



Sorbents can tailor nitrogen release from organic wastes to match the uptake capacity of crops



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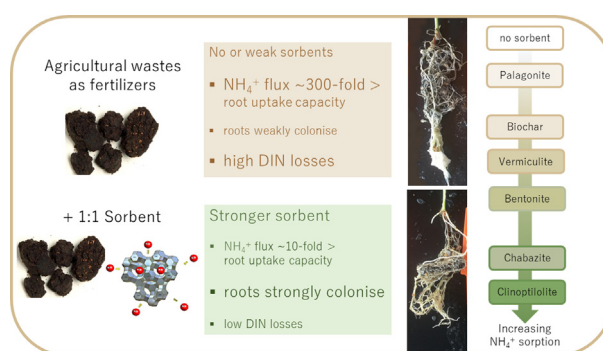
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HIGHLIGHTS

- Aim to synchronize nitrogen release from organic wastes and crop uptake capacity.
- NH_4^+ retention capacity of sorbents translates to sorbent-waste formulations.
- Efficient sorbents strongly attenuate NH_4^+ release and reduce leaching losses.
- NH_4^+ fluxes in efficient sorbent-waste mixtures more closely match root uptake.
- Sorbents have a role in formulating organic wastes as efficient fertilizers.

GRAPHICAL ABSTRACT



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ABSTRACT

Delivering nutrients from mineral or organic fertilizers out of synchrony with crop uptake causes inefficiencies and pollution. We explore methodologies for evaluating sorbents as additives to organic agricultural wastes to retain nitrogen in an exchangeable form and deliver at rates that approximate the uptake capacity of roots. Focussing on ammonium (NH_4^+) as the main inorganic nitrogen form in the studied wastes (sugarcane mill mud, poultry litter), we tested geo-sorbents and biochar for their ability to retain NH_4^+ . Sorption capacity was ranked palagonite < bentonite, biochar, vermiculite < chabazite, clinoptilolite (5.7 to 24.3 $\text{mg NH}_4^+ \text{g}^{-1}$ sorbent). Sorbent-waste formulations were analysed for sorption capacity, leaching and fluxes of NH_4^+ . Ammonium-sorption capacity broadly translated to sorbent-waste formulations with clinoptilolite conferring the strongest NH_4^+ attenuation (80%), and palagonite the lowest (7%). A 1:1 ratio of sorbent:waste achieved stronger sorption than a 0.5:1 ratio, and similar sorption as a 1:1.5 ratio. In line with these results, clinoptilolite-amended wastes had the lowest *in situ* NH_4^+ fluxes, which exceeded the NH_4^+ uptake capacity (I_{max}) of sugarcane and sorghum roots 9 to 84-fold, respectively. Less efficient sorbent-waste formulations and un-amended wastes exceeded I_{max} of crop roots up to 274-fold. Roots preferentially colonized stronger sorbent-waste formulations and avoided weaker ones, suggesting that lower NH_4^+ fluxes generate a more favourable growth environment. This study contributes methodologies to identify suitable sorbents to formulate organic wastes as next-generation fertilizers with view of a crop's nutrient physiology. Efficient re-purposing of wastes can improve nutrient use efficiency in agriculture and support the circular nutrient economy.

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1. Introduction

Pollution caused by off-site losses of fertilizers is a global problem (Steffen et al., 2015), and technological advances have to enable effective nutrient delivery. At the core of the problem is the difficulty of striking a balance between delivering sufficient nutrients to crops while avoiding the accumulation of soluble or dissolved nutrients in soil, or their conversion into crop-unavailable forms. While conventional mineral fertilizers readily dissolve in soil and are immediately available to crops, organic fertilizers such as manures and composts combine short- and long-term nutrient release, with some nutrients being soluble and immediately available to crops and others having to undergo transformations (Ball et al., 2004; Eghball et al., 2004; Helgason et al., 2007). Irrespective of the type of fertilizer, an ideal fertilizer will release nutrients in response to crop demand, rather than to abiotic or soil biological factors.

Despite considerably higher costs, mineral fertilizers with slowed release (also termed 'controlled', or 'enhanced efficiency') are increasingly used in broad-acre agriculture (Dave et al., 1999; Sistani et al., 2014; Trenkel, 2010). Fertilizer granules are surrounded by physical barriers such as plastic coating that become porous and allow solubilization and subsequent release of nutrients (Shaviv et al., 2003), or are coated with microbial inhibitors such as sulphur or lignin-derivatives, contain biocides such as urease or nitrification inhibitors, or have an oil-based matrix (Subbarao et al., 2006; Trenkel, 2010). These fertilizers respond passively to environmental factors such as soil moisture, temperature and microbial activity, or slow the rate of microbe-driven nutrient conversions in soil (Azam et al., 2001; Carmona et al., 1990; Chu et al., 2004). These fertilizers are not specifically designed to match a crop's nutrient uptake capacity, and are not suitable to all conditions (Li et al., 2014).

An alternative to physical barriers or chemical inhibitors to control nutrient release is to bind nutrients reversibly to a matrix from which they can be removed by crop roots. Such nutrient-matrix interactions mimic the function of soils in natural ecosystems that continuously release nutrients from decaying organic materials and the soil matrix (Gillman and Noble, 2005). While natural systems also incur some nutrient losses, these are generally orders of magnitude lower than losses from agricultural soils over a given timeframe (Ventura et al., 2013). The underlying concept is that materials with high ion exchange and sorption capacity will selectively bind target molecules or ions and reduce their mobility in soil. Sorbents such as zeolites have the capacity to synchronize nutrient supply and crop demand, releasing nutrients when nutrient concentrations in the soil solution decline (Gillman, 2011; Gillman and Noble, 2005; Redding et al., 2016). As materials of geological origin, and often locally available, zeolites and related sorbents may be well suited for next-generation fertilizers. The efficacy of sorbents has been demonstrated for reducing nitrogen (N) losses, increasing N availability and crop yields (Aghaalkhani et al., 2012; Ding et al., 2010; Gholamhoseini et al., 2013; Hill et al., 2016; Pratt et al., 2016; Redding, 2011, 2013; Redding et al., 2016). Sorbents can increase the nutrient use efficiency of organic wastes by avoiding nutrient excess (Parnaudeau et al., 2009; Smith et al., 2001).

Here we formulate sorbents with nutrient-rich agricultural wastes to confer a slower and more sustained nutrient release. Agricultural wastes often benefit soil fertility, crop nutrition and root growth through input of organic carbon and a broader range of nutrients than typically contained in mineral NPK fertilizers (Drinkwater and Snapp, 2007; Gómez- Muñoz et al., 2017; Jiang et al., 2006; Paungfoo-Lonhienne et al., 2012). However, organic wastes also carry inefficiencies - from excessive nutrient release to inadequate nutrient delivery (Bosshard et al., 2009; Edmeades, 2003; Helgason et al., 2007; Redding, 2011), which necessitates innovation. Most studies compare two sorbents concurrently, which limits broader comparisons. Sorbents differ in their physicochemical properties geologically, and wastes differ in their nutrient stoichiometry and release profiles (Mondale et al.,

1995). Thus, there is a need for empirical studies evaluating the performance of locally sourced sorbent-waste formulations.

