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Kinetics of water-extractable zinc release from seaweed (*Fucus serratus*) as soil amendment

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ABSTRACT

Soil fertilization with trace-metal rich organic fertilizers such as *Fucus serratus* seaweed may be an effective way to combat micronutrient deficiency. In this study the kinetics of zinc release from *Fucus serratus* seaweed was investigated in a packed soil column leaching experiment over 1,776 hours. The release of zinc from control (soil only) and treatment (soil + seaweed; equivalent zinc application rate of 1.42 kg ha^{-1}) columns, measured by ICP-MS, demonstrated two distinct release stages. The cumulative zinc release data for each phase were fitted to five kinetic models: zero order, first order, Elovich, power function and parabolic diffusion. In the first stage (0-400 hours) the release of zinc from both control and treatment was best described by a parabolic rate law, indicating release of zinc from a soluble soil reservoir. In the second stage (400-1,776 hours) zinc release followed a zero order rate law indicative of slow release from an essentially insoluble reservoir. The modelled difference between the amount of zinc released from treatment and control columns in stage 1 (230 ± 11 µg) represented the total amount of zinc added *via* seaweed. The parabolic rate constant for seaweed zinc release was 12.09 µg g^{-1} $h^{-0.5}$. In summary, the addition of *F. serratus* to soil is a viable source of labile zinc and a low cost agronomic option for mitigating zinc deficiency in soils.

1 Introduction

Zinc is an essential nutrient needed for normal growth in plants, animals and humans, and its entry into the food chain is directly related to its solubility in soils (*Alloway*, 2008 and *Poblaciones et al*., 2017). However, more than fifty percent of the world's agricultural soils have been reported to suffer medium to widespread zinc deficiency (*Sillanpää*, 1990; *Alloway*, 2008; *Welch* et al., 2013; *RLF*, 2015). This has significantly contributed to poor crop yield (*Noulas* et al., 2018) and aggravated poor-diet-induced zinc deficiency in humans (*Cakmak* et al., 1999; *Alloway*, 2009), thus making it of global concern (*WHO* and *FAO*, 2006; *Cakmak*, 2009; *Sharma* et al., 2016).

In recent years, soil Zn fertilization with inorganic Zn sources has become widespread with $ZnSO_4$ being the major source used for correcting Zn deficiency (*Karak* et al., 2005; *Shaver* et al., 2007; *Alloway*, 2008; *Cakmak*, 2008; *Taheri* et al., 2011). Organic farming methods seek to provide inexpensive and sustainable agricultural approaches. Recent research has investigated the potential of organic amendments as Zn fertilizers. Suitable potential sources include: sewage sludge (*Motaghian* and *Hosseinpur*, 2013), green manures made from red clover and sunflower (*Aghili* et al., 2014), poultry manure (*Ravindran* et al., 2017), cow manure and vermicompost (*Motaghian* and *Hosseinpur*, 2017), biogas slurry (*Malav* et al., 2015 and *Dey* et al., 2019), brewery waste sludge (*Ahmed* et al., 2019) and seaweed (*Possinger*, 2013).

Generally, seaweeds contain higher concentrations of micronutrients than terrestrial plants (*Strik* et al., 2003; *MacArtain* et al., 2007; *Rohani-Ghadikolaei* et al., 2012; *Astorga-Espana* et al., 2015). Seaweed has been used by humans as source of food, medicine, fodder and fertilizer for millennia (*Kenicer* et al., 2000; *Dillehay* et al., 2008; *Possinger*, 2013). It is a naturally abundant resource; in the coasts of Britain alone, more than 600 species of different seaweed flora have been identified (*Kenicer* et al., 2000). Thus, seaweed plays a great role as an organic fertilizer especially in coastal agriculture where soil fertility is traditionally maintained by direct seaweed application (*WSH*, 2016), either as compost (*Eyras* et al., 1998;

Kenicer et al. 2000) or dried amendment (*Possinger* et al., 2013). For instance, such practice has been carried on in the coastal regions of Scotland, and especially in the Machair community till date (*Angus* and *Dargie*, 2002). Machair community has a cultural tradition of crofting which involves spreading harvested or beach-cast brown seaweeds on arable farm lands as soil conditioners or fertilizers. The seaweeds are usually collected at low tides during autumn and winter months when large quantities of brown seaweed are washed ashore (*WSH*, 2016). The seaweed types usually harvested in large quantities in Scotland include *Ascophyllum,Laminaria* species and *Fucus serratus* (*WSH,* 2016). The Scottish Natural Heritage organization promotes soil application of seaweed as part of sustaining small-scale, diversified agriculture (*Angus* and *Dargie*, 2002). In the present study, two locally abundant species of coastal, benthic brown seaweed (*Fucus serratus* and *Laminaria digitata*) were harvested from the sea at low tide for further processing and analysis. *F. serratus* was selected as the model fertilizer for this study because its Zn composition is approximately double that of *L. digitata*.

