hose that sprays the clay into the drain for immediate adjustments of the clay flow rate if required.
- Consider using pumps specifically designed for slurries with a high solids content.
- Install purpose-built structure for more accurate drain discharge measurements.
- Develop a more efficient method to homogenise the clay slurry in the tank, especially if larger clay volumes or a thickened slurry will be used.
- Deploy water quality loggers for several weeks as part of a future trial to evaluate any effects of the clay treatment on variables such as dissolved oxygen.
- Deploy auto-samplers when dosing over several days.

References

ANZECC & ARMCANZ 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality Paper No. 4. Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand

Bureau of Meteorology (BOM) climate data website: www.bom.gov.au/climate/data/

- Kelsey, P, Hall, J, Kretschmer, P, Quinton, B and Shakya D 2011, Hydrological and nutrient modelling of the Peel-Harvey catchment, Water Science Technical Series, Report no. 33, Department of Water, Western Australia
- Kilminster, KL 2010, Sediment quality in three south-western Australian estuaries, Water Science technical series, Report no. 18, Department of Water, Western Australia.
- Tulipani, S. 2019. Lower Vasse River water treatment trials 2016–2018: synthesis report. Single column report Water Science Technical Report

Appendices

Appendix A - Additions to method section

Estimation of drain discharge

Drain discharge estimations involved measuring the cross-sectional area of the drain and the average flow velocity across this area.

The discharge estimation was calculated as: $Q = 0.85 \times V \times A$. where Q is flow in m³/s, V is average velocity in m/s and A is the cross-sectional area (m²).

The discharge was estimated at two locations near the clay dosing site. The sites were chosen at narrow and straight sections of the drain with a relatively uniform riverbed. Efforts were made to avoid sections where water ponds.

The cross-section of the semicircular channel was estimated as 2/3 x width x depth.

The flow velocity was measured using a Valeport Model 801 electromagnetic open channel flow-meter, taking 85 per cent of this value to estimate the average cross-sectional velocity. Three velocity measurements were taken across the drain width and the average was used for the discharge calculation.

Equation used to estimate discharge:

 $Q = 0.85 \times V \times 2/3 \times D \times W$

Where:

- Q: Discharge in m³/s
- V: Flow velocity in m/s
- D: Depth in the middle of the drain/culvert (in m)

W: Drain width (in m)

Spiking of the drain with sodium phosphate

Because of the unexpectedly low FRP concentrations we had to spike the drain with a small amount of phosphate in order to be able to observe a phosphorus reduction by the clay treatment. This was achieved by adding 0.5 M sodium phosphate solution (NaH₂PO₄) at a pumping rate of 0.0018 L/s to the drain about 100 m upstream of the clay dosing site. The peristaltic pump used for this purpose was started one hour before to clay dosing and stopped shortly after the end of the trial when the tank had run empty.

Removal of supernatant water from the tank

To enhance the solid content in the clay slurry the supernatant water which had accumulated above the clay slurry as a result of further settling over several weeks was removed from the tank by using a 50 mm diameter hose and a petrol pump. The end of the hose which was fed through the manhole of the tank was equipped with a one-way valve to enable priming of the hose with drain water.

Determination of clay solid content

Three clay slurry samples were collected from different depths within the tank using a grab pole sampler, and 20 mL from each sample were weighed and dried in small aluminium trays in an oven at 105°C for eight hours. The dry residues were weighed immediately once removed from the oven.

Calculations of clay amounts and dosing rates

The total clay slurry volume was calculated from the measured fill-height in the tank and the tank diameter. The total weight of dry-weight clay was calculated from the average of the measured solid contents and the total slurry volume.

The targeted clay dosing rate was 1 g dry weight clay/mg P. The required clay pumping rate of 0.6 L/s was calculated from the targeted spiked FRP concentrations (0.2 mg P/L), the estimated drain discharge (0.17 m³/s) and the clay volume and solid content.

Adding sodium bromide to the clay

A total of 75 kg of sodium bromide was added to the clay as a tracer to follow the clay movement. The salt was mixed with the clay slurry in an external 1000-L bulky box outside of the tank to reduce manual handling risks of the 25 kg bags (see Figure 20). The targeted bromide concentration in drain water was 20 mg/L. The required sodium bromide amount was calculated based on the previously determined clay flow rate and estimated drain discharge.



Figure 20: Method used to dose sodium bromide to the clay. Inner diameter of hoses was 50 mm.

Water quality sampling procedures

Water samples were collected with a grab pole just below the surface, avoiding any surface scum and debris. To avoid contamination, nitrile gloves were worn during collection and when handling the samples. Filtering of the samples for the analysis of filterable nutrients and dissolved organic carbon was conducted in the field immediately after sample collection using syringes and 0.45 μ m single-use filter cartridges. Grab pole sampler, syringes, filter cartridges and sample containers were pre-rinsed three times with the appropriate sample before using them.

