Entry to the Stockholm Junior Water Prize 2020

CRACK for the FUTURE:

The use of eggshell waste as a bio-adsorbant of phosphates for water and soil quality

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PERSONAL INTRODUCTION:

I am part of gen Z, often depicted as boring, sensible and hopelessly screen addicted. Am I? Or do I just feel an overwhelming responsibility for our future by having to address the consequences of older generational choices?

Growing up on a remote rural property instilled responsibility, problem solving techniques and time management into my psyche. It also exposed me to the unique balance within ecosystems and the absolute power of nature and its forces.

I have always asked questions and researched their answers. In 2018 I attended the International Science and Engineering Fair (ISEF) in Pittsburgh as part of the Australian Young Scientist Team, after being named NSW Rural Young Scientist of the Year. In 2019 I was again named NSW Rural Young Scientist of the Year and attended ISEF in Phoenix, where I was awarded third place in my category. In 2020 I was hoping to represent Australia at ISEF in Anaheim, however this was cancelled due to the Covid-19 pandemic.

My perusal of scientific research has given me a platform to promote my passion, which is giving rural young people, particularly women, a voice in STEM on the world stage. Rather than being boring and sensible, STEM is exciting, progressive and the key to our future which so many of my generation have the ideas, determination and technology to preserve.

I am currently studying a Bachelor of Mathematics and MD at the University of Queensland. I will continue to mentor and challenge young scientists, particularly those from a rural background, to pursue the answers to their questions.

SUMMARY:

Phosphate run-off into natural waterways from agricultural fertilisers and animal manures can cause eutrophication. Agricultural operations are large consumers of non-renewable fertilisers and large producers of biowaste materials. These issues come at great economic and environmental cost.

This study's aim was to offset these issues by identifying eggshell as a potential biowaste adsorbent, examining its effectiveness in decreasing the orthophosphate concentration in aqueous solutions, and its direct application to run-off areas as adsorbents and soil conditioners. Eggshell was selected based on its abundance, availability, cost, renewability and biodegradable properties. Tests conducted in simulated superphosphate run-off rainwater over 24 hours, indicated that eggshell decreased orthophosphate levels by 62% on average. Testing on eggshell waste, at 6 hourly intervals and in manure/rainwater run-off simulation, showed average orthophosphate reductions of 59% and 55%, indicating effective adsorption. Costs and benefits were investigated comparing the use of eggshell waste for the dual purpose of phosphate adsorption and soil conditioning. A mathematical model and website (www.po4cleaner.com) was developed to calculate cost savings and application rates of eggshell. History has shown that global change is achieved through action on a local scale. The website provides farmers with a free, accessible tool to help counteract their environmental footprint and create global change. This study concluded that the economic and environmental benefits of agricultural use of biowaste products, such as eggshell, as an adsorbent and soil conditioner, appear to have been undervalued and underutilised.

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LITERATURE REVIEW

Phosphorus is essential for growth and development of living organisms *(Nguyen et al. 2012)* and as such is critical to maintaining food security and life on earth. It is also a principal material of many industries, such as fertilisers, detergents, paints, corrosion inhibitors, beverages and pharmaceuticals *(Biswas et al. 2008)*. Such anthropogenic use of phosphorus and resultant high phosphorus waste streams from these industries plus animal manures, human excreta and human food waste impact on naturally existing ecosystem services and biodiversity. *(MacDonald et al. 2016)*.

Human-induced phosphorus loss to surface waters is considered one of the main culprits in eutrophication (*Scavia et al. 2014)*, and is recognised as the single greatest cause of water quality deterioration in freshwater and coastal marine ecosystems worldwide (*Smith and Schindler, 2009; Schindler, 2012*). Eutrophication occurs when elevated nutrient concentrations in the water stimulate the growth of bacteria, algae and aquatic macrophytes, leading to the degradation of bodies of water from reduced sunlight and changes in water oxygen levels, detrimental to aquatic life. In freshwater environments, biomass production is most often proportional to phosphorus concentrations (*Schindler 1977, Baird and Cann 2005*). Eutrophication affects the aesthetic and ecological values of these ecosystems, but can also cause economic loss and adverse effects on people's health(*Nguyen et al. 2007*). Decreasing the load of phosphorus already in and entering natural waterways is central to preventing eutrophication and environmental damage (*McDowell et al. 2007*).