We focus on the early burst release of nutrients that characterises many wastes by testing six sorbents with the aim to identify suitable methodologies to evaluate nutrient release of sorbent-waste formulations. Five sorbents were locally sourced in Australia, and one from Italy, and we aimed to identify favourable properties for next-generation fertilizers. The overarching aim is to improve N supply of tropical broadacre crops (sugarcane, sorghum, others) and re-purpose locally sourced wastes. The chosen wastes were sugar mill mud (low in N, high in phosphorus and potassium), and chicken litter (manure + bedding material; high in N and phosphorus). Both wastes were mixed to emulate next-generation fertilizers composed of wastes with different nutrient composition to achieve ideal nutrient stoichiometry for a particular crop. Ammonium (NH_4^+) is the prevalent form of inorganic N in the studied wastes (Wiedemann et al., 2008) and was the target N forms here. Ammonium can be toxic to crops at higher concentrations, lost from soil *via* leaching or gaseous emissions, or be converted to nitrate (NO_3^-), which is the most loss-prone N form in soil (Pagans et al., 2006). The sorbents represent Australian analogues of commonly studied vermiculite, bentonite, clinoptilolite, chabazite and biochar, and, for the first time, an Australian palagonite. We tested these sorbents for NH_4^+ selectivity and sorption capacity and compared sorbent-waste mixtures for their ability to mitigate leaching of dissolved inorganic N (DIN, ammonium & nitrate).

Further, we quantified in real time DIN fluxes in sorbent-amended organic wastes from a plant root perspective using microdialysis, an emerging high-resolution tool for quantifying the dynamics of plant available N in soil (Brackin et al., 2015, 2017; Buckley et al., 2017; Inselsbacher et al., 2011). Our study contributes knowledge in support of nutrient stewardship by targeting nutrient-rich agricultural wastes formulated with sorbents as next-generation fertilizers.

2. Materials and methods

2.1. Organic wastes and sorbent materials

Ten kilograms of spent broiler poultry litter consisting of faeces and hardwood shavings was supplied by the Darwalla Group, a poultry meat producer (Mount Cotton, South-East Queensland, Australia). Immediately after collection, the litter was thoroughly mixed by shovel, and larger materials removed by passing the litter through a 2 mm sieve. Sugarcane mill mud was supplied by the Manildra Group (Gladesville, New South Wales, Australia) and stored frozen (-20°C) for approximately eight months before use. Throughout the experiments, poultry litter and mill mud were stored at 4°C until use. Of the six sorbents examined, five were sourced in Australia, and a chabazite was sourced from Naples, Italy (Table 2). Sorbents were stored in the laboratory under ambient conditions in air-tight containers protected from direct light.

2.2. Physicochemical analysis of organic wastes and sorbents

The moisture content of poultry litter and mill mud was determined after oven-drying samples in triplicate at 55°C for 16 h. The pH of poultry litter and mill mud was measured after a 1:5 solid:water extraction with five replicates. Elements in poultry litter and mill mud were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Varian Vista Proc instrument) on samples that were open-vessel digested (using a 5:1 ratio mixture of nitric and perchloric acids, (Achilli et al., 1991)). Elemental analysis of sorbents was performed by ICP-OES, with samples digested using a Milestone ethos-1 microwave digester and a 5:3:1 combination of nitric, hydrochloric and hydrofluoric acids (Achilli et al., 1991). Carbon and N of poultry litter and mill mud was analysed with a LECO TruSpec combustion analyser (Bremner, 1996). Water soluble and total ammonia and

ammonium contents of sorbents, poultry litter and mill mud were determined following a 1:5 solid:water or KCl extraction *via* colorimetric assay using a modified indophenol reaction (Kandeler and Gerber, 1988). From the same extraction, water soluble and total nitrate and nitrite content were determined *via* reduction of nitrate to nitrite using vanadium (III) chloride (VCl_3) with detection by Griess reaction (Miranda et al., 2001). Exchangeable cations and the cation exchange capacity of sorbents was determined *via* the silver-thiourea extraction method (Pleysier and Juo, 1980). Briefly, a 1:50 sorbent to 0.01 M silver thiourea solution was mixed for 24 h, after which extracts were centrifuged and filtered, with cation exchange capacity (CEC) determined by measuring the amount of silver ions exchanged and exchangeable bases being determined by ICP-OES.

2.3. Ammonium sorption capacity of sorbents

To determine NH_4^+ sorption capacity, sorbents were suspended in 6.25, 12.5, 25, 50 and 100 mM NH_4^+ solutions prepared from analytical reagent (AR) grade ammonium sulfate (Sigma-Aldrich). For each sorbent type and concentration of NH_4^+ solution, one gram of sorbent was placed into a 50 mL centrifuge tube with 20 mL of NH_4^+ solution added. This procedure was repeated in triplicate for all sorbents. Samples were placed on an orbital shaker and shaken for 18 h before centrifuging for three minutes at 4754 RCF. 1 mL of supernatant was collected from palagonite, chabazite and clinoptilolite treated solutions. Since particles remained in suspension in the bentonite, vermiculite and biochar containing solutions, 1 mL of solution was subsampled and centrifuged at 52,826 RCF for 15 min. Supernatant from all sorbent treated solutions was analysed for NH_4^+ using the colorimetric assay described above. NH_4^+ sorption was calculated by subtracting the NH_4^+ remaining in the supernatant from the original NH_4^+ solution concentration. The NH_4^+ sorption of sorbents was determined by the Langmuir sorption isotherm equation (McGechan and Lewis, 2002), where Q_{max} (mg NH_4^+) corresponds to the maximum sorption capacity of sorbents and k_L refers to Langmuir constants related to adsorption capacity and rate.

$$Q = Q_{max} \left[\frac{k_L C}{1 + k_L C} \right]$$

2.4. Nitrogen leaching from sorbent-amended organic wastes

Leaching experiments were conducted using $50 \times 50 \times 120$ mm seedling tubes and sorbents combined with poultry litter and mill mud at approximately 65 kg N ha^{-1} , equivalent to 32 t of mill mud and 2.6 t of poultry litter per hectare. To facilitate contact of NH_4^+ with reactive sites, sorbents and organic wastes were incubated for three days following the protocol of Redding (2011). Briefly, materials for each treatment level were prepared in 119×60 mm (474 mL) plastic containers, moistened to saturation with deionised water and thoroughly mixed by hand for 3 min using a spatula. Samples were incubated for 72 h in the dark at 30°C and ~80% humidity (Clayson Incubator, Clayson Laboratory Apparatus Pty. Ltd., Narangba, Australia). Three ratios of sorbent:waste mixtures were prepared with 2:1, 1:1 and 1:1.5 sorbent:waste on a dry matter basis, similar to bentonite ratios used by Redding (2011). Following incubation, sorbent-waste mixtures were placed into tubes with 100 mL of washed sand that was mixed with sorbent-waste mixtures to simulate subsurface application. Five replicates were prepared for each sorbent type and sorbent:waste ratio. Tubes were placed into small plastic bags without covering the tops to collect leachate, and incubated in the dark (30°C , ~80% humidity) for 21 days. On days 0, 3, 7, 14 and 21, tubes were watered with 5 mL of deionised water until at least 5 mL of leachate accumulated in the bag. Approximately 1.5 mL of leachate was subsampled and stored at -20°C until DIN analysis (see above). Excess

leachate was returned to the tubes. This approach allows obtaining a relative measure of DIN leached and minimizes variability in nutrient concentration as the leached volume would be small compared to pore volume.