After collection the water samples were placed in an esky with ice bricks for transport and then stored in a refrigerator at 0-4°C. Water samples for magnesium and aluminium analysis were preserved with small amounts of nitric acid. Analyses were performed in the laboratories of ALS within appropriate sample holding times and according to standard APHA methods.

Appendix B – Quality control (QC) sampling

QA protocols for fieldwork described below have been derived from AS/NZ 5667.1:1998. QC samples were taken at a random site and at a random sampling time.

Field blanks

Field blanks look at the quality of the sampling procedure as well as the integrity of the DI water being used to rinse sampling equipment. Field blanks are prepared in the field with the same DI water used to rinse the equipment.

At the randomly selected QC-sampling site a spare set of bottles for each of the analysed laboratory variables was filled with DI-water, using the same bottle types and procedures for each variable as in the collection of field samples (e.g. filtering vs. not-filtering, preservative in bottles and pre-rinsing of sample bottles).

The blank samples were treated and analysed in the same way as the normal field samples.

Field Replicates

Field replicates look at the amount of variability in a sample at a site. One set of field replicates for each of the analysed variables were collected immediately after the actual field samples, while treating them as a completely different set of samples (e.g. rinsing of equipment after collection of the original sample, use of a new filter cartridge etc.). After collection the replicate samples were treated and analysed in the same way as the normal field samples.

Field duplicate samples

Field duplicate samples look at sampler error in sample handling and processing. A set of field duplicates is collected together with the original field sample in a large pre-rinsed container, which is then split up to fill the appropriate sample bottles for each variable and perform filtering where required (one set of bottles for original field sample and one set of bottles for duplicate samples).

Results of QC sampling

, .				
	Original sample	Field Duplicate	Field Replicate	Field Blank
Sampling time	16:15	16:15	16:30	16:10
TSS (mg/L)	65	75	72	<1
Br ⁻ (mg/L)	13.8	13.9	13.2	<0.010
Total Alkalinity (mg CaCO₃/L)	41	40	40	<1
HCO₃ ⁻ Alkalinity (mg CaCO₃/L)	41	40	40	<1
CO₃ ⁻ Alkalinity (mg CaCO₃/L)	<1	<1	<1	<1
OH ⁻ Alkalinity (mg CaCO₃/L)	<1	<1	<1	<1
Mg (mg/L)	20	19	18	<1
AI (mg/L)	4.48	4.36	4.23	<0.01
Reactive Silica (mg Si /L)	2.21	2.15	2.17	<0.005
TN (mg/L)	0.657	0.681	0.744	<0.025
TP (mg/L)	0.100	0.121	0.125	<0.005
FRP (mg P/L)	0.012	0.025	0.02	<0.005
DOC (mg/L)	9	8	8	<1

Table 8: Results from quality control sampling. A duplicate and a replicate sample of a regular sample at PD-fenceline were collected during clay dosing. The field blank sampling was conducted with Milli-Q water.

Appendix C – Discussion of discharge measurements

The drain discharge was estimated on the day before the trial at two locations near the dosing site based on flow-velocity measurements with a portable flow-meter (see Appendix A). There was no significant amount of rainfall overnight at the clay dosing site or further upstream (Bureau of Meteorology climate data website), therefore we did not expect any variations of the drain discharge from the previous day.

Nevertheless, the measured bromide tracer and spiked phosphorus concentrations were substantially lower than the targeted concentrations, suggesting that the drain discharge was likely underestimated (see Section 3.4, Table 6).

The estimated drain discharge varied significantly when using different calculation methods:

- measuring flow velocity and cross sectional drain area (was used to calculate trial parameters); 0.170 m³/s
- using bromide concentrations in the drain water and clay pumping rates for retrospective calculations; 0.27 m³/s
- correlating previous discharge estimates at the trial site (based on flow velocity measurements) to discharge data from a gauging station 3.4 km upstream; 0.22 m³/s (see correlation in Figure 21)

Each of these methods has benefits and but also specific sources of error:

