RESEARCH ARTICLE

Integration of silicate minerals for ammonium and phosphate removal with an on-site wastewater treatment prototype

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Abstract

Inadequately treated wastewater exiting from on-site water treatment systems (OWTS) contains high levels of ammonium and phosphate, which contribute to environmental nutrient pollution. Nutrient removal in small-scale OWTS can be challenging because the most effective known methods are designed for large-scale systems and rely on biological processes. This work focuses on the implementation of two natural silicate-based minerals, clinoptilolite and Polonite, as non-biological sorptive media for nutrient removal in an OWTS. Lab-scale batch sorption experiments showed that Polonite performance is maximized after suspended solids have been removed from blackwater via ultrafiltration. In contrast, clinoptilolite shows robust performance even with untreated blackwater. With both minerals installed in our full-scale OWTS prototype, nutrient removal performance increased from 47.5 ± 15.0% to 84.1 ± 6.3% removal for total N and from 32.3 ± 2.3% to 78.9 ± 5.9% removal for total P. Nevertheless, the target removal performance (>80%) for total P was only achieved with high Polonite loading, which increased effluent pH outside the target range of 6 < pH < 9. Additionally, no loss in nutrient removal performance was observed when the OWTS was restarted after a 150-day idle period. To investigate the potential for media reuse and nutrient recovery, various media regeneration solutions were evaluated. For clinoptilolite, 1 M HCl, NaCl, and KCl all showed good regeneration ability at 2 h contact time, with KCl showing the highest (>86%) ammonium recovery. For the first time, we demonstrated that a minor fraction (30–40%) of binding sites in Polonite can be regenerated using 1 M NaOH or KOH. We also found that the same 1 M HCl regeneration solution could be reused for four clinoptilolite regeneration cycles with no loss in performance. From these results, we discuss opportunities and limitations for implementing these materials in small-scale OWTS.
1. Introduction

Nutrient pollution is a consequence of the uncontrolled release of bioavailable ions containing nitrogen and phosphorus into the environment. The severe negative impacts of nutrient pollution are not only environmental [1, 2], but also affect human health and the economy [3–7]. While agricultural runoff is the largest contributor to nutrient pollution, a growing global concern arises from inadequate on-site wastewater treatment discharges [8] which are likely underreported [9]. Inadequately treated blackwater–toilet effluent which contains a mixture of water, feces, and urine [10]–contains high levels of ammonium and phosphate (NH$_4^+$ and PO$_4^{3-}$) ions. Therefore, uncontrolled discharge of inadequately treated blackwater also results in loss of valuable nutrient resources which are crucial for agriculture. Fertilizers containing phosphate are almost entirely produced from phosphate rock, which is a non-renewable and unevenly distributed natural resource [11, 12]. Ammonia-based fertilizers are almost exclusively produced using the Haber-Bosch process, which accounts for approximately 2% of annual energy consumption and 1.2% of greenhouse gas emissions globally [13]. The potential to recover NH$_4^+$ and PO$_4^{3-}$ from wastewater for reuse in agricultural applications is becoming increasingly attractive from the perspective of sustainability and growing interest in “circular economies” [4, 14].

There are myriad technical challenges to implementation of adequate nutrient removal at small scales, and many hinge on the interrelated issues of scalability, sustainability, and resource scarcity. In particular, the growing global prevalence of water scarcity is also a pressing concern [8, 10], and strategies for enabling reuse of treated wastewater for non-potable applications are in high demand [15–17]. Newly adopted regulatory standards reflect this trend by providing metrics for safe discharge and/or reuse of wastewater from small-scale on-site wastewater treatment systems (OWTS) and non-sewered sanitation systems (NSSS) [18–20]. However, some new standards for nutrient effluent concentrations are difficult to reach for many state-of-the-art small-scale treatment systems, even for non-potable, restricted reuse applications. For example, the ISO 30500 standard for NSSS requires minimum removal thresholds of $\geq$ 70% total N and $\geq$ 80% total P regardless of whether the effluent is to be reused or discharged [18]. We recently reported laboratory testing and a preliminary techno-economic analysis of an OWTS prototype for treating the liquid fraction of blackwater [21]. The prototype is based on sequential processes of ultrafiltration, granular activated carbon filtration, and electrochemical disinfection, and was evaluated with respect to the ISO 30500 metrics for non-potable water reuse. This prototype system showed excellent performance for disinfection of effluent, reduction of chemical oxygen demand (COD), and removal of total suspended solids (TSS). However, like many systems designed for similar scales and wastewater influents [4, 22–24], the prototype could not reach the performance targets for total N and total P removal due to high levels of NH$_4^+$ and PO$_4^{3-}$ remaining in the effluent.

There is a lack of non-biological nutrient removal options which can operate effectively at small scales and low cost while also limiting the use of consumables and the generation of side-product waste streams (e.g. brine) [4, 23]. One non-biological option for NH$_4^+$ and PO$_4^{3-}$ capture is the use of sorptive media based on low-cost silicate minerals. Some of these materials (e.g. clinoptilolite) have been used for millennia [25] and intensely studied in recent decades [26–30], while others (e.g. Polonite, derived from opoka) are emerging in commercial products only within the last 10–20 years [31–35]. A persistent issue with practical implementation of sorptive media is determining the functional sorptive capacity of a particular material for a given wastewater stream. The primary mechanisms of sorption on these silicate minerals are ion-exchange, electrostatic interactions, and/or precipitation [36–40]. The clinoptilolite mineral lattice has negative charge which is counterbalanced by...
cations such as sodium, calcium, and potassium [41]. These cations can be replaced by \( \text{NH}_4^+ \) during the ion-exchange process, giving clinoptilolite great selectivity for \( \text{NH}_4^+ \) sorption [41]. Polonite has been shown to have selective sorption capacity for \( \text{PO}_4^{3-} \) by ion-exchange and/or hydroxyapatite precipitation [42]. Due to the presence of competing ions and differences in speciation as a function of pH, sorptive media often show lower capacity for target ions when tested with real wastewaters as compared to model solutions [26, 43–45]. Furthermore, maximum reported sorption capacities are often extrapolated from experimental results using theoretical models which may not account for competitive sorption processes or dynamic pH conditions [46–49]. Therefore, testing promising nutrient removal media with real wastewater under relevant operational conditions is essential to successfully move prototype technologies from laboratory to field testing.

Here, we report an evaluation of the silicate-based minerals clinoptilolite and Polonite for removal of \( \text{NH}_4^+ \) and \( \text{PO}_4^{3-} \), respectively, in our OWTS prototype. The goal of the present work is to determine if these minerals will be effective at scale when deployed in field tests, with a secondary aim of enabling nutrient recovery in future works, e.g., by directly using the regeneration byproduct as a fertigation solution. We evaluate the performance of clinoptilolite and Polonite with real blackwater by investigating (1) whether placement of the sorbents at different points in the OWTS treatment process affects their sorptive capacities; (2) whether these sorbents are effective in a single-pass filter configuration at prototype scale; and (3) if the use of different regeneration solutions can maximize media reuse and enable nutrient recovery. Finally, we will discuss the implications for use of these materials in field testing and suggest appropriate use-case scenarios.