2.5. Estimating DIN availability using diffusive fluxes with microdialysis

Sorbents with high (clinoptilolite), moderate (bentonite) and low (palagonite) NH_4^+ sorption capacity were used for further testing using microdialysis to quantify diffusive fluxes of DIN as a real-time estimate of ammonium (NH_4^+) and nitrate (NO_3^-) availability from a plant root perspective. The microdialysis system consists of a syringe pump (CMA 4004, CMA Microdialysis AB, Kista, Sweden) housing four micro-syringes (2.5 mL, Hamilton, Bonaduz, Switzerland) that are connected to microdialysis probes (CMA 20). The perfusate is collected into 1.5 mL Eppendorf tubes placed in a styrofoam box on ice. Probes of 1 mm length and 0.5 mm diameter with polyarylethersulfone membrane with a 20 kDa molecular weight cut-off were used (Brackin et al., 2015).

Sorbent-amended mixtures of poultry litter + sugar mill mud were prepared as described above with the 1:1 sorbent:waste ratio as optimal for most sorbents. Samples were transferred into modified 50 mL centrifuge tubes that were cut in half to facilitate probe placement with mesh fitted over the bottom conical base to separate solids from leachate and prevent anaerobic conditions (Inselsbacher et al., 2011; Brackin et al., 2015). Samples were randomly placed into form-fitting styrofoam blocks to shield samples from light and kept at field capacity for the entirety of the experiment with four replicates for each treatment. Samples were incubated in the dark at 30°C and ~80% humidity for 21 days and were removed for 1 h on day 0, 3, 7, 14 and 21 to insert microdialysis probes and collect perfusate at a flow rate of $5 \mu\text{L min}^{-1}$ to obtain 300 μL of perfusate (Brackin et al., 2015). The collected samples were stored at -20°C and analysed for DIN as described above.

2.6. Plant responses to sorbent-amended organic wastes

All treatments were prepared as described in the leaching experiment. To facilitate visual inspection of root morphology, seedling tubes were modified by precutting the vertical sides of one panel from each pot, allowing one side to be removed at a later point. Tubes were wrapped in three layers of cling wrap to restore structural integrity. Using the same sorbent-organic waste ratios described earlier, sorbent-waste mixtures were placed in a single layer, approximately halfway down between two layers of sand. Two sorghum (*Sorghum bicolor*) seeds were placed 10 mm below the sand surface, directly adjacent to the removable side, and one germinant was removed upon emergence to allow one seedling to grow. Tubes were placed in a naturally lit glasshouse at The University of Queensland, St Lucia Campus, for 21 days during July–August 2017, with temperatures ranging from -20 – 30°C . Tubes were watered to field capacity every two days. After day 21, root morphology was inspected *via* the removable panel. Plants were harvested and substrate carefully washed from roots. Shoots and roots were dried at 55°C for 48 h and biomass recorded.

2.7. Statistical analysis

Nitrogen data from microdialysis were analysed using one-way ANOVA followed by Tukey's *post hoc* analysis to determine significant differences between treatments (GraphPad Prism version 7.00). Confidence intervals (95%) were determined from two-tailed *t*-tests ($P = 0.05$).

The effect of sorbent on the leaching test was analysed at each time using two-way correlated analysis of variance (sorbent as categorical variable, dose level as continuous variable), and a three-way ANOVA used to determine overall model including time (as above, time as continuous variable). The Matlab 2016b command `anovan` was used.

Table 1

Sorbents examined in this study, their distributors, source location and range in particle sizes as provided by the distributors.

Sorbent	Distributor	Source location	Particle size (mm)
Chabazite	John Webster Innovations	Naples, Italy	>0.1–0.2
Clinoptilolite	Castle Mountain Zeolites	Quirindi, NSW	>0.1–0.5
Vermiculite	Brunnings	Brunnings, AUS	0.3–4.0
Biochar	Chaotech	Rocklea, QLD	0.2–2.0
Sodium bentonite	Bentonite Resources	Ebenezer, QLD	2.2–3.5
Palagonite	Mount Sylvia Soil Conditioners	Mount Sylvia, QLD	0.1–2.0

Interaction effects were significant, but generally masked the primary effect, without a substantial improvement in model quality, and only primary effects are reported. Linear model residuals were normally distributed, noting this is not critical, given the very large numbers of degrees of freedom (112 at each time, 587 for 3-way ANOVA). Rstudio was used to fit Langmuir curves isotherm equations for NH_4^+ sorption.

3. Results

3.1. Physicochemical traits of organic wastes and sorbents

Sources, physicochemical traits including element composition of the materials are summarized in Tables 1, 2 and Supplementary Table 1. Carbon and N concentrations were higher in poultry litter than sugar mill mud, and NH_4^+ concentration in poultry litter was 16-fold higher than nitrate (Table 2). Poultry litter had a 14-times higher NH_4^+ concentration than mill mud in line with higher total N content (Supplementary Table 1). Exchangeable cations in vermiculite, biochar, bentonite and palagonite were dominated by one or two cations, which varied between the sorbents, and were more evenly distributed in clinoptilolite and chabazite. Sorbent CEC stratified into three categories: low (<10 cmol(+)/kg; biochar and chabazite), medium (~26 cmol(+)/kg; palagonite) and high (>45 cmol(+)/kg; vermiculite, bentonite, clinoptilolite) (Table 2; further analysis in Supplementary Tables 1 and 2).