- The discharge estimation used for the current trial uses approximations for (a) the average flow velocity (which is not uniform over the entire cross section of the drain) and (b) the calculation of the cross section itself from measurements of drain width and depth in the middle of the channel (Appendix A). Furthermore, small obstructions (e.g. plants) or some unevenness in the drainage channel, may lead to errors in the flow velocity measurements, despite choosing shallow and narrow drain sections with a near-uniform bed and measuring at two different locations.
- The correlation of drain discharge estimations at the trial site to discharge measured by the upstream gauging station also relies on the same discharge estimation method. However, despite some outliers, there was a clear linear relation of the discharge at both locations (R²= 0.96; Figure 21B). In addition, the quality control measurements with the same discharge estimation method at the gauging station showed good agreement to the gauging station measurements (Figure 21A). The discharge was monitored fortnightly at HNNCULV (current trial site) from 10/05/2016 to 05/09/2017 and at PD1 (location of gauging station) from 03/11/2016 to 27/06/2017.
- The subsequent discharge estimation calculated from the concentrations of the bromide tracer may have been influenced by some variations in the clay pumping rate, which did occur over the trial. The calculation also assumes complete mixing of the bromide in the drain water. The average bromide concentration in the drain during the trial was 14.2 mg/L (12.7-15.4 mg/L), the

average bromide concentration measured in the clay slurry was 6.34 g/L (0.606 and 0.661 g/L) and the clay pumping rate during most of the trial was 0.6 L/s. The discharge calculated from the first bromide measurement at the beginning of the trial (shortly after setting the clay pumping rate) was similar to the average discharge calculated over the entire trial duration (0.27 m³/s).

 Even the highest drain discharge calculated by any of these methods cannot solely explain the low spiked FRP concentrations, which were only ca. 1/3 of the target value. This indicates some loss of phosphate in the upstream drain section, incomplete mixing or some variation in the pumping rate used for P-spiking.



Figure 21: Comparison of discharge estimates from fortnightly flow velocity measurements at Punrak Drain with Hydstra discharge records from a gauging station 3.4km upstream of the clay dosing site (PD1).



Appendix D - Additional figures

Figure 22: Total alkalinity and pH at the different sample locations along Punrak Drain during HT-clay dosing. Coloured labels indicate when the clay was present at a particular sampling site, 'DS' stands for downstream of the clay dosing site.



Figure 23: Total solid content (TSS) vs. Turbidity during clay application along the treated drain section.

Appendix E - All Data

Table 9: Water quality data in water samples collected during the clay dosing trial on 25/10/2017. A coloured cell background indicates that the clay plume was present at the site (based on in-situ clay tracers and visual observations). These samples were used to calculate average values during clay dosing. n.d. = not determined

Time	TSS (mg/L)	Br ⁻ (mg/L)	HCO₃ ⁻ Alkalinity (mg CaCO₃/L)	CO ₃ ⁻ Alkalinity (mg CaCO ₃ /L)	OH ⁻ Alkalinity (mg CaCO₃/L)	Total Alkalinity (mg CaCO₃/L)	Mg (mg/L)	Al (mg/L)	Reactive Silica (mg Si/L)	NH₃ (mg N/L)	NOx (mg N/L)	DON (mg/L)	TN (mg/L)	TP (mg/L)	FRP (mg/L)	DOC (mg/L)
10 m	upstrea	am of d	osing site (P	PD-10m Upst	r)											
10:50	2	0.27	30	<1	<1	30	10	0.53	2.17	0.032	0.105	0.62	0.809	0.197	0.076	14
11:40	0	0.26	29	<1	<1	29	10	0.44	2.25	0.028	0.109	0.61	0.68	0.191	0.064	18
12:30	2	0.26	28	<1	<1	28	10	0.46	2.25	0	0.114	0.2	0.717	0.187	0.046	15
13:20	2	0.27	30	<1	<1	30	9	0.44	2.24	0.027	0.109	0.63	0.724	0.166	0.066	16
14:10	2	0.27	25	<1	<1	25	9	0.46	2.37	0.015	0.113	0.51	0.735	0.17	0.053	14
15:00	1	0.26	30	<1	<1	30	10	0.45	2.24	0.012	0.115	0.62	0.721	0.169	0.059	18
15:50	2	0.27	28	<1	<1	28	10	0.56	2.22	0.072	0.114	0.6	0.741	0.179	0.072	19

Time	TSS (mg/L)	Br ⁻ (mg/L)	HCO ₃ - Alkalinity (mg CaCO ₃ /L)	CO ₃ ⁻ Alkalinity (mg CaCO ₃ /L)	OH ⁻ Alkalinity (mg CaCO₃/L)	Total Alkalinity (mg CaCO ₃ /L)	Mg (mg/L)	Al (mg/L)	Reactive Silica (mg Si/L)	NH ₃ (mg N/L)	NOx (mg N/L)	DON (mg/L)	TN (mg/L)	TP (mg/L)	FRP (mg/L)	DOC (mg/L)
30 m	downst	tream o	of dosing site	e (PD-30m D	ownstr)											
11:05	103	13.90	42	<1	<1	42	21	5.55	2.13	0.026	0.128	0.16	0.734	0.096	0.02	8
11:55	113	15.40	41	<1	<1	41	22	6.35	2.26	0.026	0.128	0.43	0.61	0.089	0.019	8
12:45	108	14.30	44	<1	<1	44	22	5.83	2.25	0.026	0.129	0.17	0.76	0.094	0.021	11
13:35	109	14.70	42	<1	<1	42	22	5.77	2.12	0.023	0.13	0.5	0.605	0.094	0.019	9
14:25	117	14.40	43	<1	<1	43	22	5.84	2.13	0.028	0.133	0.45	0.602	0.1	0.019	11
15:15	100	12.70	41	<1	<1	41	20	5.21	2.14	0.028	0.134	0.52	0.706	0.114	0.026	11
16:05	4	0.34	30	<1	<1	30	10	0.55	2.24	0.029	0.113	0.47	0.764	0.165	0.073	16