The total zinc available for plant uptake is largely determined by the amount of zinc released from soil surfaces into solution (*Dang* et al., 1994). Hence, an understanding of the kinetics of zinc release at the solid-liquid interface is of fundamental importance to a complete understanding of the dynamics of zinc in soils. Most studies on zinc sorption-desorption by soils have been based on equilibrium conditions whereby thermodynamic approaches are used to predict only the final state of reactions (*Taylor* et al., 1995; *Reyhanitabar* and *Gilke*s, 2010; *Reyhanitabar* et al., 2011). However, processes of ionic exchange in soils rarely assume equilibrium state due to fertilizer addition, slow chemical reactions, plant uptake, edaphic and climatic factors (*Dang* et al., 1994; *Taylor* et al., 1995; *Reyhanitabar* et al., 2011). Therefore, a more comprehensive approach to understanding the dynamics of zinc release in soils requires an investigation of the kinetics of zinc sorption-desorption processes at a given time.

In recent years, the kinetics of zinc release from different soils has drawn considerable attention as different kinetic models have been employed to describe Zn release patterns. The models include parabolic diffusion (*Dang* et al., 1994; *Taheri* et a*l*., 2011), power function (*Reyhanitabar* and *Gilkes*, 2010; *Ghasemi-Fasaei* et al., 2012; *Motaghian* and *Hosseinpur*, 2013), *Elovich* (*Taylor* et al., 1995; *Reyhanitabar* et al., 2011), zero order (*Padidar*, 2015), first order and second order equations. The models were employed to investigate the nature of reactions and zinc release patterns in acid-leached soils (*Alghanmi* et al., 2015; *Padida*r, 2015), DTPA- extracted soils (*Dang* et al., 1994; *Motaghian* and *Hosseinpur*, 2013), zinc sulphate-amended and cropped soils (*Taheri* et al., 2011).

Eghball et al. (2002) reported that, in order to apply manure or compost to fulfil the nutrient requirements of a crop, knowledge of the amount of nutrients mineralized following application is needed as this should be considered when determining application rates. Hence, *Dey* et al. (2019) engaged kinetic studies to assess nutrient release from different organic amendments so as to decide the rates and frequency of application. Kinetic studies of nutrient release from organic amendments are now gaining attention while investigation of zinc release kinetics from organic fertilizer-amended soils is very limited. *Motaghian* and *Hosseinpur* (2013) investigated the kinetics of Zn release in wheat rhizosphere of some sewage sludge amended soils, their study indicated that zinc desorption rate was higher in wheat rhizosphere than in bulk soils and that the process was modelled by the power function model.

Thus, it is important to study zinc kinetics in an uncropped organically amended soil with a view to understanding zinc dynamics in soils and organic fertilizers, and ameliorating soil zinc reservoirs. Understanding zinc release kinetics is useful for synchronization of zinc release peak in soils with zinc peak demands of prospective crops. For instance, *Taheri* et al. (2011) employed kinetic models to investigate patterns of Zn release from fertilizers into soil so as to understand application timing, frequency and magnitude of Zn dose application (as suggested

by *Eghball* et al., 2002). They reported that, similar to soluble $ZnSO_4$, tire ash is a fast-release Zn fertilizer which supplies plants with readily available Zn, hence lower application rates may be required. On the other hand, they observed that ground rubber is a slow-release fertilizer of which intermittent application of higher Zn rates is required; as such, they recommended application of ground rubber in Zn deficient soils before seeding, to provide long term Zn fertilization. This is key to achieving high nutrient use efficiency hence maximization of crop productivity and minimization of negative environmental impacts.

In assessing the relevance of seaweed as a source of zinc in organic agriculture, understanding zinc release rate into the soil solution is an important factor in regulating zinc supply to plants, informing timings and scale of fertilizer applications. Here, we present the first study of zinc release kinetics from seaweed. Specifically, we present the results of a study of zinc release kinetics in uncropped, water-leached, seaweed-amended soil employing a soil column protocol.

2. Material and methods

2.1 Collection and Preparation of Soil Samples

Soil samples were collected from surface soils (0 – 15 cm) of an uncultivated garden (54° 34′ 48.75″ N, 1° 19′ 29.81″ W) in Stockton, County Durham, UK in August 2016. The soil samples were air dried, passed through a 2 mm sieve and stored in polythene bags. Soil physical properties were determined using standard methods as described for soil particle-size determination (*Kettler* et al., 2001), pH (*Hendershot* et al., 2006), bulk density and porosity.