The overexploitation of phosphorus ores leads to concern about the decline in global reserves of these natural resources, estimated to reach their peak in the next 50-100 years (*Aryal and Liakpolou-Kyriakides, 2011, Yoshida et al 2013*). Phosphorus must be managed more judiciously in the food chain to ensure future availability of phosphorus supply and affordability (*Cordell and Neset 2014, Mew 2016*). This highlights a pressing need for innovative, cost-effective and sustainable solutions for phosphorus removal plus re-use and recovery from all available waste streams, including run-off into, and phosphorus already in natural waters. (*Drizo et al. 2016*). This is important as Australia uses around 4 million tonnes of superphosphate annually (*NSW DPI 2018).*

Two forms of phosphorus, particulate and dissolved, can be transported via surface run-off and subsurface flow into surface waters (*Penn et al. 2012*). Dissolved phosphorus is 100% bio-available upon reaching a water body and can be transported in moving water even if erosion is eliminated. This is becoming more prevalent in areas where soil is becoming saturated in phosphorus from historical phosphorus inputs (legacy phosphorus), which increases phosphorus mobilisation (*Withers, 2016*), as well as directly from recently surface applied and non-incorporated fertiliser and manure application in urban and agricultural areas. To manage dissolved phosphorus, remedies have been studied to remediate phosphorus contaminated waters.

Techniques employed to remove phosphorus from water include adsorption and chemical precipitation, enhanced biological removal and constructed wetlands (*Ramasahayam et al, 2012*). Factors that influence phosphate adsorption capacity and rate are initial phosphate concentration, contact time, sorbant dosage, temperature, pH of the solution, surface area and ionic strength. A growing trend is establishing treatment methods that are environmentally friendly and inexpensive. Absorption of phosphorus enables possible recovery and re-use of the resource. Phosphorus sorbents can be categorised as natural materials, industrial by-products and manufactured material (*Klimeski et al 2012, Cucarella and Renman 2009*). Successful sorbing materials tested can be chemically classified into metals (Fe and Al) containing materials, materials containing soluble divalent earth metals (Ca, Mg) and mixtures of the two. Other materials have also been tested (*Ramasahayam et al, 2012*). Of particular relevance to an environmentally friendly, abundantly available, economically efficient and sustainable solution are the phosphorus adsorption properties of bio-waste materials which have the potential to be directly regenerated as a fertiliser in agricultural and urban situations (*Ismail, 2012*). Most of these studies have been performed with modified biosorbents. There are uncommonly few papers employing biosorbents in natural/raw form for this purpose (*Nguyen et al 2012*), with a view to possible direct application to sources of run-off such as fertilisers and manures on pastures in a primary production environment. This is particularly relevant to phosphate adsorbent capacity and rate, where influencing factors vary according to the location.

Farming processes generate different kinds of wastes that potentially cause environmental problems from their disposal. On a global scale, the management of agricultural wastes is essential and a crucial strategy as it becomes a critical factor for humans, animals and vegetation. (*Al Seadi, Holm-Nielsen 2004*). Agricultural processes also consume large amounts of limited natural resources such as fertilisers and soil conditioners. During the twelve months to June 2015, it was estimated that 1.4 million tonnes of phosphate based fertiliser were applied to 11 046 thousand hectares and over 3 million tonnes of lime and dolomite were spread to condition Australian soils. (ABS, 4627.0 - Land Management and Farming in Australia, 2014-15).

The present work has tried to develop simple methodologies for controlling and capturing phosphate run-off by evoking sorption abilities of biowaste materials. This study focuses on recycling eggshell that (1) produces environmental damage by current disposal methods, (2) is readily available to agricultural producers, (3) has the capacity to adsorb and capture phosphorus by direct application to soils, and (4) has additional benefits by direct application and incorporation into soils and pastures (5) is inexpensive and easy to utilise.

SCIENTIFIC RESEARCH QUESTIONS

What effect does the application of eggshell have on the orthophosphate concentration in polluted water?

1. What effect does the agricultural bio-waste - eggshell have on the levels of orthophosphate in polluted waters, under certain conditions and over time?
2. Does application of the eggshell act as an effective bioadsorbant of phosphorus run-off in a practical environment, under natural conditions?
3. What are the economic and environmental costs and benefits of readily available, natural, inexpensive, agricultural bio-waste products being applied in a practical farming situation, as a source and adsorbent of nutrients?