2. Materials and methods

2.1 Ethics statement

Procedures for collection of human feces and urine from anonymous, healthy donors (with written informed consent) were approved by the Duke University Institutional Review Board.

2.2 Blackwater generation

Unless otherwise specified, blackwater (BW) was generated as described previously [21] using a ceramic pedestal toilet with 6 L tap water per flush and assuming \( \sim 1.5 \text{ L urine and } \sim 150 \text{ g feces per person per day} \) [50], spread across a total of five flush events [51]. Bulk solids were separated from the blackwater liquid fraction (BW-\( l \)) after the flush using a coarse sieve with \( \sim 10 \text{ mm diameter holes as a solid/liquid separator. The BW-} l \text{ was stored at room temperature (20–22} \degree \text{C) in a 50 L tank prior to use, which enabled some gravity settling of larger solid particles. However, advanced solids settling techniques, such as those described previously [52], were not used in this study.}

2.3 Sorptive media

Clinoptilolite (mesh size 8 × 14; 1.00 × 1.41 mm) was obtained from KMI Zeolite. Polonite (particle size 2–6 mm) was obtained from Ecofiltration Nordic. Mineral properties as reported by the suppliers can be found in S1 Data. Both minerals were rinsed with ultrapure water (18.2 M\( \Omega \text{ cm) to remove dust particles and dried in an oven at 105} \degree \text{C prior to use. Other than rinsing and drying, both minerals were used as-received and not further processed (e.g., sieving; grinding) prior to experiments.}
2.4 Description of the OWTS prototype and water sample nomenclature

A full-scale on-site wastewater treatment system (OWTS) prototype was used in this study and has been described previously in detail [21]; a brief description of the treatment process and relevant features of this prototype is given here. The OWTS prototype consists of three subsystems operating in series: (1) a cross-flow ultrafiltration (UF) unit, providing removal of suspended solids; (2) a granular activated carbon (GAC) packed-bed filter, providing sorption of soluble organic species; (3) an electrochemical oxidation reactor (EC), providing disinfection of the treated effluent. The three subsystems are connected in series by polypropylene tubing and quick-disconnect fittings. In the current study, the order of the three subsystems (UF followed by GAC followed by EC) was never changed. The use of quick-disconnect fittings allows for liquid to be easily diverted to sample collection containers between the individual subsystems. For simplicity and clarity, we name liquid samples in this work according to the last subsystem the water exits from before collection, as depicted in Fig 1. For example, a "UF-l" sample has only encountered the UF subsystem prior to collection. Likewise, an “EC-l” sample consists of liquid that has been treated using all three subsystems (UF followed by GAC followed by EC).

2.5 Analytical methods and chemical reagents

All calculations (average, standard deviation, percent removal, percent recovered) were performed using Microsoft Excel. Values with error bars are reported and plotted as average ± standard deviation. Data were plotted using OriginPro 2018. See the S1–S3 Datas files for additional details of calculations and all underlying data.

Fig 1. Simplified depiction of the OWTS prototype used in this study. Dashed arrows indicate liquid sampling points, and solid arrows indicate process flow. The blackwater liquid fraction (BW-l) is introduced into the feed tank and then encounters the three sequential treatment subsystems (UF, GAC, and EC). After the EC disinfection process, the treated effluent is pumped to the effluent tank. Liquid samples in this work are named according to the last subsystem process completed before sample collection.

https://doi.org/10.1371/journal.pwat.0000048.g001
For bench-scale batch sorption experiments, liquid samples were collected in clean, sterilized 1 L plastic containers. Untreated BW-1 samples were pulled directly from the OWTS feed tank using sterile, disposable serological pipettes; similarly, EC-1 liquid samples were collected using sterile, disposable pipettes from the effluent tank after the EC batch process was completed. UF-1 and GAC-1 liquid samples were collected by detaching the quick-disconnect fittings from the appropriate location between subsystems (see Fig 1) and allowing liquid to drain directly into sterile 1 L collection containers. Batch sorption experiments were performed on an orbital shaker (ThermoScientific MaxQ 4450) operating at 250 rpm. Total suspended solids (TSS) were measured according to EPA method 160.2. Conductivity and pH were measured using a Myron L 6PFC UltraMeter II. Samples for a three-tube most probable number (MPN) assay [53, 54] were collected from the feed tank and treated water tank using clean, sterile pipettes and stored at 4°C.

Water chemistry analyses were performed using the appropriate HACH reagent kits and methods (chemical oxygen demand, COD, HACH method 8000; total P, HACH method 8190, measured as mg PO₄³⁻ L⁻¹; reactive P, HACH method 8048, measured as mg PO₄³⁻ L⁻¹; total N, HACH method 10072; and NH₃, HACH method 10031), and results were measured with a HACH DR 900 colorimeter. A HACH DRB200 reactor was used for methods requiring digestion (COD, total P, and total N). Ultrapure water (18.2 MΩ cm) was used for samples requiring dilution prior to analysis. Safety note: The NH₃ test kit contains sodium nitroferricyanide, which can release hydrogen cyanide gas when mixed with strong acids. To test the 1 M HCl regeneration solutions for NH₃, we combined equal volumes of 1.45 M NaOH solution (HACH) with the acidic sample in the test kit tube, capped the tube and inverted several times to mix, and then added the nitroferricyanide reagent to the tube. Control measurements of only the 1.45 M NaOH showed no detectable NH₃ in this solution.

2.6 Integration of nutrient sorption media into the OWTS prototype and batch testing conditions

Silicate minerals were added to the OWTS to serve as the nutrient removal module (NRM). The NRM consisted of two 4-gallon (15.1 L) tanks placed between the GAC column and the EC oxidation tank. Fig 2 depicts the flow of water through the prototype with the NRM connected. The water flow rate through the NRM was dictated by the permeate flow rate from the UF subsystem which was typically 0.1–0.3 L min⁻¹. Water first entered the NRM into the clinoptilolite tank from the bottom port. The clinoptilolite tank was connected to the effluent port of the GAC column in a quick-disconnect fitting and polypropylene tubing. For laboratory testing at Duke, the Polonite tank was connected similarly to the influent port of the EC subsystem. The junction between the clinoptilolite and Polonite tanks consisted of three U-shaped ports made from 2” OD (5.08 cm) PVC centered 2.5” (6.35 cm) from the top of the tanks. Water exited the Polonite tank via a 1/2” (1.27 cm) PVC elbow pipe leading to the bottom of the tank. Only the clinoptilolite tank was installed at the Coimbatore field testing site. In that case, the effluent from the top of the clinoptilolite tank was connected to the influent port of the EC subsystem.