2.2 Collection and Processing of Seaweed (*Fucus serratus*)

Live samples of brown seaweed (*Fucus serratus*) were collected at low tide from Saltburn-by-the-Sea, Yorkshire, England (54° 35′ 16.1″ N, 0° 57′ 24.3″ W) on 31st of August 2016 at low tide 10 am BST. They were transported to the laboratory within two hours of collection and immediately stored in a fridge at 4°C until the next day (i.e. for 17 hours). After refrigeration, samples were thoroughly washed, detached from other sea plants and fauna and soaked in deionized water for 17 hours. They were then drained, weighed and oven-dried to constant weight at 50°C. In order to increase the surface area of dried biomass for faster biodegradability, the seaweed was ground to powder in an agate planetary ball mill (*Fritsch, Pulverisette 6*) for 40 minutes at rotational speed of 200 rpm. Ground seaweed was then sieved to determine its particle size distribution. The particle size distribution of seaweed, shown in Figure 1, ranged from 0.15 – 0.5 mm. Seaweed pH was measured using the procedures described by *Singh* et al. (2017) as follows: 1g of seaweed was added to 10 mL of deionised water and mixed for 1 hour using a reciprocating shaker. The mixture was then allowed to stand for 30 minutes after which pH was measured using a benchtop pH / mV meter (*Fisher Scientific AE150*).

((Figure 1))

2.3 Total Zinc Determination

Total zinc concentrations in soils and seaweed were determined before and after the experiment through microwave-assisted 70% nitric acid digestion (*Mars- 6, CEM, One Touch Technology*). Approximately 0.1 g of each biomass was weighed in twelve replicates into Teflon tubes (50 mL), and blanks were also prepared for each biomass. Concentrated nitric acid (70 %, 10 mL) was added to each sample. The tubes were equidistantly arranged on the circular tube rack and then loaded into the microwave digester and digested for 105 minutes at 1800 W. The digestion process was followed by multi-element analyses on inductively coupled plasma mass

spectrometer (ICP-MS) *Agilent 7500 series, Octopole Reaction System*. Prior to analysis the digested samples were serially diluted as follows: each digested sample was made up to 100 mL in a volumetric flask with deionised water, diluted (1:10) in deionized water and further diluted (1:10) with 2% nitric acid. This solution was analysed on the ICP-MS. Estimation of error in total zinc concentration was reported as 95% confidence interval.

2.4 Zinc Leaching Experiment

The apparatus used for the zinc leaching experiment is shown in Figure 2. A transparent cylindrical acrylic (pexiglass) tube measuring 250 mm long and 54 mm internal diameter was used as soil column. The bottom of the column was sealed with a rubber stopper having a 2 mm hole outlet tube at the center. The rubber stopper was overlaid with perforated acrylic circular disc (having seventeen 1 mm holes) on top of which was a Whatman #54 filter paper. The filter paper was covered with a 1 cm layer of quartz sand. The column was then filled with 300 g of 2 mm-sieved and air-dried soil, following the protocols of soil column set-up for unsaturated dry-packing (*Lewis* and *Sjöstrom*, 2010; DEMEAU, 2012). For the treatment, 3 g of the processed *F. serratus* (that is, 213 ± 6 µg of zinc) was mixed evenly throughout the soil column, an application rate equivalent to 20 tonnes of seaweed per hectare (*Motaghian* and *Hosseinpur*, 2013) since the mass of soil per hectare at 15 cm surface depth is 2 million kg ha^{-1} (*Hinrich* et al., 2002).

((Figure 2))

After filling, the top of the soil was first overlaid with Whatman #54 filter paper, followed by 1 cm layer of quartz sand and then by a perforated acrylic circular disc (of similar column diameter) having thirteen 1 mm holes. The top of the column was sealed with a rubber stopper fitted with an inlet valve through which there was a continuous flow of irrigation (deionized) water from a reservoir. The flow rate of irrigation water was manually controlled and set at 30 mL h^{-1}. Leachate in each 24 hour period was collected and analysed for zinc by ICP-MS. The

transparent part of the column was wrapped with an aluminum foil to simulate light conditions encountered in the subsurface and prevent the growth of photolithotrophic microorganisms and photodegradation of organic fertilizer resulting from exposure to light. There were two soil columns set-up – treatment and control – with the control having no seaweed. The experiment was conducted from September 29 to December 12, 2016 during which zinc release was monitored daily for 1,776 hours (74 days) at ambient temperatures of between 15 – 20^{o}C.

2.5 Models for Zn Release Kinetics

Amounts of zinc released from treatment and control columns with time were modelled using five kinetic models: zero order, first order, Elovich, power and parabolic diffusion functions, as detailed in (Table 1). The models that best described zinc release in both conditions were determined by linear regression using Microsoft Excel. Total zinc release from seaweed was modelled as the difference between zinc release from the treatment and control columns.