3.2. Ammonium sorption capacity of sorbents

The amount of NH_4^+ retained by sorbents increased with increasing NH_4^+ concentration until an equilibrium was reached under the test conditions (Fig. 1). Sorbents grouped into low, medium and high NH_4^+ retention capacity with 5.7 mg NH_4^+ g⁻¹ sorbent (palagonite) ≤ 13.1–7.7 mg NH_4^+ g⁻¹ (vermiculite, biochar, bentonite) ≤ 24.3–16.2 mg NH_4^+ g⁻¹ (chabazite, clinoptilolite, Table 3). Sorbent CEC (Table 2) did not accurately predict NH_4^+ sorption capacity. For example, although chabazite had the lowest measured CEC (8.1 cmol(+)/kg), NH_4^+ sorption capacity was highest of all tested sorbents (24.3 mg NH_4^+ g⁻¹ chabazite, Table 3). Similarly, palagonite with an intermediate CEC had the lowest maximum NH_4^+ sorption capacity

(5.7 mg NH_4^+ g⁻¹ palagonite). At lower NH_4^+ concentrations (6.25–25 mM NH_4^+), clinoptilolite, chabazite and bentonite sorbed a greater proportion of the NH_4^+ ions present in solution (58–75%) than biochar, palagonite and vermiculite which sorbed only ~34 to 44% of NH_4^+ .

3.3. Ammonium leached from sorbent-amended wastes

Nutrient leaching from soil in response to rainfall or irrigation was studied by watering the tubes in excess and collecting the leachate. Untreated wastes (control) released NH_4^+ into the leachate in an initial burst (days 0 to 7) followed by a gradual decline in NH_4^+ release (days 7 to 14) that approached the detection limit before reaching an equilibrium (14 and 21 days, Fig. 2). In contrast, sorbent:waste mixtures attenuated the peak release of NH_4^+ and achieved equilibrium sooner than the waste-only control. The level of attenuation depended on sorbent type and application rate, with sorbent type and application rate highly significant ($P = 8 \times 10^{-11}$, $P = 1 \times 10^{-32}$, respectively). The 3-factor linear model had an R^2 of 0.67, indicating a large fraction of the total variance was explained, with much of the residuals due to non-linear effects in time. At each time point, sorbent type was significant ($P < 0.05$), with dose being significant at all times except day 14 (all P values are shown in Supplementary Table 3). Clinoptilolite had the strongest sorption overall (except at time 0), with significantly higher sorption than all other sorbents at $t = 7$ and 14 days. Clinoptilolite reduced NH_4^+ release in the first three leaching events (days 0, 3, 7) by 65, 97 and 94% at the highest sorbent-manure addition compared to un-amended wastes (control). Chabazite performed the best at $t = 0$, significantly better than the next best sorbent (Clinoptilolite) ($P < 0.05$), but was similar to most sorbents at later leaching events.

Vermiculite, bentonite and biochar achieved similar reductions in NH_4^+ leaching of 34 to 49%, 15 to 57% and 27 to 55% respectively, and an equilibrium phase ~7 days earlier than the control. Palagonite amended wastes exhibited NH_4^+ leaching patterns that more closely mirrored the no sorbent control. In general, all sorbents apart from palagonite, significantly ($P < 0.01$) reduced NH_4^+ leaching rates compared to the control, with the main effect occurring in the first week.

Table 2

Physicochemical traits of poultry litter, mill mud and sorbents reported on an oven-dry basis. pH of sorbent amended manures at an application rate of 1:1 are reported only as changes in pH across different levels of sorbent application were generally negligible (pH ± 0.04) or minor in the case of bentonite and chabazite (pH ± ~0.29).

	Organic wastes		Sorbents					
	Poultry	Mill mud	Chabazite	Clinoptilolite	Vermiculite	Biochar	Bentonite	Palagonite
Moisture %	41.3 ± 0.51	72.2 ± 2.6	n/a	n/a	n/a	n/a	n/a	n/a
pH	8.23 ± 0.03	4.78 ± 0.01	5.69 ± 0.02	5.03 ± 0.01	4.98 ± 0.02	5.32 ± 0.01	5.38 ± 0.09	5.01 ± 0.02
Total C %	30.73	6.04	n/a	n/a	n/a	n/a	n/a	n/a
Total N %	2.14	0.34	n/a	n/a	n/a	n/a	n/a	n/a
NH_4^+ mg/kg	4514 ± 216	321 ± 11	1.35 ± 0.17	1.29 ± 0.05	1.55 ± 0.21	1.74 ± 0.05	1.45 ± 0.08	1.25 ± 0.04
NO_3^- mg/kg	279 ± 13	<d/l	1.2 ± 0.14	0.72 ± 0.08	0.2 ± 0.40	0.88 ± 0.27	15.07 ± 1.61	0.46 ± 0.06
Exchangeable Ca ^a	n/a	n/a	2.74	19.54	1.46	0.78	20.92	18.23
Exchangeable K ^a	n/a	n/a	2.02	9.52	0.72	5.91	0.29	0.01
Exchangeable Mg ^a	n/a	n/a	0.87	8.65	43.53	1.51	7.14	7.68
Exchangeable Na ^a	n/a	n/a	2.50	8.52	0.06	0.45	21.85	0.26
CEC ^a	n/a	n/a	8.12	46.24	45.77	8.65	50.21	26.18

^a cmol(+)/kg.