SCIENTIFIC HYPOTHESIS

I hypothesise that if crushed, untreated eggshell is added to contaminated water, the orthophosphate levels will reduce. Eggshell with its texture and mineral composition will exhibit phosphorus adsorbent properties, with there being a maximum phosphorus uptake creating an equilibrium. Time will affect the rate of adsorption.

I predict that in an agricultural application, eggshell will provide an effective adsorbent of orthophosphates from manure and fertiliser run-off, resulting in a reduction in water pollution eutrophication, providing a beneficial addition to soil morphology via essential mineral additions to the soil.

H_0 - Eggshell will not decrease the mean level of orthophosphate in solution regardless of time

H_a - Eggshell will decrease the mean level of orthophosphate in solution.

METHODOLOGY

a) Materials:

1. *The bio-waste product eggshell was chosen with the following rationale:*

Eggshell is easily accessible as a kitchen and primary production waste product. It contains calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%). The shell is a complex, porous structure which can be divided into six different layers of membranes, crystals and cuticles (Stadelman 2000). The eggshells were crushed to size > 10mm side, rinsed in rain water and air dried (<230C). Over 250 000 tons is produced annually (Verma et al. 2019), and can be used as a limestone substitute in agriculture.

2. *Other materials required*

- Scales
- Thermometer
- Litmus paper
- Funnel
- Clean rainwater
- Dried animal manures
- Syringes
- Sample pots
- Gloves
- Blender
- Spectrophotometer
- Sterile 300ml & 1000ml containers with lids
- Superphosphate fertiliser (Incitec Super Perfect 0:9:0:0)

b) Scientific Testing

1. Trial 1: Testing of eggshell as a biosorbent
    1.1. pH of water was measured
    1.2. Three trials were undertaken - 95 grams eggshell soaked in 500ml rainwater/phosphate solution (concentration 17.3 mg/L).
    1.3. Water samples taken 6 hour intervals over 24 hour period for filtration and analysis in numbered sample pots
    1.1. pH was measured every 6 hours
    1.4. Sampling syringe was washed between samples
    1.5. Samples were transported to lab for testing.
    1.6. Testing of water sample for orthophosphate (colorimetric "blue" method)
        1.6.1. Water sample pots kept refrigerated until transported to lab
        1.6.2. Filter water sample using a syringe filter (0.45 micron) into cuvette
        1.6.3. Performed necessary dilutions 1:5
        1.6.4. Put water sample into cuvette
        1.6.5. Add reagent containing ascorbic acid and ammonium molybdate to react with orthophosphate and turn blue
        1.6.6. Intensity of blue colour is directly proportional to the amount of orthophosphate in the water

Table 1: Experimental Variables Trial 1

Variable		
Amount of P adsorbed or released	Measured	Dependant
Adsorbate concentration	17.3 mg/L	Controlled
Volume rainwater added	500ml	Controlled
Contact Time	24 hours	Controlled

pH of solution	Measured	Controlled
Samples taken	Every 6 hours	
Adsorbent material	Eggshell crushed <10mm	Independent
Temperature	17-19ºC	Controlled
Surface area	Based on crushing	

2. Trial 2: Field testing of eggshell adsorption on manure/water run-off
    2.1. pH measured
    2.2. Three trials and one control were set up
    2.3. Collected dried animal manures and mixed them
    2.4. 75g eggshell soaked in 500 ml rainwater
    2.5. 500 ml rainwater added after 24 hours (pH measured)
    2.6. Sampling syringe washed between samples
    2.7. Water samples taken
    2.8. Samples transported to the lab.