((Table 1))

2.6 Statistical Analysis

Column soil data before and after the experiment were analyzed using the one-way ANOVA to evaluate significant difference among means at $P < 0.05$. Also, the significance or otherwise of differences at the 95% confidence level between modelled rate constants was established using t-tests for slope coefficient difference (*Paternoster* et al., 1998).

3. Results

3.1 Properties of Studied Soil and Seaweed fertilizer

The initial textural classification of the column soil was loam (37% sand, 40% silt, 23% clay) with bulk density of 1.15 g cm^{-3} and porosity of 57%. This is ideal for plant growth and water infiltration; the bulk density is less than the maximum 1.40 g cm^{-3} recommended by USDA-NRCS (2014). The soil pH was 6.35 and that of the seaweed was 5.72, both within the range (5.5 – 6.5) at which soil Zn is most available.

The initial concentration of total zinc in the soil was 210 ± 30 mg kg^{-1}, within the acceptable total Zn concentration for agricultural soils (10 – 300 mg kg^{-1}; *Barber* (1995)). The initial chemical characteristics of the *F. serratus* used in this study are presented in Table 2. . The total zinc concentration of seaweed was 71 ± 2 mg kg^{-1}. At the end of the experiment, concentration of zinc in soil (control) was 200 ± 40 mg kg^{-1} while it was 200 ± 20 mg kg^{-1} in seaweed-amended soil (treatment). That is, there is no statistically significant difference between the zinc content of the original soil and of the control and treatment after the experiment (F (2, 12) = 0.069, P = 0.93).

((Table 2))

3.2 Cumulative Release of Zinc from the Soil Column

The cumulative mass of zinc released between 0 and 1,776 hours from both the control and treatment columns are as presented in Figure 3. Both columns show a steady increase in cumulative zinc release over time and there is an apparent discontinuity at about 400 hours defining two distinct stages of zinc release. In stage 1 (0 – 408 hours) the control column displays an initial rapid loss of zinc that slows over the period, whereas in stage 2 (>400 hours) the zinc loss rate is essentially constant. The treatment column exhibits behavior similar to that of the control in both stages but the cumulative mass of zinc release from the treatment is positively offset relative to that of the control, reflecting the additional labile zinc present.

((Figure 3))

3.3 Kinetics of Zinc Release

In order to understand the processes by which Zn is released, data were fitted to the kinetic models detailed in Table 1. The results of model fits are presented in Table 3. Based on the values of coefficient of determination (R^2) and standard error of the slope of each kinetic model, the best model fit for zinc release was selected in both stages. In stage one, zinc release was

best described by the parabolic diffusion model for both treatment and control (Figure 4). In stage 2, zinc loss was best described as a zero order process for both treatment and control.

((Table 3))

((Figure 4))

It is of interest to note that, out of all the tested models, only the zero order and parabolic diffusion models had their rate constant values higher in treatments than in controls (Table 3): that is, for only these two models is seaweed acting as a source of zinc. For the best kinetic models in both stages of Zn release, *t-tests* were done to establish significant differences in rate constants (k) between treatment and control. In stage 1, there was a significant difference between parabolic rate constants, k of the treatment (k = 28.95, SE = 0.52) and control (k = 16.85, SE = 0.26), t (15) = 20.67, $p < 0.05$ whereas in stage 2, there was no significant difference in k for treatment (k= 1.13, SE = 0.02) and control (k = 1.11, SE = 0.01), t (53) = 0.917, $p >$ 0.05. That is, zinc release is faster from the treatment than from control during stage 1 but there is no difference in rate between treatment and control during stage 2.

The cumulative zinc release from seaweed was estimated as the difference between the parabolic models for treatment and control in stage one. Hence, seaweed released 230 ± 11 µg of zinc during stage 1 and there was no statistically significant difference between this amount and the actual amount of zinc added to the system by seaweed (213 ± 6 µg). The modelled rate constant for parabolic release of zinc from *F. serratus* in this experiment was 12.09 µg g^{-1} $h^{-0.5}$.

4. Discussion

4. 1 Seaweed Decomposition

With C/N ratio of 25:1 (Table 2), seaweed degradation is expected to happen over a somewhat longer timeframe than that of the experiment. However, Zn release in stage 1 (0-408

hours) is parabolic, indicating that trans-membrane transport processes are not rate limiting for zinc release.