In batch testing, a total of 91 experiments with this full-scale OWTS prototype were performed in our laboratory, with batch sizes between 7.5 L to 20 L, to give a total treated liquid volume of 1005 L. The first 52 experiments (dataset 1; up to 425 L; performed between December 2019 –February 2020) were collected using the prototype as described in our previous publication, with liquid flowing through the GAC column in an up-flow configuration, and clinoptilolite and Polonite tanks added between the GAC column and the EC reactor tank [21]. Samples were taken from the feed and effluent tanks. The full datasets for all experiments
Fig 2. Nutrient removal module (NRM) integration with the OWTS prototype. (a) Schematic depicting installation of the NRM into the treatment system process flow (not to scale). Solid arrows show process flow between the different subsystems. Dashed arrows show direction of liquid percolation through the media in the nutrient removal module tanks. Due to high pH after contact with Polonite, the clinoptilolite tank (clin.) was placed before the Polonite tank (Pol.). (b) Photo of the NRM connected to the OWTS prototype in the Duke laboratory. Number labels for different process components are the same as in part (a).

https://doi.org/10.1371/journal.pwat.0000048.g002
can be found in the S2 Data. The first 12 experiments (0–98.0 L) were performed without connecting to the NRM in order to establish a baseline (Note: these 12 baseline experiments were also reported in our previous work [21]). After the initial baseline experiments, the NRM was disconnected on two occasions in order to (1) add the elbow exit port to the Polonite tank as shown in Fig 2 (experiments 22–25, 183.5–209.5 L) and (2) troubleshoot the EC disinfection process (experiments 30–31, 259.5–267.0 L), which was not working properly as indicated by high MPN values measured in the effluent. We determined by disconnecting and reconnecting that the NRM was not the cause of inadequate disinfection; consistent with our previous work, we observed that low conductivity (and thus low chloride concentration) of the influent and effluent during these experiments was the likely cause of inadequate disinfection [21]. (See S2 Data for full data set.)

Several other events occurred between collection of the two datasets; these changes did not impact the performance of the NRM, but we list them here for the sake of transparency. First, the membrane in the UF subsystem was changed from a polymeric membrane to a hollow-fiber ceramic membrane. Measurements performed immediately after changing the membrane indicated no change in performance of the UF subsystem. Secondly, dataset 2 was collected between July 2020 –September 2020, after the NRM had been idle for 150 days due to lab shutdown during the beginning of the COVID-19 pandemic. At the start of this idle time, all liquid was drained from the NRM. Finally, for dataset 2 we only measured reactive P (as PO$_4^{3-}$) and ammonium (as NH$_3$), rather than total N and total P which had been measured for dataset 1, due to limited availability of the different test kits. We know from baseline testing that the UF subsystem removes essentially all the organic fractions of total N and total P, leaving only NH$_3$ and reactive P in the effluent, so these are appropriate proxy measurements for total N and total P. To calculate total N and total P percent removal based on the measured NH$_3$ and reactive P values, we first determined the average fraction of total N present as NH$_3$ (0.762 ± 0.110) and the average fraction of total P present as reactive P (0.721 ± 0.026) in the influent. We then use these values to estimate the influent total N and total P values from the measured influent NH$_3$ and reactive P values. (See S3 Data for all data and calculations.)

3. Results and discussion

3.1 Batch evaluation of nutrient sorption from real wastewater

Clinoptilolite and Polonite were investigated as nutrient removal sorptive media to be implemented in our OWTS prototype. The prototype consists of three sequential treatment steps: ultrafiltration (UF), granulated activated carbon (GAC), and electrochemical oxidation (EC). Before implementation of the sorptive media into the OWTS, it is crucial to identify where in the water treatment process their sorption performance will be maximized. Hence, batch sorption experiments were carried out using liquid samples taken after each water treatment step. The batch processing time for our OWTS prototype is approximately 2 h, which gives a lower limit of the contact time for the nutrient removal media if no additional pumps or recirculation loops are added to the system. Fig 3 shows batch sorption results for clinoptilolite (Fig 3A and 3B) and Polonite (Fig 3C and 3D) as a function of mineral loading, with measurements performed after 2 h and 24 h of contact time in the orbital shaker. Initial nutrient concentrations ranged from 104–188 mg L$^{-1}$ for NH$_3$ and 51.4–67.9 mg L$^{-1}$ for PO$_4^{3-}$ (see S4 Data for complete data sets). For both minerals, nutrient removal increases with increasing loading up to 20–40 g L$^{-1}$. For Polonite, this steady trend is slightly disrupted at low loadings < 20 g L$^{-1}$, due to the broader distribution of particle sizes compared to clinoptilolite (See S1 Data). At 24 h, clinoptilolite loadings ≥ 20 g L$^{-1}$ remove > 80% NH$_3$ in all water samples (Fig 3B). At 2 h, clinoptilolite loadings < 20 g L$^{-1}$ appear to have a slight enhancement for NH$_3$ removal in
Fig 3. Nutrient removal performance at different media loadings in OWTS water samples. Media loading data points correspond to 0.1, 0.25, 0.5, 1.0, 2.5, and 5.0 g of sorptive media in 50 mL of water sample. Clinoptilolite placed in the orbital shaker for (a) 2 h or (b) 24 h; initial NH$_3$ concentration in the water samples ranged from 104–108 mg L$^{-1}$. Polonite placed in the orbital shaker for (c) 2 h or (d) 24 h; initial PO$_4^{3-}$ concentration in the water samples ranged from 51.4–67.9 mg L$^{-1}$. At 2 h, clinoptilolite loadings $>40$ g L$^{-1}$ removed $>80\%$ NH$_3$. At 24 h, clinoptilolite loadings $>20$ g L$^{-1}$ removed $>80\%$ NH$_3$. Clinoptilolite performance is largely unaffected by the water sample used. At 2 h, Polonite
GAC-l and EC-l samples (Fig 3A). In contrast, Polonite removal of PO₄³⁻ is consistently lower in BW-l samples regardless of the contact time. At 2h, Polonite loading > 50 g L⁻¹ remove 90% PO₄³⁻ in the GAC-l sample compared to 67% PO₄³⁻ removal in the BW-l sample (Fig 3C). At 24 h, Polonite loading 50 g L⁻¹ removes 97% PO₄³⁻ in the GAC-l sample compared to 84% PO₄³⁻ removal in the BW-l sample (Fig 3D). The key takeaway from these data is that, at shorter contact times, Polonite performance is maximized when the sorptive media is implemented after the GAC subsystem. Therefore, all following bench-scale batch experiments were carried out using GAC-l liquid samples to inform placement of the minerals at this point in the prototype.