Table 2: Experimental Variables Trial 2

Variable		
Amount of P adsorbed or released	Measured	Dependant
Adsorbate concentration	17.3 mg/L	Controlled
Volume rainwater added	500ml+500ml	Controlled
Contact Time	24 hours	Controlled
Manure		Controlled
Samples taken	24 hours	
pH of solution	Measured	Controlled
Adsorbent material	Eggshell crushed <10mm	Independent
Temperature	17-19ºC	Controlled
Surface area	Based on crushing	

3. Economic and environmental modelling of biowaste applications to practical farming situations

- Obtain actual costings of existing superphosphate, lime and potential costing of biowaste applications.
- Examine economic and environmental costs and benefits of biowaste utilisation.
- Build a mathematical model in Excel and website to show weekly eggshell application required to negate phosphate run-off, taking into account the following:
  - Total phosphorus production in manure based on the type and number of animals
  - Average amount of rainfall run-off from proposed area based on annual rainfall based on ground coverage
  - Actual costing of lime and superphosphate applications for area

c) Validity

To ensure this study was valid, all variables apart from the independent variable and dependent variable were kept constant through the use of controls, careful experimental design and clear assumptions. Trials were run in parallel for each separate test

- Variables (pH, temperature, time, concentrations) consistent for each trial
- A common, mixed source was used for water and biowaste material samples
- The source of water was constant temperature (18-19^{0}C).
- Superphosphate fertiliser was added to water at a rate representative of run-off from a rain event after super was applied at a rate of a bag to the acre and 10mls of rain in a short period of time
- Dried animal manures were used to ensure results in trial 2 were reflective of water run-off from a current paddock after a theoretical rain event.
- The eggshells used were from a cross section of chicken breeds and ages but were washed and processed in one batch from which samples were taken to ensure consistency across all trials.
- Suitable measuring equipment was used including a spectrophotometer correct to two decimal places, a measuring scale accurate to two decimal places as well as graded measuring cylinders and beakers.
- Samples were analysed in accordance with "Standard Methods for the Examination of Water & Wastewater", 23rd edition, 2017, APHA

These measures and controls ensured in a fair test and controlled experiment, resulting in valid data and conclusions.

Assumptions:

- Samples of crushed eggshells surface area same by mass
- Manure profile for three samples the same
- Phosphorus content of manure samples the same
- Bioadsorption will reach an equilibrium over time
- Rainfall and run-off simulation is representative of actual event
- 4.85 mg/L indicative of superphosphate water run-off situation

d) Accuracy

The accuracy was increased with respect to the phosphate measurement in polluted water (input and output) by using the ammonium molybdate Spectrophotometric method. A spectrophotometer was used at 700nm, with results given to two decimal places in mg/L. All calculations were made using appropriate formulas on Microsoft Excel and Google Sheets to at least five significant figures, adding further accuracy to the presented data. Measuring scales accurate to two decimal places were used, cleaned and stored between use. All equipment was rinsed with rain water to avoid cross-contamination, and tests were conducted inside and covered to avoid contamination. Graded measuring apparatus were used to measure additions and samples of water.

e) Reliability

Reliability and reproducibility of results were assessed and improved through:

- Calculation of averages where possible
- Replicated and repeated trials
- Careful experimental design
- Minimisation of propensity for error in measurements
- Contamination control
- Detailed mathematical analysis

f) Risk Assessment

Table 3: Risk Assessment and Matrix

Risk	**Hazard**	**Precaution**	**Level**

Animal Manures	May contain infectious diseases or other harmful contaminants that can be transmitted	Wear gloves when handling, store in disposable containers, wash hands following use, do not inhale.	High
Contaminations on eggshell	Possibility of contamination with bacteria, such as Salmonella enteritidis	As above	Low
Handling superphosphate	Chemical exposure may cause harm to humans or animals if in excess	Use gloves when handling. Dispose of carefully to ensure that no animals/wild life are impacted adversely.	High

g) Interpretation

Nutrient concentrations of phosphate of water were analysed using a t-test (one tailed independent samples t-test assuming unequal variances) to determine significant differences in control and treatment sample means. The significance level ($p \leq 0.05$) was chosen for statistical difference between control and sample results as this is a standard level, indicating the acceptable risk of rejecting the null hypothesis and accepting the evidence for the alternative. A t-test was chosen as the data was examined and appeared to be a relatively normal distribution (small number so difficult to determine), and it was used to compare means. One tail was chosen as the data was one-directional.