Time	TSS (mg/L)	Br ⁻ (mg/L)	HCO ₃ - Alkalinity	CO₃ ⁻ Alkalinity	OH ⁻ Alkalinity (mg CaCO₃/L)	Total Alkalinity	Mg (mg/L)	Al (mg/L)	Reactive Silica	NH₃ (mg N/L)	NOx (mg N/L)	DON (mg/L)	TN (mg/L)	TP (mg/L)	FRP (mg/L)	DOC (mg/L)
4.0 1		- 1	(mg CaCO₃/L)	(mg CaCO ₃ /L)		(mg CaCO₃/L)			(mg Si/L)							
1.2 KN	n aown	stream	i of dosing s	ite (PD-Fenc	eline)											
12:54	0	5.51	31	<1	<1	31	12	1.46	2.16	n.d.			0.676	0.143	0.035	14
13:46	69	14.40	39	<1	<1	39	18	4	2.04				0.643	0.112	0.015	8
14:45	73	13.30	39	<1	<1	39	18	4.01	2.21				0.632	0.108	0.018	8
15:26	67	11.40	39	<1	<1	39	19	3.76	2.17				0.671	0.113	0.022	10
16:15	65	13.80	41	<1	<1	41	20	4.48	2.21				0.657	0.1	0.012	9
17:06	24	11.50	40	<1	<1	40	18	3.89	2.17				0.708	0.123	0.018	10
18:07	9	1.51	32	<1	<1	32	12	1.13	2.26				0.763	0.144	0.043	15

Time	TSS (mg/L)	Br [.] (mg/L)	HCO ₃ - Alkalinity (mg CaCO ₃ /L)	CO ₃ ⁻ Alkalinity (mg CaCO ₃ /L)	OH ⁻ Alkalinity (mg CaCO₃/L)	Total Alkalinity (mg CaCO₃/L)	Mg (mg/L)	Al (mg/L)	Reactive Silica (mg Si/L)	NH₃ (mg N/L)	NOx (mg N/L)	DON (mg/L)	TN (mg/L)	TP (mg/L)	FRP (mg/L)	DOC (mg/L)
1.8 kr	n down	stream	of dosing s	ite (PD-Delta	a)											
13:04	0	0.27	29	<1	<1	29	10	0.49	2.13				0.748	0.126	0.025	14
14:18	4	4.09	30	<1	<1	30	12	1.09	2.16				0.709	0.122	0.029	16
15:05	35	13.10	35	<1	<1	35	16	2.82	2.11				0.618	0.094	0.017	9
15:55	51	13.90	38	<1	<1	38	17	3.53	2.11				0.631	0.097	0.01	16
16:45	54	11.40	36	<1	<1	36	17	3.16	2.11				0.653	0.108	0.014	17
17:35	56	13.70	39	<1	<1	39	19	3.68	2.12				0.652	0.096	0.013	8
Samp	ling sit	es with	nin Delta just	t upstream o	f Lake Amar	illo										
17:45	19	12.80	37	<1	<1	37	17	3.44	2.01				0.674	0.102	0	12
17:50	56	13.00	39	<1	<1	39	17	3.5	1.97				0.671	0.1	0	11