Fig 4 shows the effect on nutrient removal as a function of increasing contact time. The sorption experiments were performed using GAC-l samples with 50 g L⁻¹ media loading. 50 g L⁻¹ was chosen because it achieves the target removal performances of >70% NH₃ and >80% PO₄³⁻ at 2 h contact time, as shown in Fig 3. The pH of GAC-l water varies somewhat depending on day-to-day variations in the composition of human excreta, with an average value of pH = 7.38 ± 0.93. Fig 4A shows two stages for nutrient sorption as described by other works on clinoptilolite [28, 29] and Polonite [33–35]. In the first sorption stage (0–2 h), nutrient removal gradually increases with contact time as sorption of NH₄⁺ and PO₄³⁻ occurs initially on the mineral surfaces. In the second stage (2–24 h), most of the available sorption sites have been occupied and nutrient removal reaches a plateau after ~4 h for both minerals at ~90% nutrient removal. After 24 h, nutrient removal was 96% for NH₃ and 97% for PO₄³⁻. These measurements were performed in triplicate to evaluate reproducibility; the larger error bars for PO₄³⁻ removal data reflects the broader particle size distribution of the Polonite media (see S1 Data).

PO₄³⁻ and NH₃ sorption is pH-dependent because the pH of the solution determines the speciation of the compound and the sorption mechanisms at play [45]. Hence, it is crucial to evaluate the sorption performance of the minerals with real blackwater without artificially controlling the pH. Fig 4B shows that pH increases with increasing contact time for each mineral, this change in pH is more pronounced at short contact times (<2h). For clinoptilolite, the pH stabilizes at 8.43 after 4 h because the main sorption mechanism is ion-exchange (NH₄⁺ displaces Ca²⁺ or other metal cations during sorption [36, 37, 55]) which does not cause a significant change in pH. For Polonite, the pH increases from 9.06 at 2 h to 9.74 after 24 h. PO₄³⁻ precipitation on Polonite [40, 42, 56] causes a greater increase in pH due to the release of OH⁻ ions into the solution. The acceptable pH range for most water reuse/discharge standards is 6 ≤ pH ≤ 9 [18–20]. At 50 g L⁻¹ loading, the pH of clinoptilolite-treated GAC-l is within the standard range at all contact times, while the pH of Polonite-treated GAC-l is too high after ~2 h contact time. This indicates that Polonite can meet the strict P-removal standard (> 80% removal), but the amount of Polonite and contact time necessary for meeting the P-removal target may cause the overall system to fail at meeting pH effluent standards unless an additional pH adjustment is performed prior to reuse/discharge.

From Fig 3B and 3D, we provide an estimate for clinoptilolite and Polonite sorption capacity to be 20.0 mg NH₃ g⁻¹ and 3.2 mg PO₄³⁻ g⁻¹, respectively. This estimate was obtained from the amount of target nutrient removed by smallest batch loading experiment (2 g L⁻¹) at 24 h contact time in GAC-l. We provide an estimate for the sorption capacities obtained from the experimental data rather than from an isotherm model because the experimental data do not fulfill the model requirements; namely, the Langmuir and Freundlich isotherms fail to predict
Fig 4. Batch sorption experiments for nutrient removal from GAC-I at 50 g L⁻¹ media loading. Media loading value corresponds to 5 g of sorptive media in 100 mL of GAC-I. Nutrient percent removal (a) and liquid pH (b) are shown for experiments using clinoptilolite (green triangles) and Polonite (black squares). Clinoptilolite and Polonite experiments were performed separately. Each data point is the average of three replicate experiments. (Some error bars are smaller than symbols.)

For clinoptilolite experiments, initial NH₃ concentrations ranged from 100–112 mg L⁻¹. For Polonite experiments, the PO₄³⁻ initial concentration was 51.4 mg L⁻¹.

https://doi.org/10.1371/journal.pwat.0000048.g004
pH-dependent adsorption effects \cite{44, 49, 57}. Jeppu and Clement \cite{49} presented a modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects, however this model requires a constant (controlled) pH throughout the experiment. For interested readers, our attempt at fitting the sorption data to Langmuir-Freundlich isotherm model can be found in S1 Data. While the calculated sorption capacity values from the model are similar to those estimated from the data, the model fails at high Polonite loadings (where the pH is most strongly affected).

In summary, the results from these batch sorption tests can be used to decide the optimal placement of the sorptive media in the OWTS prototype. In the case of Polonite, performance at low contact times is substantially improved by being placed after the UF treatment step and marginally improved by being placed after the GAC treatment step. In contrast, clinoptilolite performance does not strongly depend on its location in the wastewater treatment process, and so other performance factors must be taken into consideration. For example, we can consider the background removal of N and P by the OWTS prototype. Our previous results showed that the original OWTS prototype (mostly via the UF subsystem) on average removed $20.0 \pm 1.9\%$ of $\text{PO}_4^{3-}$ \cite{21}. This again supports that Polonite be placed after the UF subsystem in order to have the greatest additive effect on total P removal. However, $\text{NH}_3$ removal by the OWTS was less consistent in the original prototype, highly correlated to the influent $\text{NH}_3$ concentration, and occurred primarily during the EC disinfection process. This suggests that the greatest additive effect for $\text{NH}_3$ removal would come by placing clinoptilolite after the EC step, thereby allowing some $\text{NH}_3$ removal to occur before clinoptilolite sorption and reduced the $\text{NH}_3$ load on the sorptive media. However, if nutrient removal is the last treatment step, the effluent disinfection could be negatively impacted by the growth of a biofilm on the mineral particles \cite{58}. Therefore, clinoptilolite should be placed before the EC disinfection process to prevent microbial (re)growth in the treated effluent.

### 3.2 Implementation of clinoptilolite and Polonite in OWTS prototype

In batch testing, Polonite increased the pH of the treated wastewater outside the acceptable range of 6–9. However, the pH remained below 9 at low contact times (< 2 h), and it is unclear from these small-scale batch tests what the pH of Polonite-treated wastewater will be when implemented in a single-pass, fixed-bed media filter configuration. Therefore, we tested clinoptilolite and Polonite by adding a nutrient removal module (NRM) to our OWTS prototype as shown in Fig 2. Samples were taken from the feed and effluent tanks, and results for nutrient removal (total N and total P) and pH of the treated effluent are shown in Fig 5. It is important to establish a baseline for nutrient removal without connecting the NRM to the OWTS. Hence, the gray data points in Fig 5 (0–98.0 L) represent those baseline experiments resulting in effluent pH $= 7.8 \pm 0.3$, total N removal $= 47.5\% \pm 15.0\%$, and total P removal $= 32.3\% \pm 2.3\%$. (Other gray points indicate times the NRM was briefly disconnect are described in Section 2.6 of Materials and Methods.)