RESULTS

1. Testing of eggshell over time: Trial 1

Table 4: Trial 1 Orthophosphate concentrations over time:

Sample	0 hours (mg/L)	6 hours (mg/L)	12 hours (mg/L)	18 hours (mg/L)	24 hours (mg/L)
1	17.3	13.1	10.7	8.14	7.50
2	17.3	12.7	10.4	7.32	6.96
3	17.3	12.9	9.82	7.94	7.00
pH	6	6.5	7	7	7
Mean	17.3	12.9	10.31	7.8	7.15
Std dev	0	0.2	0.45	0.43	0.3
p*		0.000344	0.000681	0.000337	0.000146

** p probability derived from t-test*

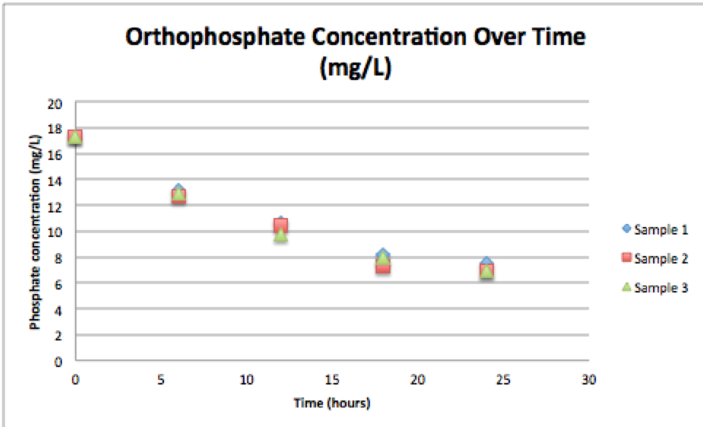


Figure 1: Orthophosphate concentration over time

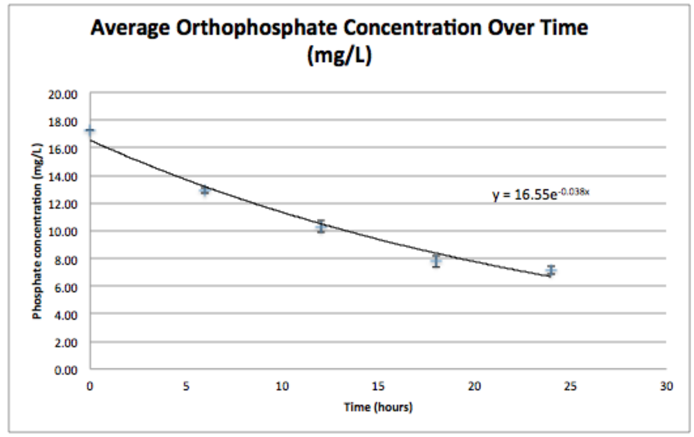


Figure 2: Avg. orthophosphate conc. over time

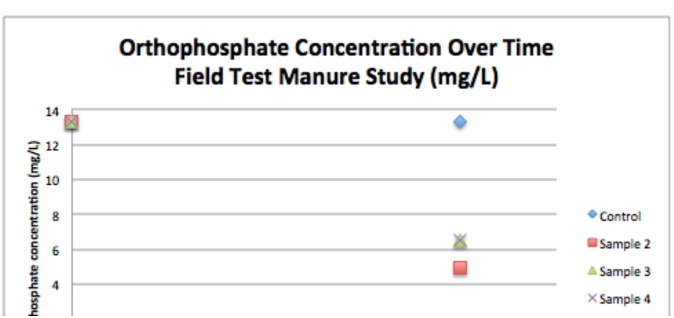
2. Field Test Results: Manure treatment with eggshell waste, run-off simulation - Trial 2

Table 5: Trial 2 - 75g eggshell in 200g dried manure after 24 hours - simulated rain event

Sample	Orthophosphate Concentration (mg/L)	% change	pH
1 (Control)	13.3		6
2	4.92	63.01%	7
3	6.56	50.68%	7
4	6.50	51.13%	7
Mean	5.99	54.96%	
Std dev	0.93		
p*	0.0026785		

p* derived from t-test

Figure 3: Orthophosphate over time trial 2



DISCUSSION

Trial 1: Testing on eggshell over time

All three samples indicated that, from an initial concentration of 17.3 mg/L (indicative of actual run-off rates from animal manures in an agricultural environment), there was a rapid initial adsorption uptake rate of phosphates and, thereafter, the absorption rate decreased gradually. This uptake rate appeared to be consistent between the trials with 95 grams of adsorbent utilised. The inference from this result is that initially all uptake sites on the surface of the adsorbent were vacant and the solute concentration gradient was relatively high. Consequently, the extent of phosphate uptake decreases significantly with the increase in contact time, which results from the decrease in the number of vacant sites on the surface of the eggshell. Also, after a lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules of the solid surface and the bulk phase. This is consistent with other adsorption studies reported. (Wang et al, 2008).