Time	Site	TSS (mg/L)	Br ⁻ (mg/L)	HCO₃ ⁻ Alkalinity (mg CaCO₃/L)	CO₃ ⁻ Alkalinity (mg CaCO₃/L)	OH ⁻ Alkalinity (mg CaCO₃/L)	Total Alkalinity (mg CaCO₃/L)	Mg (mg/L)	Al (mg/L)	Reactive Silica (mg Si/L)	NH₃ (mg N/L)	NOx (mg N/L)	DON (mg/L)	TN (mg/L)	TP (mg/L)	FRP (mg/L)	DOC (mg/L)
'Before'	monitoring 2	4/10/20 1	17														
14:10	HNCCULV	1	0.751	31	<1	<1	31	10	0.42	2.19	0.023	0.122	0.61	0.717	0.123	0.029	12
13:38	PD-Fenceline	2	0.274	29	<1	<1	29	10	0.51	2.2				0.74	0.118	0.024	14
12:20	PD-delta	2	0.267	28	<1	<1	28	10	0.46	2.03				0.715	0.119	0.012	16
11:29	AMRLOUT	19	0.655	67	<1	<1	67	24	0.99	0.599				0.812	0.057	0.007	20
10:50	AMAR	3	0.748	76	<1	<1	76	27	0.31	1.22				0.904	0.072	0.023	19
Average	e during clay a	applicat	ion 25/1	0/2017													
11:00 - 15:15	PD-30m downstr	108 ±6.25	14.2 ±0.90	42 ±1.17	<1	<1	42 ±1.17	21.50 ± <i>0.84</i>	5.76 ±0.38	2.17 ±0.06	0.03 ±0.00	0.130 ± <i>0.00</i>	0.37 ±0.16	0.67 ±0.07	0.10 ± <i>0.01</i>	0.02 ±0.00	10 ±1.51
13:15 - 17:00	PD-fenceline	68.5 ±3.42	13.2 ±1.30	40 ±1.00	<1	<1	40 ±1.00	18.75 ±0.96	4.06 ± <i>0.30</i>	2.16 ±0.08				0.65 ± <i>0.0</i> 2	0.11 ± <i>0.01</i>	0.02 ±0.00	9 ±0.96
14:30 - 18:00	PD-Delta	49 ±9.56	13.0 ±1.14	37 ±1.83	<1	<1	37 ±1.83	17.25 ±1.26	3.30 ±0.39	2.11 ±0.01				0.64 ±0.02	0.10 ± <i>0.01</i>	0.01 ±0.00	13 ± <i>4.6</i> 5

Table 10: Water quality data in water samples collected during 'before' and 'after' monitoring of the clay dosing trial and average water quality data during clay dosing (± standard deviation).

Hydrotalcite clay trial at Punrak Drain, Peel Harvey Catchment (Oct 2017)

Time	Site	TSS (mg/L)	Br ⁻ (mg/L)	HCO₃ ⁻ Alkalinity (mg CaCO₃/L)	CO₃ ⁻ Alkalinity (mg CaCO₃/L)	OH ⁻ Alkalinity (mg CaCO₃/L)	Total Alkalinity (mg CaCO ₃ /L)	Mg (mg/L)	Al (mg/L)	Reactive Silica (mg Si/L)	NH₃ (mg N/L)	NOx (mg N/L)	DON (mg/L)	TN (mg/L)	TP (mg/L)	FRP (mg/L)	DOC (mg/L)
'After' m	onitoring 26/	10/2017															
11:27:00	HNCCULV	0	0.263	28	<1	<1	28	10	0.45	2.27	0.036	0.082	0.55	0.749	0.111	0.027	14
11:11:00	PD-Fenceline	2	0.269	28	<1	<1	28	10	0.54	2.26				0.741	0.1	0.018	15
10:48:00	PD-delta	0	0.275	28	<1	<1	28	10	0.61	2.24				0.74	0.107	0.021	14
10:11:00	AMRLOUT	186	0.756	82	<1	<1	82	28	3.45	0.556				0.85	0.027	0.009	19
9:38:00	AMAR	5	0.889	80	<1	<1	80	31	0.28	0.717				0.987	0.044	0.013	21

Table 11: Water quality data measured in-situ during the clay dosing trial on 25/10/2017. A coloured cell background indicates that the clay plume was present at the site (based on in-situ clay tracers and visual observations). These samples were used to calculate average values during clay dosing.

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
10 m upstream	n of dosing si	te (PD-10m U	pstr)			
10:04	19.763	0.4962	6.61	78.6	7.17	7.65
10:14	19.798	0.4964	6.6	78.9	7.2	7.57
10:24	19.801	0.4961	6.6	79.1	7.21	7.46
10:34	19.862	0.4962	6.61	79.6	7.24	7.54
10:44	19.958	0.4964	6.61	80.2	7.29	7.54
10:54	20.027	0.4966	6.61	80.5	7.31	7.52
11:04	20.173	0.4967	6.61	81.3	7.36	7.48
11:14	20.318	0.4968	6.62	82.2	7.42	7.4
11:24	20.446	0.4969	6.62	83	7.47	7.41
11:34	20.485	0.4969	6.62	83.4	7.51	7.46
11:44	20.507	0.4968	6.63	83.8	7.53	7.43
11:54	20.594	0.4969	6.63	84.4	7.57	7.38
12:04	20.681	0.497	6.63	85	7.61	7.38
12:14	20.763	0.497	6.63	85.6	7.65	7.47
12:24	20.913	0.4971	6.63	86.2	7.69	7.32
12:34	21.069	0.4974	6.64	87.1	7.75	7.39
12:44	21.173	0.4975	6.64	87.9	7.8	7.37
12:54	21.274	0.4977	6.64	88.5	7.83	7.42
13:04	21.414	0.4979	6.64	89.2	7.87	7.34