We set the NRM performance targets relative to the ISO 30500 standards \cite{18} for reuse or discharge of treated effluent (total N $\geq 70\%$ removal; total P $\geq 80\%$ removal; $6 \leq$ pH $\leq 9$); these performance targets are represented in Fig 5 by the light green shaded areas. Before the NRM was incorporated into the prototype, the total N and total P concentrations in the effluent did not achieve the performance targets, while pH was within the target range. After incorporation of the NRM, there is an immediate improvement in the total N and total P removal, however performance still failed to meet the target thresholds. Therefore, the loadings of clinoptilolite and Polonite were increased (Fig 5, first dashed vertical line near 130 L) from 5 kg and 4 kg to 9 kg and 7.5 kg, respectively. The increase in clinoptilolite loading resulted in total
N removal > 70%. While the total P removal initially exceeded 80% after increasing the Polonite loading, this performance was not sustained in subsequent experiments. Then, a small amount of sorptive media was removed (Fig 5, second dashed vertical line near 220 L) due to configuration changes in the NRM, this decrease caused the total N and total P removal to slightly decrease. Next, the remaining media was added back into the NRM tanks (Fig 5, third dashed vertical line near 340 L) bringing the total media loading back to 9 kg clinoptilolite and 7.5 kg Polonite, this resulted in an immediate increase in performance. These data clearly demonstrate that, as expected, simply adding more media increases nutrient removal performance. However, the increased loading of Polonite also increases the effluent pH outside of the target range, and the NRM configuration changes (addition of the elbow port, see Section 2.6 for
details) did not noticeably improve total P removal. Addition of more Polonite to increase total P removal would require a larger tank and would also further increase the effluent pH. For all subsequent experiments 53–91 (dataset 2; 437–1005 L), the amounts of clinoptilolite and Polonite were kept constant in the NRM.

Fig 6 shows clinoptilolite and Polonite performance after 150 days of idle time for the NRM. Data points plotted from 350–425 L volume treated are from dataset 1, which were performed before the idle period (indicated by the solid black vertical line) and are included in Fig 6 as reference points. The first four experiments after the idle time, shown in gray, were performed with the NRM disconnected from the prototype. Connecting the NRM shows immediate removal of both target nutrients with similar performance to that measured before the idle time. On average, after the idle time, clinoptilolite removes 78.2 ± 7.6% of NH\(_3\) and Polonite removes 63.8 ± 14.0% of reactive P, giving average calculated values of 83.4 ± 5.8% total N removal and 73.9 ± 10.1% total P removal. The dashed vertical line indicates when a backwash cleaning of the UF membrane was performed by flushing tap water through the UF permeate port and into the feed tank. The wastewater in the feed tank was therefore diluted with tap water for experiments immediately after the backwash and had lower initial concentrations of NH\(_3\) and reactive P decreasing from 95.0 and 39.8 mg L\(^{-1}\) to 60.0 and 26.8 mg L\(^{-1}\), respectively. Polonite performance decreased from 56.7% to 34.9% total P removal immediately after the backwash, but recovered during the next experiment. Clinoptilolite performance is largely unaffected by the changes to the feed after backwashing, showing only a small dip in total N removal from 79.9% to 72.1%.

Based on the total loadings of clinoptilolite (9 kg) and Polonite (7.5 kg) in the NRM, the estimated maximum capacities of the media (20.0 mg NH\(_3\) g\(^{-1}\) for clinoptilolite and 3.2 mg PO\(_4^{3-}\) g\(^{-1}\) for Polonite), typical concentrations of nutrients in the GAC-liquid (around 165 mg NH\(_3\) L\(^{-1}\) and 50 mg PO\(_4^{3-}\) L\(^{-1}\)), and the average performance values (78.2% NH\(_3\) removal and 63.8% PO\(_4^{3-}\) removal) in the NRM (assuming that this performance remains steady), we can estimate the volume of liquid that can be treated by the NRM integrated with the prototype before media exhaustion. We estimate that 9 kg of clinoptilolite should be able to treat approximately 1397 L, and 7.5 kg of Polonite should be able to treat approximately 752 L. During the COVID-19 pandemic, our access to fecal donations was severely curtailed, and so we were unable to generate additional blackwater in order to run the NRM to full exhaustion. However, it is notable that the Polonite is still removing P in excess of the estimated 752 L. One possible explanation is that the Polonite P removal capacity during long-term use is boosted by microbial activity. It is known that biofilms readily form on clinoptilolite and other natural zeolites [59], including biofilms consisting of ammonia-oxidizing microbes which consume ammonium adsorbed to the media surface [58, 60]. It is possible that phosphate-reducing microbes establish biofilms on the Polonite mineral surface and consume sorbed phosphate, extending the lifetime of the media before exhaustion. Additional work would be required to characterize microbial communities on the Polonite surface, which is outside the scope of the present study.

The data in Fig 6 also show a trend of decreasing effluent pH correlating with decreased P removal performance, with pH eventually falling within the performance target range after ~900 L volume treated. However, only one experiment with the NRM (at 615 L volume treated) was able to simultaneously meet both the effluent pH (8.87) and total P removal (83.2%) performance targets at the given Polonite loading. This tradeoff between P removal performance and pH shows that, at the loading required for effective P removal, Polonite is likely not practical in our OWTS without implementation of an additional pH adjustment process (e.g., acid dosing; electrochemically-driven acid production). In conclusion, the results from laboratory testing of the NRM show that it is possible to incorporate clinoptilolite into
our OWTS while meeting the required standards. Unfortunately, the quantity of Polonite that would be required in the NRM to achieve performance targets will result in an effluent pH > 9, which is too high for on-site discharge or water reuse.

Based on the results of laboratory testing at Duke, we decided not to install the Polonite in the NRM for field-testing deployment, as the effluent pH > 9 is too high for on-site discharge or water reuse. Installation of an identical clinoptilolite tank was performed at our field-testing site in Coimbatore, India. The clinoptilolite-only NRM was installed on February 28, 2020 and performance data were collected for nine days until the COVID-19 pandemic forced closure of the field-testing site. Despite the limited testing period, the NRM module demonstrated immediate removal of ammonium, and improved the total N removal from 10% to 99.5%. (See S5 Data complete dataset and final report from the field-testing site.) Of particular note is that the OWTS had been struggling with chlorine production prior to the installation of the NRM, and troubleshooting efforts to correct the issue had stalled. As soon as the NRM was installed, chlorine production was observed. We suspect that the high levels of ammonium in the effluent may have been consuming the available free chlorine [61] prior to installation of the NRM. Additional testing would be required to definitively determine the role of the NRM in supporting chlorine production. However, the COVID-19 pandemic prevented further testing of the NRM at the Coimbatore field site. We are currently field testing a next-generation OWTS prototype which utilizes clinoptilolite for NH₃ removal and will report the results of that study in a future publication.