4.2 Cumulative Zinc Release from Soil Column

As shown in Figure 3 there was a discontinuity in the slope of cumulative zinc release at about 408 h suggesting that different mechanisms of release are operating in stages one and two. Over the 1,776 hours of the experiment, approximately 2 mg of zinc (~1% of total soil zinc) was released from the column in both treatment (soil + seaweed) and control (soil only) conditions. This is in line with our expectations because more than ninety percent of soil zinc is insoluble (*Broadley* et al., 2007). The total cumulative zinc release from the treatment condition was higher than that from the control condition, indicating that seaweed is a source of zinc. Furthermore, the offset between the two conditions was constant over stage 2 and was equal to the zinc content of the seaweed. That is, all the seaweed zinc is released in the experiment and this release happens exclusively in stage 1.

4.3 Kinetics of Zinc Release in Stage 1

The observation of two stages of zinc release suggests the existence of two types of zinc reservoir in this system. The zinc release in stage 1 was rapid and exhibited parabolic kinetics implying that the overall rate of zinc release from this reservoir was controlled by diffusion phenomena (*Aharoni* et al., 1991 and *Rao* et al., 1998). For highly soluble material, diffusion processes, for example, exchange/replacement of surface zinc in the solid and/or diffusion of dissolved zinc away from surfaces and into the bulk liquid are expected to be rate limiting. That is, any additional steps that may be operating in the mechanism of zinc release from this reservoir are fast with respect to diffusion. The initial rapid release of zinc during the first 408 h is considered to be due to desorption of zinc from soil particle surfaces with weak binding energy (e.g. weakly bound zinc on macro-aggregate surfaces or on the outer surfaces of micro-aggregates) or sources with high zinc-solubility. Soluble zinc is typically at low

concentration in soils (approximately 10^{-8} M; *Barber* (1995)), hence the short duration of stage 1 release.

The suitability of the parabolic diffusion model in adequately describing zinc release in stage one is consistent with the finding of *Ghiri* et al. (2012). They investigated the kinetics of zinc desorption in calcareous soils of southern Iran; of all the tested models, the parabolic diffusion model best described zinc desorption from the soils. Metals release from soils is, however, complex and is influenced strongly by the particular nature (mineral content, organic matter content, pH, particle size, etc.) of the soil under study. A recent study by *Wisawapipat* and *Pongpom* (2019) investigated the kinetics of ligand-controlled Zn release in acid sulfate paddy soils of Thailand, using ethylenediaminetetraacetic acid (EDTA) as extractant. Their result showed that, over the course of 192 hours at soil pH 4.0, kinetics of Zn release was best described by the parabolic model, compared with other models. Hence, they concluded – equivocally – that diffusion-controlled exchange was one of the processes governing ligand-controlled Zn dissolution in the studied soils. Similar to the present study, *Hosseinpur* and *Motaghian* (2013) observed a two-stage pattern of nutrient release when they studied the kinetics of potassium release from calcareous soils of central Iran, and they reported that the parabolic diffusion model best described potassium release in the second stage (168 – 2017 h). However, in an investigation of zinc release kinetics in different soil orders by *Ghasemi-Fasaei* et al. (2012) using time-dependent zinc extraction techniques, it was shown that the parabolic diffusion model did not adequately describe zinc release from the soils whereas the power function did. Nonetheless, based on the rapid and short-lived parabolic release seen in our experiment, we conclude that the first stage represents loss of soluble zinc.

The amount of zinc released from the seaweed alone during stage 1 can be modelled as:

$$Zn\ released\ from\ seaweed$$

$$= zinc\ released\ from\ treatment - zinc\ released\ from\ soil$$

Using the parabolic models in Table 1 to describe zinc release from the treatment and control conditions, the amount of zinc released from seaweed was 230 ± 11 µg. That is, the zinc contributed to the system by the seaweed (213 ± 6 µg) augments the soluble zinc reservoir, and only this reservoir. Hence, seaweed is a potential zinc fertilizer from a soil-application perspective.

Rate constants are good indices for measuring the mineral supplying capacity of a material (*Hosseinpur* and *Motaghian*, 2013 and *Li* et al., 2015). The difference between the modelled parabolic zinc release from treatment and control in stage one yields a parabolic rate constant for zinc release from seaweed only of 12.09 µg g^{-1} $h^{-0.5}$.