Table 6: Trial 1 Average and Percentage Changes:

Sample	0 hours (mg/L)	6 hours (mg/L)	12 hours (mg/L)	18 hours (mg/L)	24 hours (mg/L)
Mean	17.3	12.9	10.31	7.8	7.15
Percentage change		25.43%	40.40%	54.91%	58.67%
Incremental change		25.43%	20.08%	24.35%	8.33%

The mean incremental percentage change indicates that sorption equilibrium is approaching around 24 hours. Other studies have indicated that phosphorus absorption by modified biowastes reached equilibrium at variable times according to the initial concentration of phosphate. The higher the initial concentration of phosphate species, the larger is the amount of phosphate adsorbed. This increase in uptake capacity by the adsorbent may be attributed to the increase of sorbate quantity. (Mezenner etal, 2008). This is of relevance only to the estimated levels of phosphorus run-off under different agricultural conditions, and as such modifications could be made to ensure this is considered in practical situations. Adsorbent quantity also has been shown to influence the sorption equilibrium. As the dosage of adsorbent increased, the adsorption of phosphate also increased until saturation level was reached. Temperature also influenced phosphate uptake capacity for adsorbents. (Mezenner etal, 2008). Adsorbent levels would need to be calculated in accordance with estimated phosphorus run-off levels and temperature to determine an optimal balance, as per models.

Statistical testing of the sample indicates that, at a significance level of 0.05, evidence is provided that indicates a rejection of the null hypothesis and acceptance of the alternative hypothesis is reasonable.

Trial 2: Field test with manure treated with eggshell waste - run-off simulation

All three samples indicated that, from an initial concentration of 13.3 mg/L, the eggshell biowaste additives effectively adsorbed phosphorus, at a similar rate to Trial 1. An estimated equation, shown as equation 1, for this relationship between the adsorbate, and adsorbent, namely phosphate and eggshell can be depicted as follows and is proven relevant in a practical agricultural environment:

$$y = 16.55e^{-0.038x} \quad (1)$$

This equation is applicable until saturation point between the adsorbent and adsorbate has been reached. At this point, additional adsorbent would have to be applied.

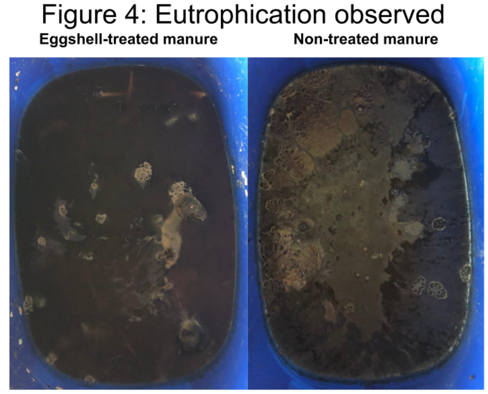
The chemical equation for the acid-carbonate reaction is shown as equation 2:

$$2H_3PO_{4\,(aq)} + 3CaCo_{3\,(s)} \rightarrow Ca_3(PO_4)_{2\,(s)} + 3CO_{2\,(g)} + 3H_2O_{\,(l)} \quad (2)$$

After 72 hours the control sample in trial 2 indicated signs of eutrophication (figure 4), whereas the eggshell treated sample did not. This was a visual sign of a green tinged film of algae on top of the water in the sample. The ratio applied in this trial was 75 gram waste eggshell to 200 gram dried manure. In a practical pasture application, this ratio could be reduced, depending on the many variables as to potential phosphorus run-off. Some considerations are as follows:

- Other decomposers such as dung beetles working on manures
- Variation in rainfall and rainfall history
- Variation in pasture species and height
- Slope of paddock
- More effective erosion control in some places
- High risk areas with high manure concentrations and run-off
- Different stocking capacities
- Variation in animal manure phosphorus concentrations
- Manures in paddocks contain higher water concentrations when fresh

Figure 4: Eutrophication observed



4. Economic and environmental modelling of biowaste applications to practical farming situations

Many studies have been performed on alternate use for eggshell waste. However the potential for use in agriculture as an adsorbent and soil conditioner and the economic and environmental benefits from this appear to have been underinvestigated and undervalued. The following analysis attempts to show biowaste applications as best methods of farming practice, providing significant economic and environmental benefit.