Fig 6. Results of OWTS experiments in dataset 2. Data points for volume treated between 350–425 L are from dataset 1 (Fig 5) and are duplicated here for reference. The solid vertical line indicates the 5-month NRM idle time. Effluent pH (pink circles), calculated total N percent removal (green triangles), and calculated total P percent removal (black squares) are shown for all experiments. Experiments where the NRM was disconnected from the prototype are shown as gray data points. All open data points with error bars (425–1005 L) are calculated from estimates of total N and total P influent values based on measured NH₃ and reactive P influent values. Some error bars are smaller than data symbols. Performance targets for each parameter are indicated by the shaded green areas. The vertical dashed line indicates a UF filter backwash event, during which the feed tank was temporarily diluted with tap water.

https://doi.org/10.1371/journal.pwat.0000048.g006
3.3 Evaluation of media regeneration and nutrient recovery

Sorptive media that rely on ion exchange or weak surface adsorption for nutrient removal can be “regenerated” by treatment with an appropriate salt solution. In many cases, media regeneration is only practical and economical if the regeneration process does not produce large quantities of byproducts which need to be further processed or disposed as waste. During regeneration, sorbed nutrients are released into the salt solution; this nutrient-rich regeneration solution can then function as a nutrient recovery product, e.g., for direct reuse as a fertigation solution. Typical regeneration solutions for sorptive media include sodium chloride (brine) or sodium hydroxide, both of which are incompatible with fertigation reuse due to the high sodium content and sodium intolerance of many plants. Strong acid solutions are also commonly used for regeneration of ion-exchange media (e.g., hybrid anion exchange resins, or HAIX); the use of strong acids may be undesirable in some contexts due to safety/handling concerns and the requirement for pH adjustment prior to reuse. Therefore, another challenge is to establish methods that allow the release of sorbed nutrients, and the reuse of sorptive media for multiple sorption cycles. To this end, we evaluated several regeneration solutions for clinoptilolite and Polonite to explore different options for nutrient recovery and reuse: (1) typically used salt (NaCl), strong acid (HCl), and strong base (NaOH) solutions, and (2) KCl and KOH as sodium-free alternatives.

Each regeneration solution experiment was performed using 10 g of new sorptive media. The media were exposed to alternating solutions for nutrient sorption (i.e., nutrient removal from GAC) and desorption (i.e., nutrient recovery in the regeneration solution). Fresh 100 mL solutions were used for each sorption and desorption step, for a total of three sorption/desorption cycles. Ultrapure water (UPW) used as the solvent to make the regeneration solutions was also tested for nutrient desorption as a control. Clinoptilolite regeneration was tested using the following 1 M solutions: KCl, KOH, NaCl, and HCl. As shown in Fig 7A and 7B, the desorption ability of each solution across three cycles is KCl > KOH > HCl ≈ NaCl >> UPW. Desorption results indicate that UPW desorbs little to no NH₃ from clinoptilolite, which was also previously reported for column batch experiments by Cyrus and Reddy [62]. KCl desorbs more than 86% of NH₃ each regeneration cycle, which is in agreement with the 80–92% regeneration efficiency reported by Kalló et al. [63]. After regeneration with KCl, NH₃ sorption decreases from 90% to 80% and remains at 80% for the third sorption cycle. This sorption capacity decrease can be explained by the higher affinity of clinoptilolite for K⁺ than ammonium, and indicates that not all K⁺ is displaced by ammonium during subsequent sorption cycles [64]. NaCl desorbs 52% of all sorbed NH₃ after three regeneration cycles without compromising clinoptilolite’s performance which remains over 90% NH₃ removal for each sorption cycle. Other works [26, 64] have reported clinoptilolite regeneration with NaCl to reach 90%; the lower NH₃ recovery percentages found in the present study could be due to insufficient contact time with the regeneration solution or lower Na⁺ concentration. KOH desorbs 78% of NH₃ during the first regeneration cycle, but NH₃ sorption performance decreases from 96% NH₃ removed during the first sorption cycle to only 8% NH₃ removed during the third cycle. This dramatic decrease in NH₃ removal performance indicates an irreversible change to the clinoptilolite surface properties upon exposure to strong base. Therefore, KOH could be used as a nutrient recovery solution for one-time-only use of clinoptilolite, but not as a clinoptilolite regeneration solution. HCl desorbs 58% of all sorbed NH₃ after three regeneration cycles, and clinoptilolite’s NH₃ sorption performance not only remains over 90% across three cycles, but also slightly increases by after the first regeneration cycle. The increase in sorption is likely due to HCl dealumination of the clinoptilolite core structure creating secondary pores, increasing existing pore size and surface area [65, 66], and/or removing other cations making more exchange sites available for ammonium [67].
Fig 7. Evaluation of different regeneration solutions for nutrient desorption from clinoptilolite and Polonite. For each experiment, 10 g of sorptive media were exposed to alternating solutions of 100 mL GAC-l for 2 h (sorption) followed by 100 mL of regeneration solution for 2 h (desorption). (a) Clinoptilolite sorption step, initial concentration of NH$_3$ in GAC-l ranged from 72–168 mg L$^{-1}$. (b) NH$_3$ desorption from clinoptilolite was evaluated using 1 M solutions of KCl, KOH, NaCl, and HCl. 1 M KCl showed the best performance for NH$_3$ desorption. 1 M KOH destroyed the NH$_3$ removal capabilities of the clinoptilolite. (c) Polonite sorption step, initial concentration of PO$_4^{3-}$ in GAC-l was 51.4 mg
Polonite regeneration was tested using 1 M solutions of HCl, NaCl, NaOH, and KOH. To the best of our knowledge, investigating the regeneration of the Polonite surface in this way has not been previously reported. As shown in Fig 7C and 7D, the PO$_4^{3-}$ regeneration ability (i.e., sustained sorption performance after regeneration) for each regeneration solution is KOH ≈ NaOH > UPW > NaCl >> HCl. KOH and NaOH have comparable sorption and desorption results. While KOH shows limited desorption of PO$_4^{3-}$ (only 22% recovered after three desorption cycles), PO$_4^{3-}$ sorption remains high, with over 92% of PO$_4^{3-}$ removed in each sorption cycle. Similarly, using NaOH shows over 90% PO$_4^{3-}$ removal across all three cycles, but only 25% of PO$_4^{3-}$ is recovered. This indicates that Polonite cannot be fully regenerated, likely because irreversible precipitation (e.g. of calcium phosphates) is the predominant phosphate removal mechanism rather than ion-exchange or electrostatic interactions [68, 69]. The sustained high sorption performance with KOH and NaOH is rather simply due to the relatively high loading of media (100 g L$^{-1}$) in these experiments, and thus an abundance of available sorption sites even after three sorption cycles. NaCl desorbs 19% of all sorbed phosphate after three cycles, and PO$_4^{3-}$ sorption decreases from 95% during the first cycle to 75% for the last two sorption cycles. This decrease in PO$_4^{3-}$ sorption capacity after exposure to NaCl, but not to NaOH, indicates that exposure to a high concentration of chloride ions interferes with the phosphate sorption mechanism at a fraction of surface sites. Exposure to HCl causes a rapid decrease in sorption capacity from 90% to 6%. Exposure to strong acid destroys the structural integrity of Polonite particles, as indicated by significant Polonite mass loss upon exposure to HCl (see S1 Data), likely via dissolution of calcium (hydr)oxides [33, 70]. Nevertheless, an estimated 56% of sorbed phosphate is recovered from Polonite with the first HCl desorption, or ~3.3 g L$^{-1}$-1. Fig 8A shows that across six sorption/desorption cycles, the amount of NH$_3$ sorbed onto clinoptilolite each cycle oscillates around an average value of 10.2 mg g$^{-1}$, while the amount of NH$_3$ desorbed per cycle remains relatively constant near 8.8 mg g$^{-1}$. This oscillation in the sorption behavior could be due to continued changes to the clinoptilolite structure (dealumination, pore opening, and removal of competitive cations, as mentioned previously) with each subsequent HCl treatment. (Note: The values for phosphate recovered in HCl are corrected for some phosphate which is leached from the mineral itself during Polonite dissolution—see S1 Data for details).