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
13:14	21.517	0.498	6.65	89.7	7.9	7.46
13:24	21.615	0.4983	6.65	90.2	7.94	7.42
13:34	21.641	0.4984	6.65	90.4	7.95	7.43
13:44	21.627	0.4984	6.65	90.3	7.94	7.44
13:54	21.581	0.4982	6.65	90	7.93	7.5
14:04	21.539	0.4981	6.65	89.6	7.9	7.41
14:14	21.606	0.4983	6.65	89.7	7.89	7.51
14:24	21.71	0.4985	6.65	89.8	7.88	7.36
14:34	21.714	0.4984	6.65	89.5	7.86	7.45
14:44	21.788	0.4985	6.65	89.8	7.87	7.49
14:54	21.922	0.4985	6.65	90.3	7.9	7.46
15:04	22.01	0.4986	6.65	90.8	7.93	7.48
15:14	22.012	0.4986	6.65	90.7	7.92	7.57
15:24	22.067	0.4985	6.65	91	7.94	7.54
15:34	22.058	0.4983	6.65	90.9	7.93	7.58
15:44	22.039	0.498	6.65	90.7	7.91	7.59
15:54	22.022	0.4977	6.65	90.5	7.9	7.52
16:04	21.999	0.4975	6.65	90.4	7.89	7.52
16:14	21.965	0.4972	6.65	90.2	7.88	7.73
16:24	21.95	0.4968	6.65	90	7.87	7.75
16:34	21.921	0.4964	6.65	89.8	7.85	7.76
16:44	21.891	0.496	6.65	89.5	7.84	7.69

		Specific		Dissolved	Dissolved	
Time	Temperature	Conductivity	рН	oxygen	oxygen	Turbidity
	(°C)	(mS/cm)	-	(% Sat)	(mg/L)	(NTU)
		(,				
16:54	21.847	0.4957	6.65	89.1	7.81	7.84
17:04	21.799	0.4953	6.65	88.8	7.79	8.02
17.14	01 747	0 40 49	6 65	00 E	7 77	7.01
17.14	21.747	0.4940	0.05	00.0	1.11	7.91
17:24	21.7	0.4944	6.64	88.2	7.75	7.78
17:34	21.645	0.494	6.64	87.9	7.72	7.73
17-44	21 593	0 4935	6 64	87 4	7 69	7 88
17.44	21.000	0.4000	0.04	01.4	1.00	1.00
17:54	21.541	0.4932	6.64	87	7.66	7.74
18:04	21.49	0.4927	6.64	86.6	7.63	7.76
18:14	21,444	0.4922	6.63	86.2	7.61	7.67
18:24	21.4	0.492	6.63	85.8	7.58	7.79
18:34	21.358	0.4914	6.63	85.5	7.56	7.7
30 m downstr	eam of dosing	g site (PD-30n	n Downst	tr)		
9:39	19.6	0.482	6.91	82.7	7.57	6.17
0.40	10.6	0.492	6.6	90 G	7 56	6 16
5.45	19.0	0.402	0.0	02.0	7.50	0.10
9:59	19.7	0.482	6.53	83.5	7.62	6.19
10:09	19.7	0.483	6.54	83.4	7.62	6.3
10.19	19 7	0 483	6 55	83 7	7 64	6 1 1
10.10	10.1	0.400	0.00	00.7	1.04	0.11
10:29	19.8	0.482	6.56	83.9	7.66	6.06
10:39	19.8	0.483	6.57	84.5	7.7	5.99
10.49	19.9	0.507	6.6	84.8	7.72	19.38
10:59	20.1	0.524	6.73	85.3	7.74	27.82
		0				
11:09	20.2	0.528	6.8	86	7.78	29.33
11:19	20.3	0.53	6.84	86.6	7.81	29.64

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
11:29	20.4	0.53	6.85	87.2	7.85	29.67
11:39	20.4	0.53	6.86	87.3	7.86	29.88
11:49	20.5	0.53	6.86	87.6	7.88	29.82
11:59	20.6	0.53	6.86	88.2	7.92	29.92
12:09	20.7	0.529	6.86	88.7	7.95	29.86
12:19	20.8	0.529	6.86	89.3	7.98	29.97
12:29	21	0.53	6.87	89.8	8	30.07
12:39	21.1	0.527	6.87	90.3	8.02	28.76
12:49	21.1	0.516	6.83	90.7	8.05	23.94
12:59	21.3	0.51	6.78	91.4	8.09	20.91
13:09	21.4	0.509	6.77	92	8.13	19.89
13:19	21.5	0.509	6.75	92.4	8.14	20.1
13:28	21.6	0.528	6.82	92.6	8.15	28.88
13:38	21.6	0.53	6.85	92.7	8.15	29.54
13:48	21.6	0.531	6.87	92.3	8.13	29.92
13:58	21.5	0.531	6.87	91.9	8.1	30.14
14:08	21.6	0.532	6.87	91.9	8.1	30.45
14:18	21.6	0.528	6.85	92.2	8.11	28.77
14:28	21.7	0.523	6.84	92.1	8.1	26.88
14:38	21.7	0.523	6.82	92.2	8.09	26.64
14:48	21.8	0.523	6.82	92.4	8.09	26.58
14:58	21.9	0.523	6.82	92.6	8.1	26.57