This study suggests that biowaste eggshell in its raw form can be used as a bioadsorbant of phosphate run-off from both manures and fertiliser applications in a practical agricultural environment. The by-product from this is a phosphorus loaded eggshell. Actual analysis of this eggshell should be obtained to ensure the de-adsorption ability of phosphorus into the soil.

Other studies have been performed on the application of eggshell as a fertiliser, showing benefits such as reduction in plant blossom-end rot disease and an increase in the nutritional intake of plants. (Hamester et al. 2012). Natural reserves of limestone ($CaCO_3$) are diminishing, non-renewable resources and studies (Neves 1998, Boron 2004) suggest that eggshell is a viable substitute, citing the low level of toxic substances present in eggshell, compared to other natural sources. As a fertiliser, eggshell waste increased the pH of soil and increased Calcium levels (Chakraborty 2007), but further testing would be required to determine whether the phosphorus adsorbed could also be reclaimed. Assuming this to be correct, the possible benefits and detrimental effects from this are discussed below:

Possible benefits:

- Important nutrients, such as phosphorus are retained within the system
- Run-off from eutrophication minerals such as phosphorus are limited, preserving pristine waterways
- Additional benefits can be obtained from addition of biowaste materials to the soil
- Potential damage caused by these biowaste materials being discarded as landfill are minimised
- Increase in soil nutrient levels such as calcium and increased pH, especially in Australian acidic soils

This is the basis for the concept of the circular economy, although not in a closed form. Possible detrimental effects of this philosophy:

- Biosecurity risks such as introduction of disease
- Possible contamination of water from other factors, such as run-off from biowaste
- Livestock consuming harmful materials, potential source of residue, contamination or disease
- Odours and pests associated with these
- Costs of transport and processing of biowaste
- Biowaste may interfere with microbiology in soil
- Introduction of harmful chemicals and pesticides

A proposed cost / benefit analysis to the environment is as follows:

Cost	Benefit	Cost	Benefit
Current: *Superphosphate and Lime application to agricultural settings*		***Proposed:*** *Use of biowaste eggshell adsorbent and lime alternative*	
Non-renewable resource		Fossil fuel costs of	Reduction in landfill

		application	including emissions
Extraction cost - use of fossil fuels, contamination of waterways, use of water		Fossil fuel cost of transport	Reduction in run-off of harmful nutrients into waterways
Processing costs - use of water, power, packaging, contamination of water, transport		Power cost of processing	Natural product being applied to soils
End-user application - use of fossil fuels, acidification of soil, potential harm to soil microbiology, possible runoff into waterways causing eutrophication		Water cost of processing	Reduction in cost of disposal of biowaste & reduction in all costs associated with extraction, processing and application of non-renewable resources (as listed)

Mathematical Model - www.po4cleaner.com

The following model has been devised for use by farmers to determine how much eggshell waste to apply as a bio-adsorbant of phosphates for water and soil quality. It aims to allow farmers to calculate eggshell application rates and frequencies and shows reductions in artificial fertiliser and lime applications required. It also shows potential environmental and economic benefits from this approach.

INFORMATION REQUIRED FOR WEBSITE MODEL

Information	Source
Rate of phosphorus adsorption	Calculation above
Mass of adsorbent	Calculated
Time	Calculated
Phosphorus captured	Calculated
Calcium of adsorbent	Secondary data
Type of manure	Input
Amount of superphosphate	Input
Annual Rainfall	Input
Phosphorus content of manure	Refer Table 7 below

Assumptions:

- Samples of crushed eggshells surface area same by mass
- Manure profile within each species the same
- Phosphorus content of manure within species the same
- Bioadsorption will reach an equilibrium over time
- Average mass of animal as per table 7
- Phosphorus content percentage as per table
- Yearly rainfall averaged over days (ie no differences in rain events)
- Factors such as evaporation, wetting, and soaking into the ground are not considered here.
- Assume equal spread of manures
- That adsorption behaves exponentially according to calculated equation (with no maximum)
- Run-off occurs over all days that entered