Similar to the results for treating clinoptilolite with KOH, Polonite could be treated with HCl to facilitate phosphate recovery if the Polonite is to be used only once.

The regeneration solutions showing the best nutrient sorption capacity after regeneration in Fig 7 (HCl for clinoptilolite and KOH for Polonite) were tested further with repeated sorption/desorption cycles at lower media loadings (0.5 g media in 150 mL of GAC-l, or ~3.3 g L$^{-1}$). Fig 8A shows that across six sorption/desorption cycles, the amount of NH$_3$ sorbed onto clinoptilolite each cycle oscillates around an average value of 10.2 mg g$^{-1}$, while the amount of NH$_3$ desorbed per cycle remains relatively constant near 8.8 mg g$^{-1}$. This oscillation in the sorption behavior could be due to continued changes to the clinoptilolite structure (dealumination, pore opening, and removal of competitive cations, as mentioned previously) with each subsequent HCl treatment. For some cycles, the amount of NH$_3$ desorbed is greater than what was sorbed during that same cycle, due to incomplete desorption on previous cycles. At the end of six cycles, 86.4 ± 2.9% of all sorbed NH$_3$ is recovered in the regeneration solution. Fig 8B shows that Polonite PO$_4^{3-}$ sorption is highest (2.4 ± 0.4 mg g$^{-1}$) during the first sorption cycle and then decreases to an average value of 0.8 mg g$^{-1}$ for subsequent sorption cycles. Desorption of PO$_4^{3-}$ is relatively constant across all cycles, near an average of 0.6 mg g$^{-1}$. During the first desorption cycle, only 32.3 ± 2.0% of PO$_4^{3-}$ is recovered, while in each subsequent cycle, the amount of desorbed PO$_4^{3-}$ per cycle is ~75% of the amount of newly-sorbed PO$_4^{3-}$. This indicates that during the first sorption cycle, the predominant PO$_4^{3-}$ removal mechanism is not reversible (e.g., precipitation) and the majority of these binding sites are exhausted on
Fig 8. Results of nutrient sorption/desorption across six cycles, using fresh regeneration solution for each cycle. Amount of nutrients sorbed and desorbed on each treatment cycle. (a) 1 M HCl was used as the regeneration solution for clinoptilolite and (b) 1 M KOH was used as the regeneration solution for Polonite. (c) Percentage of total sorbed nutrients recovered in the regeneration solutions. Sorption conditions: 0.5 g of media, 150 mL of GAC-I, 2 h contact time. Desorption conditions: 50 mL of fresh regeneration solution, 2 h contact time. Initial nutrient concentrations
the first sorption cycle. For subsequent cycles, $PO_4^{3-}$ removal is dominated by weaker, reversible surface interactions (e.g., electrostatics and ion-exchange) which allows for regeneration of these binding sites by treatment with 1 M KOH. At the end of six cycles, 55.5 ± 4.0% of all sorbed $PO_4^{3-}$ is recovered in the regeneration solution. In summary, these results indicate that almost all $NH_3$ removal capacity in clinoptilolite can be recovered for at least six regeneration cycles. In contrast, the predominant $PO_4^{3-}$ removal mechanism by Polonite is not reversible and thus only a minority fraction of binding sites in this media is able to be regenerated via traditional ion-exchange chemical treatment methods.

We also investigated reusing the same regeneration solution for all desorption cycles. As shown in Fig 9A and 9B, clinoptilolite performance drops off after sorption cycle 4; at this point, the concentration of $NH_3$ in the regeneration solution has reached 304 mg L$^{-1}$. However, the regeneration solution can recover at least 550 mg $NH_3$ L$^{-1}$, as shown for the final regeneration (cycle 9) of the experiment. This indicates that the regeneration solution is not yet saturated after cycle 4, despite the decrease in $NH_3$ removal for subsequent cycles. Therefore, increasing the contact time with or volume of regeneration solution could increase the number of regeneration cycles possible before performance loss. At the end of 9 cycles, 83.7% of all sorbed $NH_3$ was recovered in the regeneration solution (Fig 9E). In the case of Polonite (Fig 9C and 9D), there is a drop in performance from 30.2% to 19.6% $PO_4^{3-}$ removal after the first sorption cycle, consistent with the results above for experiments at high media loadings. The Polonite sorption performance decreases gradually until regeneration cycle 6 (15.5% $PO_4^{3-}$ removal), after which there is a drop to 7.4% $PO_4^{3-}$ removal, which is maintained for all subsequent cycles. After cycle 6, the $PO_4^{3-}$ concentration in the regeneration solution is 60.2 mg L$^{-1}$, but continues to increase, ending at 80.3 mg L$^{-1}$ after 10 cycles. Like the results for clinoptilolite, results for Polonite indicate that sorption performance loss occurs before the regeneration solution is saturated with $PO_4^{3-}$, and therefore it may be possible to increase the contact time with or volume of the regeneration solution to improve the regeneration ability. However, the low overall recovery of $PO_4^{3-}$ (only 39.9% of total sorbed $PO_4^{3-}$ was recovered at the end of 10 cycles, Fig 9E) may make Polonite more practical as a one-time-use sorptive media.

3.4 Implications for deployment of clinoptilolite and Polonite for nutrient removal/recovery in OWTS

This work adds insight into the performance and practicality of clinoptilolite and Polonite specifically for use with untreated blackwater and blackwater that has been pre-treated with non-biological filtration. Each material has clear strengths and weaknesses for use in OWTS. Specifically, our results demonstrate that both media perform nutrient removal immediately upon installation and show no loss in performance after several weeks of idle time (Fig 6). This is in stark contrast to many biological nutrient removal systems, which can take days or weeks to reach stable performance levels and require a constant feed of wastewater with the appropriate nutrient/carbon ratio to maintain the relevant microbial communities. One possible context where clinoptilolite and Polonite could be particularly useful is in remote locations with plenty of space to accommodate large fixed-bed filters, and where wastewater generation is relatively low in quantity, infrequent, or seasonal, e.g., small villages or outposts, backcountry/wilderness sites, or environmental monitoring stations. Our results also show that clinoptilolite can be a
Fig 9. Results of nutrient sorption/desorption experiments where the same regeneration solution was reused for all cycles. Sorption conditions: 100 mL of GAC-1 water, 24 h contact time. Desorption conditions: 50 mL of regeneration solution, 2 h contact time. Clinoptilolite regeneration reusing 1 M HCl: (a) percentage target NH$_3$ removed on each sorption cycle, initial concentration of NH$_3$ ranged from 52 to 104 mg L$^{-1}$; (b) Cumulative concentration of NH$_3$ recovered in desorption cycle. Polonite regeneration reusing 1 M KOH: (c) percentage target PO$_4^{3-}$ removed from GAC-1; (d) PO$_4^{3-}$ concentration in 1 M KOH; (e) percentage of nutrient recovered during desorption cycle.
robust ammonia-removal option for a wide variety wastewater strengths. However, additional testing would be required to demonstrate that suspended solids accumulation or biological surface fouling does not inhibit NH$_3$ removal (e.g., in unfiltered blackwater) on longer time scales.