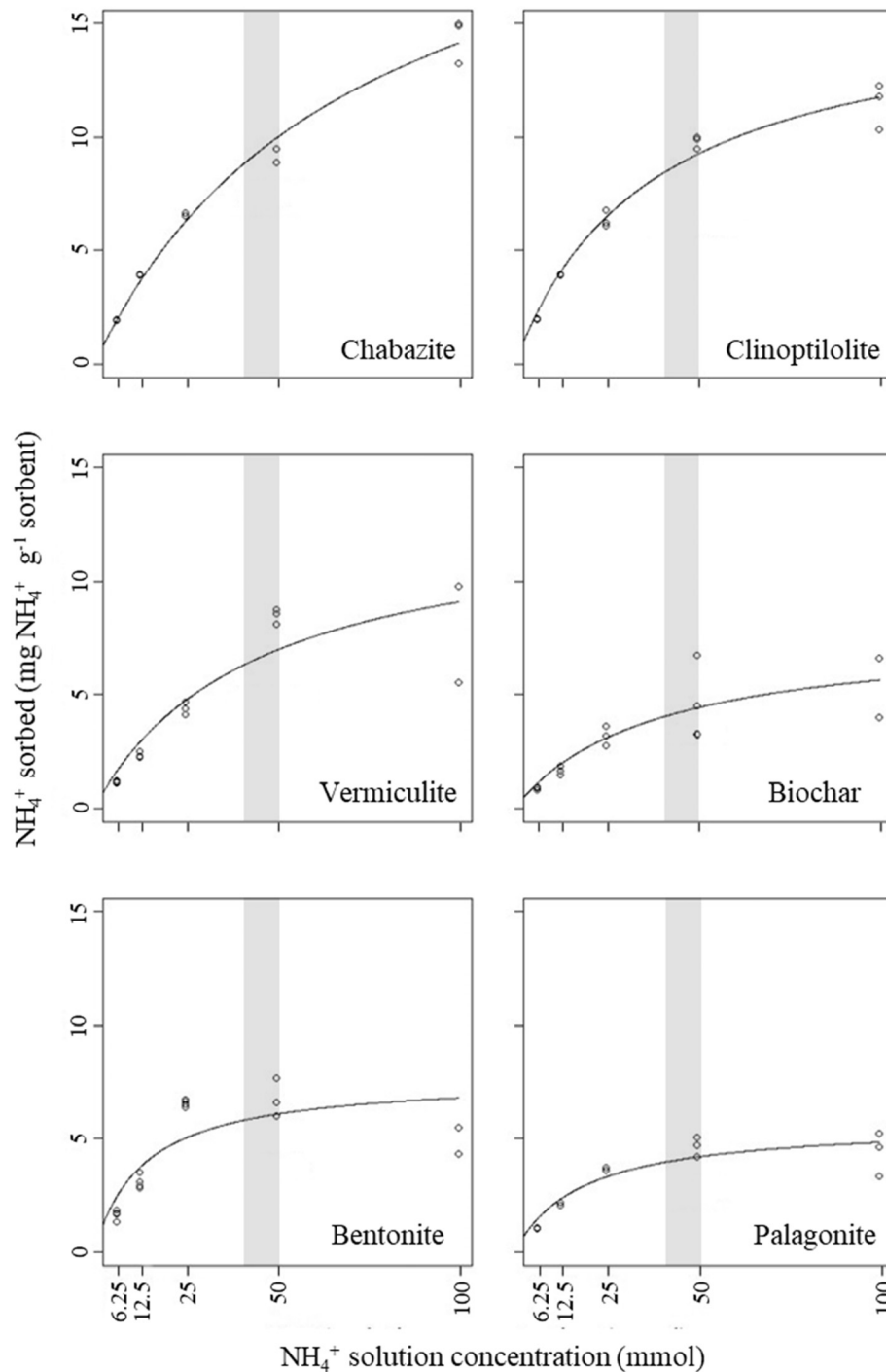


Fig. 1. Sorption isotherms for NH_4^+ on chabazite, clinoptilolite, vermiculite, biochar, bentonite and palagonite over NH_4^+ concentrations ranging from 6.25 to 100 mM NH_4^+ . The shaded area represents the NH_4^+ concentration of the sugar mill mud and poultry litter mixture used in the following experiments.

In contrast, sorbents had no effect on NO_3^- , which was consistently at, or below, the detection limit of $0.5 \mu\text{M}$ (data not shown).

Formulating sorbents and organic wastes resulted in variable reductions of the amount of NH_4^+ leached relative to the control across three levels of sorbent addition, ranging from 7% reduction with a 2:1 ratio of waste:palagonite to 80% with 1:1.5 waste:clinoptilolite (Table 4). At the highest sorbent:waste ratio, the capacity of sorbents to reduce NH_4^+ leaching reflected the same three broad categories detected for NH_4^+ sorption capacities, with 69 and 80% reduction in NH_4^+ leaching (chabazite, clinoptilolite), 49 to 57% (vermiculite, biochar, bentonite) and 23% (palagonite). Increasing sorbent:waste ratios from 1:1 to 1.5:1 resulted in further gains in leaching reduction although these

were relatively minor and ranged from ~1.5% (clinoptilolite) to ~11% (biochar).

3.4. Ammonium fluxes in sorbent-waste formulations

Diffusive fluxes of NH_4^+ in palagonite-, bentonite-amended wastes and control shared an initial period of higher NH_4^+ fluxes, followed by a substantial decline by day 14, and increase by day 21 (Fig. 3). The magnitude of NH_4^+ fluxes differed significantly ($P < 0.05$), with bentonite < palagonite < control on most sampling days, except day 14 where fluxes were similar. In contrast, clinoptilolite-amended waste maintained the lowest and most stable NH_4^+ fluxes throughout the experiment, ranging

Table 3

Calculated maximum NH_4^+ sorption Q_{max} ($\text{mg NH}_4^+ \text{g}^{-1}$ sorbent) of sorbents used in this study with k_L referring to Langmuir constants related to adsorption capacity and rate. Levels of significance are *** ≤ 0.001 , ** ≤ 0.01 and * ≤ 0.05 .

Sorbent			Std error	P value
Chabazite	Q_{max}	24.3400	1.7020	***
	k_L	0.0010	0.0001	***
Clinoptilolite	Q_{max}	16.2300	0.8560	***
	k_L	0.0019	0.0002	***
Vermiculite	Q_{max}	13.1300	2.3680	***
	k_L	0.0016	0.0006	*
Biochar	Q_{max}	7.8239	1.7398	***
	k_L	0.0018	0.0008	*
Bentonite	Q_{max}	7.7086	1.0615	***
	k_L	0.0053	0.0021	*
Palagonite	Q_{max}	5.7211	0.5253	***
	k_L	0.0039	0.0010	**

from 0.42 to 1.39 $\mu\text{mol NH}_4^+ \text{cm}^{-2} \text{h}^{-1}$, an order of magnitude lower than the control. In all treatments, nitrate fluxes were 3-orders of magnitude lower than NH_4^+ and, similar to the leaching experiment, did not differ between treatments ($< 15 \text{ nmol NO}_3^- \text{ cm}^{-2} \text{ h}^{-1}$, Supplementary Fig. 1).

3.5. Root colonization of sorbent-waste formulations

We tested how roots of sorghum seedlings respond to sorbent-waste formulations. High ion concentrations, including NH_4^+ , can cause nutritional or pH imbalances, and/or toxicity. Regardless of sorbent-waste ratios, roots intensively colonized bentonite, chabazite and clinoptilolite amended wastes that remained intact as a single layer when removed from pots (Fig. 4). In contrast, vermiculite, biochar, and palagonite amended wastes and control had lower root

Table 4

Total percentage reduction in NH_4^+ leached from sorbents combined with poultry litter and mill mud at three different sorbent:waste mixing ratios. Superscript indicates significant differences between sorbents within one ratio (uppercase) and between different ratios within each sorbent (lowercase) ($P < 0.05$).

Ratio	Chabazite	Clinoptilolite	Vermiculite	Biochar	Bentonite	Palagonite
Total % reduction in NH_4^+						
2:1	31.4 ± 2.2 ^{Ba}	65.2 ± 1.3 ^{Aa}	34.3 ± 6.9 ^{Ba}	27 ± 4.6 ^{Bca}	15.5 ± 2.4 ^{Bca}	7.1 ± 2.3 ^{Ca}
1:1	62.6 ± 2.3 ^{ABb}	78.6 ± 1 ^{Ab}	43.7 ± 2.4 ^{Ca}	43.5 ± 3.7 ^{Cab}	47.9 ± 4.4 ^{Bcb}	13.9 ± 6.2 ^{Da}
1:1.5	69.5 ± 0.3 ^{ABb}	80.1 ± 0.8 ^{Ab}	49.1 ± 3.2 ^{Ba}	54.6 ± 8.5 ^{Bb}	56.6 ± 1.6 ^{Bb}	23 ± 5.6 ^{Ca}

colonization, and the sorbent-waste layer disintegrated upon contact with water. The experiment was repeated without seedlings and all sorbent-amended wastes and control disintegrated after ~3 s of contact with water indicating that not sorbents *per se* but prolific root growth was the cause for the sorbent-waste layer staying intact.