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)	
15:08	22	0.523	6.82	92.7	8.1	26.59	
15:18	22	0.514	6.81	92.8	8.1	22.38	
15:28	22	0.495	6.73	93	8.11	12.12	
15:38	22	0.488	6.66	92.7	8.1	7.93	
15:48	22	0.486	6.64	92.7	8.1	6.83	
15:58	22	0.485	6.63	92.4	8.08	6.43	
16:08	21.9	0.484	6.62	92.1	8.06	6.29	
16:18	21.9	0.484	6.61	91.9	8.04	6.32	
16:28	21.9	0.484	6.61	91.8	8.04	6.28	
16:38	21.8	0.483	6.61	91.6	8.03	6.31	
1.2 km downs	1.2 km downstream of dosing site (PD-Fenceline)						
11:13	21	0.483	7.17	107.6	9.58	9.1	
11:23	21.19	0.483	6.94	109	9.67	9	
11:46	21.26	0.482	6.88	107.7	9.54	8.8	
11:56	21.41	0.482	6.89	109.7	9.69	8.8	
12:06	21.59	0.482	6.91	111.7	9.83	8.8	
12:16	21.79	0.482	6.92	113.7	9.97	8.8	
12:26	22.09	0.484	6.95	115.5	10.07	9.7	
12:36	22.36	0.491	7.01	117.1	10.15	12.4	
12:46	22.36	0.501	7.07	115.4	10.01	16.8	
12:56	22.52	0.511	7.14	114.5	9.9	21.2	
13:06	22.73	0.518	7.22	115.2	9.92	24.2	
13:16	22.87	0.523	7.28	115.1	9.88	26.3	

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
13:21	22.93	0.525	7.28	114.9	9.86	26.8
13:24	22.93	0.525	7.29	114.7	9.84	27.7
13:34	22.99	0.527	7.32	114	9.77	28.2
13:44	22.93	0.528	7.32	112	9.61	28.8
13:54	22.8	0.528	7.31	109.1	9.38	29.4
14:04	22.71	0.529	7.29	106.8	9.2	29.8
14:27	22.95	0.527	7.31	109.3	9.37	30.4
14:28	22.94	0.526	7.31	109.1	9.35	30.5
14:38	23.01	0.522	7.29	109	9.34	29.9
14:48	23.13	0.518	7.27	110.7	9.46	29.1
14:58	23.17	0.514	7.26	111.2	9.49	28
15:08	23.18	0.514	7.25	110.4	9.42	27.9
15:18	23.19	0.516	7.26	109.7	9.36	28.7
15:28	23.19	0.519	7.28	109.5	9.35	29.9
15:38	23.11	0.521	7.28	107.7	9.21	30.8
15:48	23.06	0.524	7.3	106.3	9.1	31.5
15:58	23.02	0.524	7.3	105.5	9.03	31.9
16:08	22.96	0.524	7.28	104.3	8.94	32
16:18	22.85	0.522	7.27	103	8.85	32.1
16:28	22.78	0.521	7.26	102.3	8.8	32
16:38	22.69	0.52	7.24	101.3	8.73	31.7
16:48	22.61	0.519	7.23	100.5	8.67	31.6

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
16:58	22.48	0.517	7.21	99.2	8.58	31.3
17:08	22.36	0.513	7.17	98.1	8.51	29.5
17:18	22.25	0.507	7.11	96.9	8.42	26.3
17:28	22.15	0.499	7.06	95.8	8.34	22.4
17:38	22.04	0.492	7	94.8	8.27	18.7
17:48	21.94	0.487	6.95	93.8	8.2	16.1
17:58	21.83	0.485	6.92	92.7	8.12	14.1
18:08	21.73	0.489	6.9	91.6	8.04	12.8
1.8 km downs	stream of dosi	ng site (PD-D	elta)			
11:54	21	0.483	6.98	101.6	9.05	8.5
12:04	21.1	0.483	6.95	102.8	9.13	8.47
12:14	21.2	0.483	6.95	103.8	9.19	8.45
12:24	21.4	0.483	6.96	105	9.27	8.46
12:34	21.6	0.483	6.97	106.8	9.4	8.46
12:44	21.7	0.484	6.98	108.2	9.5	8.43
12:54	22	0.484	6.99	109.3	9.56	8.37
13:04	22.2	0.484	6.99	110.3	9.61	8.43
13:14	22.3	0.484	7	110.9	9.63	8.36
13:24	22.4	0.484	7	111.8	9.68	8.33
13:34	22.5	0.485	7.01	112.7	9.74	8.3
13:44	22.7	0.485	7.02	113.9	9.82	8.49
13:54	22.8	0.488	7.04	114.8	9.87	9.09
14:04	22.9	0.492	7.07	114.9	9.87	10.45