WEBSITE MODEL CONSTRUCTION

Table 7: Average Phosphorus Content of Manure and urine production per animal

Animal	Phosphorus Content*
Dairy Cow lactating 600 kg	Wet manure 69 kg per day. Phosphorus content 76.9 g/day
Dairy Cow dry 600 kg	Wet manure 36.1 kg/day. Phosphorus content 26.8 g/day
Beef Cow 500 kg	Wet manure 46.6 kg/day. Phosphorus content 45.2 g/day
Horse 500 kg	Wet manure 25 kg/day. Phosphorus content 30g/day
Sheep 80 kg	Wet manure 2.5 kg/day. Phosphorus content 12.5 g/day
Pigs 250 kg	Wet manure 4.5 kg/day. Phosphorus content 18 g/day
Chickens 3 kg	Wet manure 220 gr/day. Phosphorus 1.1 gr/day

**The nutrient content of manure will vary depending on animal type and diet, type and amount of bedding, manure moisture content, and storage method. Data from* Manure Production Estimates (2019). *Dairyweb.ca*. Retrieved 11 September 2019, from http://www.dairyweb.ca/Resources/WDD62/WDD6222.pdf

Water Calculation:

The catchment area is multiplied by the depth of rain that falls on it to give the total volume of water produced. Factors such as evaporation, wetting, and soaking into the ground are not considered here.

Average Ground Cover Calculation

The average groundcover affects the rainwater run-off rates, which is relevant to potential phosphorus loss and capture. The following groundcover levels and run-off rates are assumed:

Pasture Cover	20%	40%	70%	>70%
Rainwater run-off	60%	40%	20%	10%

Costs for lime, superphosphate and biowaste to the farmer is as follows:

	Direct cost per hectare per year (approx)* **		**Cost of bio adsorbent use**
Current material		**Biowaste material*** *	
Superphosphate (one application of 225kg)	$500	Transport, processing of eggshell (estimated)*	$17
Lime (rate 1 tonne)	$150	Spreading	$60
Total cost	**$650**	**Total cost**	**$77**

*Based on transport of one tonne within 100km in a 30 tonne load, at $5 per km, application rate of 1 tonne per hectare
**Calculation based on assumption that one tonne of biowaste will capture and release the equivalent of superphosphate applied at 225kg/hectare and lime applied at 1 tonne per hectare
*** Actual current cost

Water Soluble Component of Phosphorus in Manures:

Based on the results above, the percentage of soluble phosphorus can be calculated as shown below:

Calculation of Water Soluble P Based on Trial Results			
Mass of manure		700	grams
Volume of water		0.5	Litre
Measured P concentration		13.3	mg / L
Normal sheep P levels		12.5	grams per day
P level per gram		0.0095	mg/gram
Proportion dissolvable P		0.11875	grams per day
Actual P as per table		12.5	grams
Expected P as per trial		7000	mg
Actual P as per trial		13.3	mg
Proportion soluble P		0.0019	
Percentage calculated* soluble P to manure		19.00%	

5. Further study that is recommended:

- Studies on desorption of phosphorus from eggshell
- Further understanding of phosphorus concentration in manures and current natural processes
- Studies on chemicals and residues left on biowaste materials, such as eggshell
- Extended testing on equilibrium times and rates under different natural processes, including the effect of temperature, moisture, concentration of biowaste and manure, soil pH and manure constitution.
- Comparison of calcium carbonate content compared to lime and dolomite
- Application of website in App form

6. Limitations

- Limited number of samples in each trial due to cost of water testing
- Cost of water testing

CONCLUSION

Experimental results indicated that untreated eggshell could potentially be employed as a sorbent in the removal of phosphate ions from aqueous substances containing soils, manure, or other mixtures/combinations. 24 hours of eggshell contact with phosphate contamination resulted in a decrease of phosphate concentration by an average of 61.86%. The application of this to an aqueous solution containing animal manures in a simulated run-off scenario indicated an average reduction of 55% of phosphates after 24 hours. This suggests the addition of eggshell to manure contaminated agricultural soils presents the outcomes of high phosphorus adsorption resulting in a reduction in Phosphorus runoff and eutrophication of waterways. A model has been developed which will be available to farmers as an application to allow them to solve this global problem at a local level. The potential use in agriculture of biowaste products, such as eggshell waste, as an adsorbent and soil conditioner, and the economic and environmental benefits from this appear to have been undervalued and underutilised.

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