4. Discussion

Striking the balance between adequately supplying nutrients to crops while minimizing nutrient losses from soil is a problem that has resisted resolution. Here, organic agricultural wastes were formulated with one of five geosorbents and a biochar to quantify how sorbent:waste formulations affect the release profile of NH_4^+ , a main crop-available N form. We examined the ability of crop roots to colonize sorbent-waste formulations to scrutinize the physicochemical properties of sorbents and waste:sorbent formulations in context of the biological systems that we aim to supply with N. The ammonium sorption capacity of sorbents from NH_4^+ solution fell within the documented

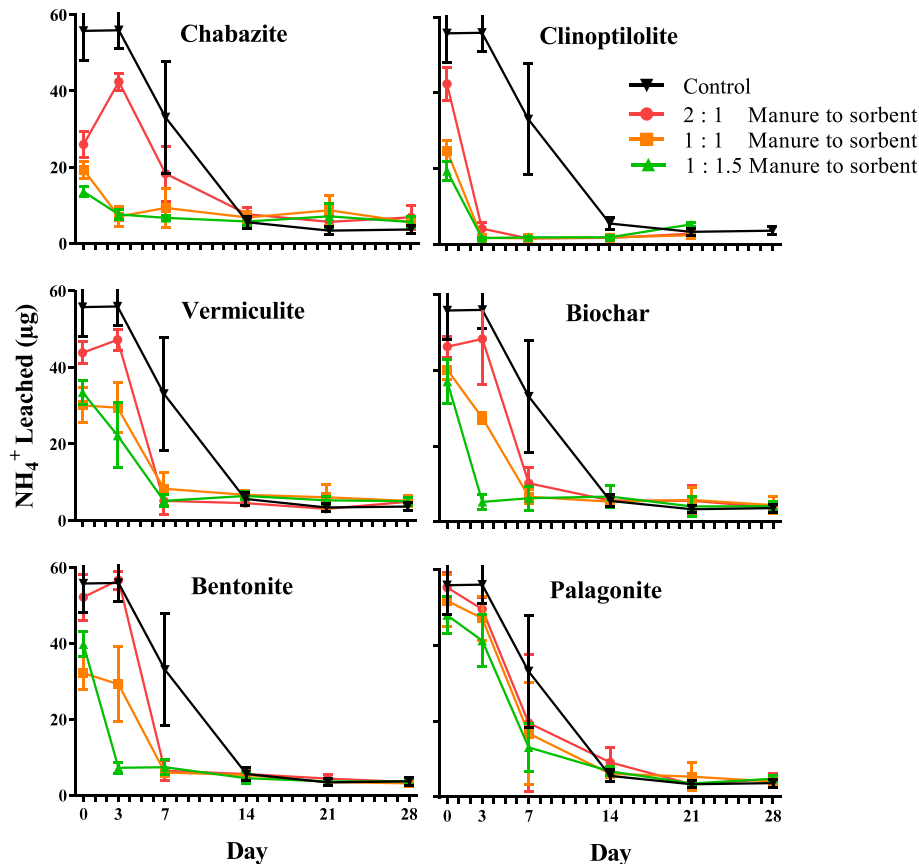


Fig. 2. Ammonium leached from sorbents combined with poultry litter and mill mud at three different sorbent application rates. Error bars represent 95% CI (n = 5) for each data point.

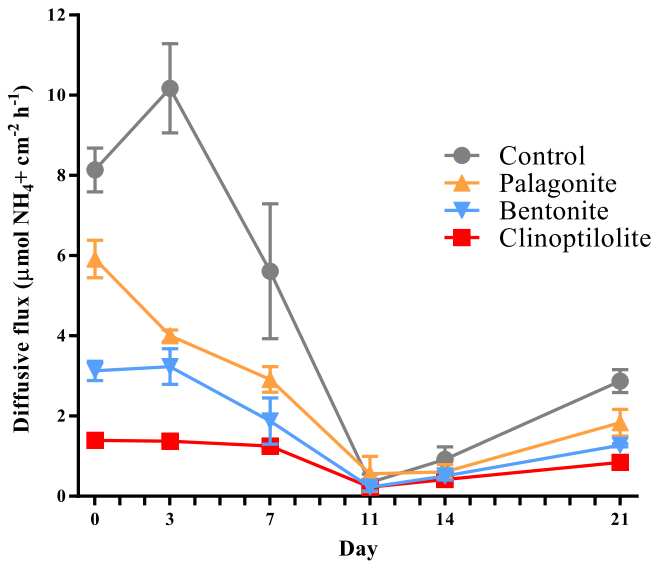


Fig. 3. Ammonium fluxes ($\text{NH}_4^+ \text{ cm}^{-2} \text{ h}^{-1}$) in clinoptilolite, bentonite and palagonite amended organic wastes (poultry litter and mill mud) at a 1:1 ratio with untreated organic waste as control. Each data point is $n = 4$ with error bars representing 95% CI.

range, ranking chabazite > clinoptilolite > vermiculite > bentonite > biochar > palagonite. This ranking also broadly reflects the behavior of sorbent-waste formulations with respect to NH_4^+ leaching, diffusive fluxes of NH_4^+ , and the preference of roots for colonizing the sorbent-waste mixtures. The best performing sorbent for the attributes studied here was clinoptilolite, followed by chabazite.

4.1. Ammonium sorption properties of sorbents

High NH_4^+ selectivity has been documented for chabazite and clinoptilolite in context of wastewater treatment (reviewed by Gupta et al., 2015), possibly caused by a high coordination between the geometry of NH_4^+ and zeolite lattice (Teunissen et al., 1995). Lin et al. (2016) reported similar maximum NH_4^+ sorption capacity in chabazite from Arizona, USA ($34.2 \text{ mg NH}_4^+ \text{ g}^{-1}$) relative to $24.3 \text{ mg NH}_4^+ \text{ g}^{-1}$ demonstrated here by Italian chabazite suggesting similar traits irrespective of source of origin. Likewise, clinoptilolite NH_4^+ sorption capacities measured here ($16.2 \text{ mg NH}_4^+ \text{ g}^{-1}$) fell within range of untreated clinoptilolite NH_4^+ sorption capacities across varying origins (ranging from 2.7 to $30.6 \text{ mg NH}_4^+ \text{ g}^{-1}$, Wang and Peng, 2010). Higher reported sorption capacities are often achieved with pretreatment of chabazite; for example, pretreatment with NaCl increased chabazite NH_4^+ exchange capacity by 40% (Leyva-Ramos et al., 2010). Whether pretreatment should be considered for increasing the capacity for NH_4^+