4.4 Kinetics of Zinc Release in Stage 2

The zero order zinc release in stage two implies release from a recalcitrant mineral phase for which the zinc concentration is large relative to the flux of zinc into the liquid phase: desorption/dissolution is the limiting step in zinc release in stage two. *Sparks* (2003) described the kinetics of zero order dissolution as a surface-controlled phenomenon in which concentrations of solutes near surfaces are equal to the bulk solution. Therefore, the slow and long term zinc release in this stage is considered to be due to zinc release from, for example, the inner surfaces of macro- or micro-aggregates with stronger binding energies and/or surface release processes There has been widespread observations of similar Zn release kinetics. For example, *Zahedifar* et al. (2012) and *Baranimotlagh* and *Gholami* (2013) studied the kinetics of Zn desorption in calcareous soils of Iran and observed a rapid Zn release phase followed by slower and long-term release. Both studies attributed the slower release to desorption of Zn from inside macro- or micro- aggregates, while *Sadusky* et al. (1987) described zero order nutrient release as a surface-controlled process attributable to weathered nature of soils. In a

laboratory study to investigate time-dependent release of Zn from biochar over the course of 120 days, *Dey* et al. (2019) observed a Zn accumulation throughout the period, which, although formally statistically non-significant, conformed to zero order release kinetics. Hence, our observation of zero order kinetics in stage 2 indicates the release of zinc from the recalcitrant soil reservoir.

5. Conclusions

This study investigated the kinetics of water extractable zinc release from seaweed using a packed soil column leaching protocol. In the treatment condition (soil + seaweed), two stages of zinc release were observed. In stage 1, zinc was released from soluble reservoirs with parabolic kinetics. In stage 2, zero order kinetics indicated release of zinc from less labile soil reservoirs. Kinetic modelling of zinc release in stage 1 allowed the kinetics of release from seaweed-only to be determined: seaweed released zinc rapidly, following parabolic kinetics. Hence, seaweed is understood to contribute all its zinc to the stage 1 labile reservoir exclusively, thereby increasing the overall flux from this reservoir. Soil application of seaweed as a low cost and readily available organic fertilizer provides a source of rapid release, labile zinc and presents potential value in meeting the challenge of zinc deficiency in soils.

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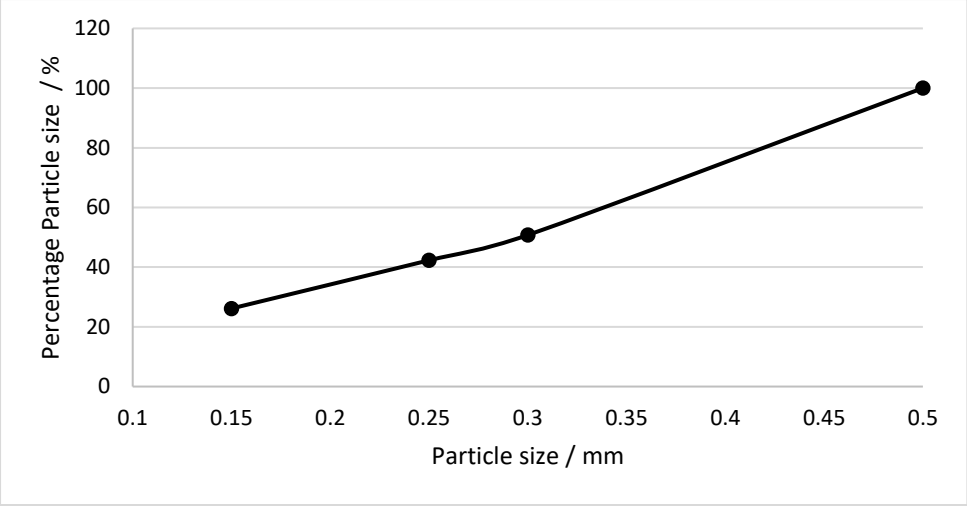