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
14:14	23	0.499	7.12	114.6	9.82	12.25
14:24	23	0.506	7.17	113.8	9.74	14.46
14:34	23.1	0.514	7.21	112.7	9.64	16.52
14:44	23.1	0.52	7.26	112	9.57	18.2
14:54	23.2	0.525	7.3	111.6	9.52	19.25
15:04	23.3	0.529	7.33	111	9.45	20.24
15:14	23.3	0.531	7.34	109.8	9.35	21.37
15:24	23.3	0.533	7.35	108.3	9.23	22.27
15:34	23.3	0.534	7.35	107.4	9.15	23.4
15:44	23.3	0.535	7.36	106.9	9.11	24.51
15:54	23.3	0.534	7.36	106.7	9.09	25.95
16:04	23.3	0.532	7.36	106.5	9.07	26.94
16:14	23.3	0.53	7.34	106.4	9.07	27.46
16:24	23.3	0.527	7.33	106.3	9.06	22.52
16:34	23.3	0.526	7.31	105.8	9.02	21.81
16:44	23.2	0.526	7.31	105.1	8.96	22.12
16:54	23.2	0.527	7.31	104.2	8.9	22.64
17:04	23.1	0.529	7.3	103.1	8.82	23.38
17:14	23	0.532	7.31	101.9	8.73	23.69
17:24	22.9	0.533	7.31	100.8	8.65	23.97
17:34	22.9	0.534	7.3	99.7	8.57	24.45
17:44	22.8	0.534	7.3	98.7	8.49	24.85

22.8

17:50

Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
17:54	22.7	0.534	7.29	97.7	8.42	24.99
Sampling sites within Delta just upstream of Lake Amarillo						
17:44	22.9	0.532	7.71	100	8.59	18.92

7.69

98.8

8.5

19.8

0.532

Site	Time	Temperature (°C)	Specific Conductivity (mS/cm)	рН	Dissolved oxygen (% Sat)	Dissolved oxygen (mg/L)	Turbidity (NTU)
'Before' moni	toring 24	/10/2017					
HNCCULV	14:10	22	0.481	6.82	95.8	8.36	6.4
PD-Fenceline	13.38	23.3	0.479	7.07	120.5	10.26	7
PD-delta	12:20	22.6	0.477	7.84	113.1	9.76	6.3
AMRLOUT	11:29	22.4	1.143	7.77	109.3	9.47	19.4
AMAR	10:50	21.3	1.246	7.47	71.2	6.29	7.1
Average durii	Average during clay application 25/10/2017						
HNCCULV	11:00 - 15:15	21.2 ±0.59	0.53 ±0.01	6.83 ±0.04	90.3 ±2.42	8.02 ±0.13	27.7 ±3.16
PD-Fenceline	13:15 - 17:00	22.9 ±0.19	0.52 ±0.00	7.28 ±0.03	108.2 ±4.61	9.27 ±0.38	29.9 ±1.76
PD-delta	14:30 - 18:00	23.2 ±0.19	0.53 ±0.01	7.32 ±0.04	105.8 ±4.35	9.04 ±0.35	22.9 ±2.74
'After' monito	oring 26/1	0/2017					
HNCCULV	11:27:22	20.3	0.473	7	86.3	7.78	6.31
PD-Fenceline	11:11:57	20.8	0.473	7.11	100.2	8.96	7.05
PD-delta	10:48:00	20.3	0.471	7.81	95.4	8.62	8.53
AMRLOUT	10:11:45	20.5	1.265	7.82	103.5	9.29	99.37
AMAR	9:38:16	21	1.408	7.41	69.6	6.18	7.16

Table 12: Water quality data measured in-situ during 'before' and 'after' monitoring of the clay dosing trial and average data during clay dosing (± standard deviation).

Shortened forms

Avg	Average
DO	Dissolved oxygen
DOC	Dissolved organic carbon (nonpurgeable)
DON	Dissolved organic nitrogen
DWER	Department of Water and Environmental Regulation
FRP	Filterable reactive phosphorus
HT-clay	Hydrotalcite clay
QC	Quality control
REI	Regional Estuaries Initiative
Stdev	Standard deviation
TN	Total nitrogen
ТР	Total phosphorus
TSS	Total suspended solids
WQ	Water quality