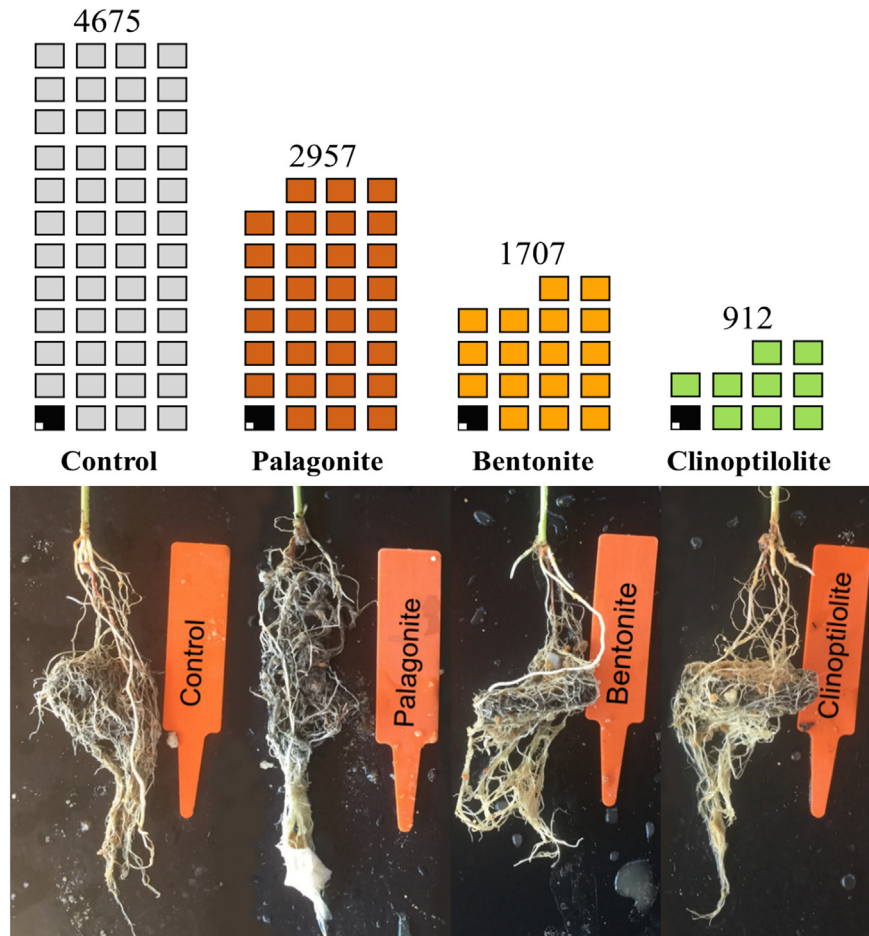


Fig. 4. Top image shows schematic NH_4^+ fluxes of sorbent-amended wastes and I_{max} , the maximum estimated root uptake rate of sugarcane (black square, $97.5 \text{ nmol NH}_4^+ \text{ cm}^{-2} \text{ h}^{-1}$) and sorghum (white square inset, $10.8 \text{ nmol NH}_4^+ \text{ cm}^{-2} \text{ h}^{-1}$). Each square represents $\sim 100 \text{ nmol NH}_4^+ \text{ cm}^{-2} \text{ h}^{-1}$ with total fluxes ($\text{nmol NH}_4^+ \text{ cm}^{-2} \text{ h}^{-1}$) shown above columns. Fluxes for each treatment represent averages of 25 replicate flux measurements over five sampling events (see Fig. 3). Bottom image shows the two distinct root morphologies detected with un-amended control (left) and palagonite (center) or clinoptilolite (right) amended wastes at a 1:1.5 sorbent to organic waste ratio after $\sim 10 \text{ s}$ of rinsing. Roots grown in palagonite, biochar, vermiculite and control treatments only loosely bound the organic waste layer with most roots developed under rather than in the layer. In the presence of clinoptilolite, bentonite and chabazite, roots intensely colonized the organic waste layer.

uptake and potentially that of other ions will require further investigation including cost-benefit analyses.

Cation exchange capacity (CEC) is used to predict sorbent behavior and the CEC measured here fell within the range reported for some sorbents (e.g. Pratt et al., 2016). However, we found CEC to be a poor predictor of NH_4^+ sorption capacity, and noted that the CEC reported for chabazite was substantially higher (250 $\text{cmol}(+)/\text{kg}$, Leyva-Ramos et al., 2010) than in our study (8.12 $\text{cmol}(+)/\text{kg}$), while others were similar (8 $\text{cmol}(+)/\text{kg}$, Kesraoul-Oukl et al., 1993). Since impurities can distort sorbent CEC, future studies may resolve such discrepancies by characterizing sorbent purity (Dohrmann, 2006), as well as resolving the most suitable methods for CEC analysis (summarized in Supplementary Table 2).

Our study confirms that the sorbents' physical properties *per se* did not define their NH_4^+ sorption capacity. While bentonite, biochar and vermiculite differ in hydraulic conductivity (e.g. high in vermiculite and biochar, low in bentonite), these sorbents have similar NH_4^+ sorption capacities and NH_4^+ leaching profiles. Similarly, while decreasing particle size increased the NH_4^+ sorption capacity of clinoptilolite and chabazite (Passaglia and Laurora, 2013; Wen et al., 2006), this is not the case for biochar (Hina et al., 2013). Rather, biochar's physicochemical traits, including electrostatic sorption, chemisorption and precipitation, affect its NH_4^+ sorption capacity, and functional groups of oxygen on the surface promote hydrogen bonding and electrostatic interaction with cations (Cai et al., 2016; Joseph et al., 2010).

The pH in NH_4^+ solutions used to test sorption decreased from 6.2 to 5.6 with increasing NH_4^+ concentration and may have altered exchange with some sorbents. For chabazite, clinoptilolite and bentonite the maximum NH_4^+ sorption capacity was detected at pH 6 (Hedström, 2001; Mazloomi and Jalali, 2017; Vassileva and Voikova, 2009) while $>\text{pH}$ 7 was optimal for biochar (Wang et al., 2015). We did not specifically explore the effects of pH on sorbents, as the pH of the sorbent:waste mixtures was in a similar range (pH ~ 5–5.8) and only minor increases of 0.04 (bentonite) and 0.29 (clinoptilolite) pH units were observed with increasing sorbent:waste ratios.