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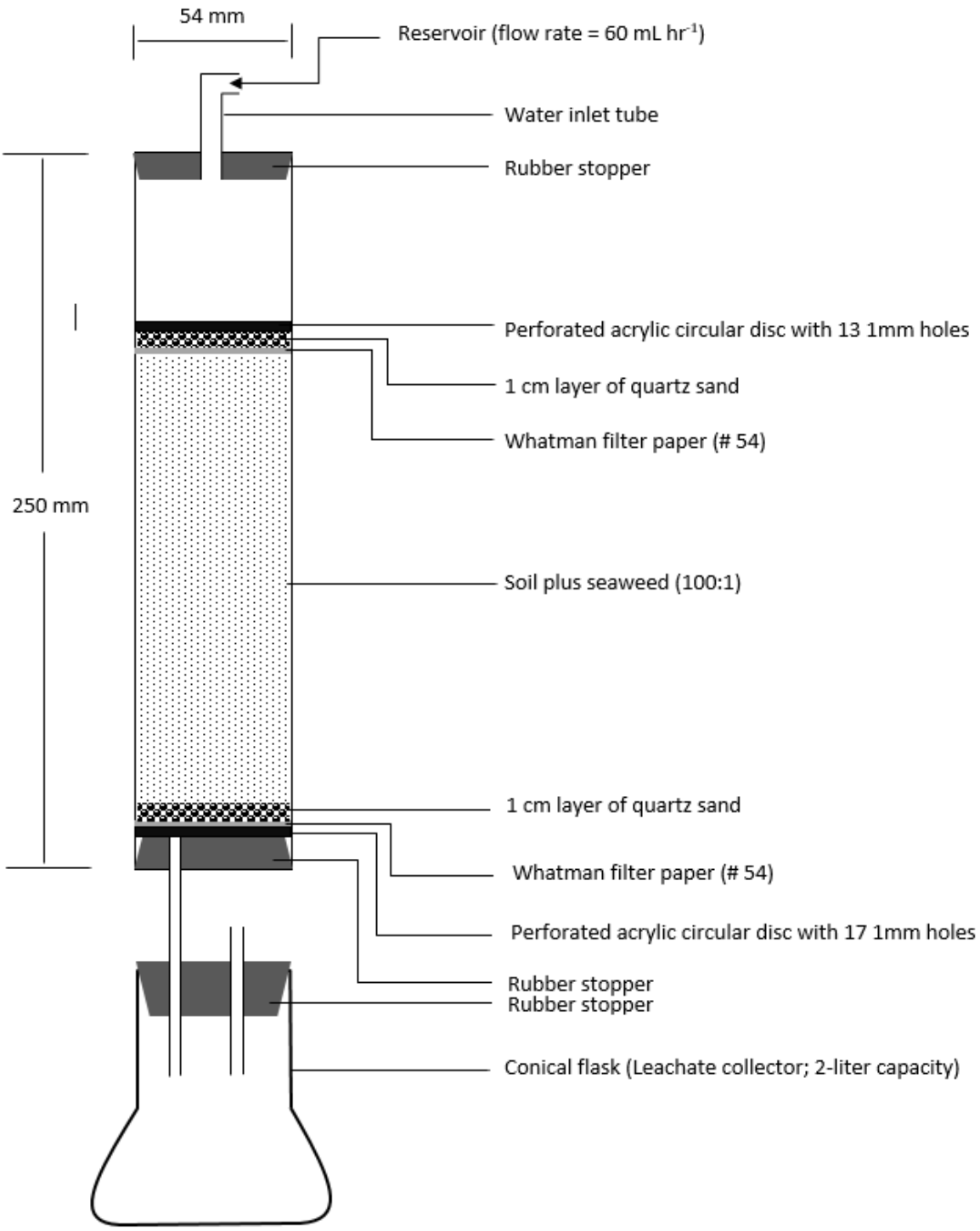
54 mm
Reservoir (flow rate = 60 mL hr-1)
Water inlet tube
Rubber stopper
Perforated acrylic circular disc with 13 1mm holes
1 cm layer of quartz sand
Whatman filter paper (# 54)
250 mm
Soil plus seaweed (100:1)
1 cm layer of quartz sand
Whatman filter paper (# 54)
Perforated acrylic circular disc with 17 1mm holes
Rubber stopper
Rubber stopper
Conical flask (Leachate collector; 2-liter capacity)

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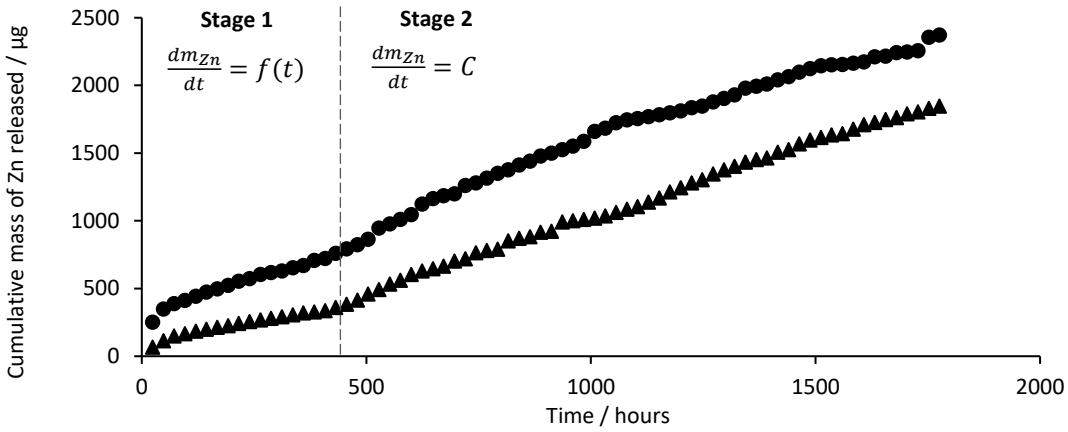
Stage 1
$\frac{dm_{Zn}}{dt} = f(t)$
Stage 2
$\frac{dm_{Zn}}{dt} = C$
Cumulative mass of Zn released / µg
Time / hours
0
500
1000
1500
2000
2500