4.2. Potential of sorbents to mitigate ammonium leaching from organic wastes

The efficiency of sorbents in reducing NH_4^+ leaching from sorbent-waste formulations clustered into the same broad categories as for the sorption capacity determined with NH_4^+ solution. Clinoptilolite and chabazite reduced NH_4^+ leaching by 80 and 69%, respectively, with bentonite, biochar and vermiculite reducing it by 49–56% and palagonite by 23%. Chabazite provided a short-term effect (<7 days), while clinoptilolite provided sustained attenuation of NH_4^+ release, which is a desirable trait for supplying N to crops over several weeks or months (Han et al., 2008). Sorbents with stronger NH_4^+ sorption capacity greatly attenuated the initial period of high NH_4^+ release characterising untreated waste, which in turn depends on the strength of the binding of ions to sorbent surfaces or structures (Sepaskhah and Yousefi, 2007). Clinoptilolite formulated at the highest rate of 1.5:1 sorbent-waste had the most pronounced effect, achieving 65 and 97% reduction in NH_4^+ leaching in the first two leaching events. Similarly, Redding (2011) reported that increasing ratios of bentonite to poultry litter from 0.32:1 to 1.56:1 increased the proportion of exchangeable NH_4^+ and decreased soluble NH_4^+ . Sorbent-enabled reductions in N leaching losses hold promise as these losses can be significant as observed during five simulated consecutive rainfall events on poultry litter that leached 21 to 24% of total N, mostly as NH_4^+ , with 60% of N leached during the first event (Robinson and Sharpley, 1995).

We propose that for most sorbents studied here an ideal formulation is a 1:1 ratio of sorbent:waste to reduce NH_4^+ leaching. Although, due to its high affinity for NH_4^+ , a 1:2 clinoptilolite:waste ratio may also prove to be cost-effective. The reason for the diminishing returns obtained by further sorbent additions beyond a 1:1 ratio may be a decreasing

proportion of free NH_4^+ relative to sorbent binding sites, which would decrease the frequency of contact between water-soluble NH_4^+ and binding sites. A further consideration is that sorbent selectivity for NH_4^+ is crucial, as demonstrated by the higher proportion of sorption of NH_4^+ from low concentration solutions (6.25–25 mM) by clinoptilolite, chabazite and bentonite tested here. This is also demonstrated by the incomplete sorption of NH_4^+ from low concentration NH_4^+ ion solutions by all sorbents tested here (Howery and Thomas, 1965; Kumar and Jain, 2013). A lower proportion of water-soluble ions to binding sites appears likely considering we applied sorbents at rates that exceeded NH_4^+ present in the wastes. We anticipated that as the tested systems moved from a pure NH_4^+ solution to complex waste mixtures that contain diverse ions, competition for binding sites would depress NH_4^+ sorption. Introduction of competing ions decreased NH_4^+ sorption in bentonite and vermiculite by up to 26 and 74%, respectively (Mazloomi and Jalali, 2017). Differing ion selectivity according to sorbent type suggests that sorption of competing ions was a likely factor in our study. Further research should explore if sorbents with differing affinities for specific ions can target particular nutrients and accommodate the properties of different wastes and requirements of crops. Taken together, our results confirm that sorption retards NH_4^+ losses from wastes, and that sorbents, especially clinoptilolite amended organic wastes, can reduce N leaching.

4.3. Ammonium fluxes in sorbent-amended wastes with view of NH_4^+ uptake capacity of roots

Microdialysis is a recent sophisticated technique to detect ion fluxes in soil and estimate rates at which solutes are transported to roots (Inselsbacher et al., 2011; Brackin et al., 2015, 2017). We found that sorbents behaved in line with our results for NH_4^+ sorption capacity and leaching. Sorbents with higher NH_4^+ retention capacity showed an increasing capacity to attenuate the initial period of high NH_4^+ flux that characterised un-amended waste. Notably, clinoptilolite:waste formulation had the most stable and lowest NH_4^+ fluxes of all sorbents. These findings are in good agreement with those of Cyrus and Reddy (2011), who noted that after flushing NH_4^+ -saturated clinoptilolite for >100 h with deionised water a considerable proportion of NH_4^+ remained bound and was only desorbed by 0.1 M HCl.

Similarly, Hedström and Amofah (2008) found that tap water only desorbed 23% of NH_4^+ -saturated clinoptilolite after flushing for 48 h (with a substantially higher flow rate than Cyrus and Reddy (2011)). Although not investigated here, C:N ratios and pH are likely to influence desorption kinetics (Kithome et al., 1998; Zaman and Nguyen, 2010), and testing a greater diversity of organic wastes would elucidate their impacts. The ability of clinoptilolite to retain and gradually release NH_4^+ shows promise for the formulation of next-generation fertilizers that avoid boom-bust patterns of nutrient release.

To investigate if sorbent-formulated wastes more accurately meet crop N demand and, specifically, match the uptake capacity of roots, we compared diffusive fluxes of NH_4^+ and I_{max} , the estimated maximum NH_4^+ uptake capacity that has been established for sugarcane (Brackin et al., 2015) and sorghum roots (Jackson et al., 1996; Rao et al., 1993). Sorghum seedlings were used as a proxy for sugarcane as both are fast growing tropical C_4 crops, and calculated that the increased NH_4^+ retention of best performing sorbent:waste formulations improves the match between NH_4^+ supply and root uptake capacity. Ratios of NH_4^+ supply-to-root uptake capacity ranged from 46:1 in un-amended waste, 30:1 in palagonite-formulation, to 9:1 in clinoptilolite formulation. The preferential colonization of roots of clinoptilolite, chabazite and bentonite amended wastes is testimony that sorbents avoid the potentially toxic levels of NH_4^+ (and potentially other ions) (Britto and Kronzucker, 2002; Li et al., 2014). These results show that sorbents with stronger NH_4^+ retention decrease the equilibrium of NH_4^+ concentration and simulate lateral root propagation. Plants strategically exploit nutrient-rich patches (Drew and Saker, 1975; Hodge et al., 1998). These findings

hold promise for sorbents with high NH_4^+ retention, as studies have demonstrated that roots require relatively large patches of nutrients ($\sim 5 \text{ cm}^3$) to colonize (Hodge et al., 1998; Jackson and Caldwell, 1991; van Vuuren et al., 1996). Further investigation has to identify if lower NH_4^+ fluxes are indeed the cause of inhibited root colonization of the wastes without or low NH_4^+ -sorbents.

5. Conclusions

There is no doubt that synchronizing the supply of nutrients with the nutrient demand of crops is the basis for efficient nutrient use that avoids excess soluble and dissolved nutrients in soil that are subject to loss. Synchronizing nutrient supply with crop demand – while avoiding losses, excess or toxicity – opens the possibility of the sustainable intensification of agriculture. Formulating combinations of wastes and sorbents with view of particular crop nutrient physiologies and environmental conditions has potential to customize nutrient supply systems. Advancing the repurposing of organic wastes will support a circular nutrient economy without waste and pollution. Sorbents will have a role in innovative formulations of next-generation fertilizers.

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Conflicts of interest

No actual or potential conflicts of interest are declared by the authors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.07.135>.

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