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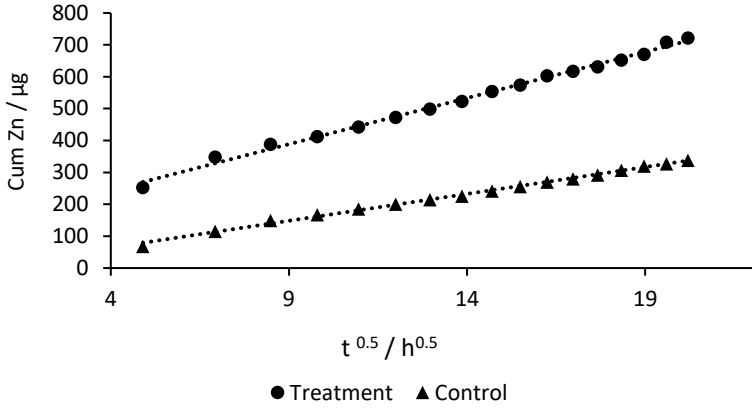
800
700
600
500
400
300
200
100
0
Cum Zn / µg
4
9
14
19
t 0.5 / h0.5
Treatment
Control

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531 Table 1: Kinetic models of Zn release from soil system used in this study

Kinetic Model	*Equation	Parameters
Zero order	$\frac{m_\infty - m_t}{\sigma} = \frac{m_\infty}{\sigma} - kt$	m_∞ mass of Zn at time infinity / µg m_t mass of Zn at time *t* / µg a, b, k: rate constants *t* time / hours σ: mass of soil / g
First order	$ln\left[\frac{m_\infty - m_t}{\sigma}\right] = \left[ln\frac{m_\infty}{\sigma}\right] - kt$	
Elovich	$\frac{m_\infty - m_t}{\sigma} = \frac{1}{b} ln(ab) + \frac{1}{b} lnt$	
Power function	$ln\left(\frac{m_\infty - m_t}{\sigma}\right) = ln\, a + b\, lnt$	
Parabolic diffusion	$\frac{m_\infty - m_t}{\sigma} = \frac{m_\infty}{\sigma} - kt^{0.5}$	

532 *Adapted from *Martin and Sparks*, 1983; *Havlin* et al., 1985; *Sparks* 2003; *Wu* et al., 2009

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Table 2: Initial chemical characteristics of *F. serratus* used in this study.

Biomass	Zn / mg kg^{-1}	C / %	N / %	pH	Hemicellulose %	Cellulose %	Lignin %	C/N ratio	Lignin/N ratio
F. serratus	71 ± 2	40.1	1.58	5.72	0.09	13.4	28.22	25	17.9

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Table 3: Parameters for each kinetic model for the two stages of Zn release (stages 1 and 2 for both control and treatment). For the Elovich model, the constant, b, is given. The units for the rate constants are as follows: μg g^{-1} h^{-1} (zero order); h^{-1} (first order); μg g^{-1} h^{-1} (Elovich); μg g^{-1} h^{-1} (power function); μg g^{-1} $h^{-0.5}$ (parabolic).

Stages		Zero order			First order			Elovich			Power function			Parabolic Diffusion		
		k	R^2	SE	*k*	R^2	SE	*b*	R^2	SE	*k*	R^2	SE	*k*	R^2	SE
Control	1	0.629	0.965	0.031	0.006	0.956	0.000	0.010	0.969	4.465	0.805	0.763	0.116	16.847	0.996	0.261
	2	1.109	0.998	0.007	0.002	0.821	0.000	0.001	0.973	25.185	2.157	0.703	0.193	71.096	0.993	0.830
Treatment	1	1.085	0.970	0.049	0.006	0.939	0.000	0.006	0.959	8.740	0.778	0.741	0.119	28.949	0.995	0.524
	2	1.130	0.980	0.022	0.002	0.859	0.000	0.001	0.997	9.203	2.001	0.769	0.151	73.165	0.996	0.679

Figure 1: Cumulative particle size distribution of ground F. Serratus.

Figure 2: Schematic representation of the soil column apparatus used to study the kinetics of zinc release.

Figure 3: Cumulative mass of zinc released from treatment (soil + F. serratus*; filled circles) and control (soil only; filled triangles) over the course of the 1,776 hour leaching experiment. The inflection at approx. 400 hours defines two stages of release kinetics: in stage 1 the cumulative release rate is a function of time; in stage 2 the rate is constant.*

Figure 4: Fit of parabolic diffusion model to the cumulative zinc release data from treatment (soil + F. serratus*; filled circles) and control (soil only; filled triangles) over the course of the 408 hours of stage 1 release. These model fits best describe the kinetics of zinc release during this time period and are used subsequently to calculate zinc release from seaweed.*