Other mineral-based sorbents to remove PO$_4^{3-}$ and NH$_3$ are typically evaluated using synthetic solutions rather than real wastewater or blackwater, this makes the direct side-by-side comparison of performance metrics (e.g., percent removal; sorption capacity) to the results of our work challenging. Nevertheless, previous studies under more controlled conditions can provide reasonable benchmarks for more general comparisons. For PO$_4^{3-}$ sorption, several other minerals and sorption capacities have been previously reported, including La/Al pillared bentonite with 13.0 mg PO$_4^{3-}$ g$^{-1}$ [71], La-modified zeolite with 24.6 mg PO$_4^{3-}$ g$^{-1}$ [72], filtrasite P with 2.5 mg PO$_4^{3-}$ g$^{-1}$ [73], and shellsand with 9.4 mg PO$_4^{3-}$ g$^{-1}$ [73]. For NH$_3^+$, several other minerals and sorption capacities have been reported, including vermiculite with 3.8 mg NH$_3^+$ g$^{-1}$ [74], Turkish zeolite (dogantepe) with 1.32 mg NH$_3^+$ g$^{-1}$ [75], and chabazite 32.4 mg NH$_3^+$ g$^{-1}$ [76]. We measured sorption capacities in this study (Polonite = 3.2 mg PO$_4^{3-}$ g$^{-1}$, clinoptilolite = 20 mg NH$_3$ g$^{-1}$) comparable to or, in the case of clinoptilolite, higher than, these other minerals, despite the use of real blackwater. Overall, clinoptilolite and Polonite performances we measured are either similar to or better than most other minerals evaluated under more controlled conditions.

Clinoptilolite showed excellent regeneration ability across multiple cycles (Fig 8), which also makes it promising for contexts where physical space is limited (e.g., dense, urban areas). However, management (e.g. storage, transport) of the regeneration solution will need to be taken into consideration. The ability to use the same volume of regeneration solution for multiple cycles may facilitate management and lower the cost of consumable media, particularly if the regeneration solution itself has value. The regeneration solutions used in this study recovered the target nutrients in quantities comparable to common liquid fertilizers. One US common commercially-available liquid fertilizer concentrate, designed for household use with a 12-4-4 N-P-K ratio, contains 150 mg L$^{-1}$ N, 66.8 mg L$^{-1}$ PO$_4^{3-}$, and 41.4 mg L$^{-1}$ K when diluted according to the manufacturer instructions (see S6 Data). The clinoptilolite regeneration solution in this study contained 304 mg L$^{-1}$ NH$_3$ after four regeneration cycles (approximately 2× that of the commercially-available liquid fertilizer) and could most likely recover even more ammonium with increased contact time. The Polonite regeneration solution in this study contained 60.2 mg PO$_4^{3-}$ L$^{-1}$ (approximately 1× that of the commercially-available liquid fertilizer). Either of these regeneration solutions on their own would require pH adjustment prior to reuse; however, combining the clinoptilolite and Polonite regeneration solutions would partially neutralize the pH and generate a combined N-P-K fertilizer solution. One issue that would need to be addressed is that 1 M KOH (or KCl, if considering only regeneration of clinoptilolite) contains approximately 1000× more K$^+$ (39,100 mg L$^{-1}$) than the 12-4-4 fertilizer. Even if the concentration of K$^+$ were decreased to 0.1 M, combining the two regeneration solutions would result in a solution with an approximate 5-1-78 N-P-K ratio (or 5-0-78, if considering only clinoptilolite regeneration with KCl). While this ratio may limit the contexts in which direct reuse is most practical, many agricultural soils are heavily deficient in potassium, particularly in low-income countries [77, 78]. There is also an increasing recognition of the importance of potassium in plant growth, with potassium imparting multiple protective

PO$_4^{3-}$ removed on each sorption cycle, initial concentration of PO$_4^{3-}$ ranged from 51.6 to 62.0 mg L$^{-1}$; (d) cumulative concentration of PO$_4^{3-}$ recovered in desorption cycle. (e) Percentage of total sorbed nutrients recovered in the regeneration solutions.

https://doi.org/10.1371/journal.pwat.0000048.g009
features in a variety of environments [78, 79], and the demand for high-K fertilizers is likely to increase in many resource-stressed areas and low-income countries [77, 78]. In any case, additional testing (e.g., for pathogens and heavy metals) would be required to show that the regeneration solutions are safe for direct reuse.

The comparatively poor regeneration ability of Polonite likely limits its use to scenarios that can accommodate large (hundreds of kg), single-use filters, and where the high effluent pH is acceptable or desired. A full techno-economic analysis of clinoptilolite and Polonite regeneration and reuse would be crucial for determining whether this is an economically-viable strategy in a given context, however, this is outside the scope of the current study. Still, we can get a good approximation of the cost and energy expenditure of the OWTS with the added NRM subsystem from a previously reported techno-economic report about the OWTS [21]. As a first approximation, we can treat the NRM subsystem as similar to the GAC subsystem, as it requires only media, a housing for the media, and tubing/connectors to integrate it into the overall OWTS. We reported [21] previously that the UF subsystem is the primary cost driving factor (contributing to more than 50% of both the energy and maintenance costs), while the GAC subsystem is only 3.5% of the overall cost. Only the UF and EC subsystems contribute to energy consumption, and we therefore do not expect the energy consumption to significantly change with the inclusion of the NRM, as no additional pumps or electrical components were added. We expect that adding the NRM would increase the material costs by around twice that of the GAC subsystem, as it contains twice the amount of media (one bed each of clinoptilolite and Polonite), and the cost per kg of GAC is similar to the costs of clinoptilolite and Polonite. Overall, the NRM at its current scale in the OWTS should not significantly increase the energy consumption or cost of the OWTS. We note however that this cursory analysis provides no insight into lifetime of the media, nor costs associated with media replacement/regeneration in the NRM. These values would be best determined based on data obtained through long-term field testing, where the NRM can be run to exhaustion and media regeneration can be tested in situ.

It is also likely that direct reuse of regeneration solutions will not be cost effective or desirable in some contexts, and that the costs associated with safe disposal or further treatment of the regeneration solution would also need to be considered. Nevertheless, it is still noteworthy that some fraction of sorption sites (our results indicate ~30–40%) in Polonite can be regenerated using strong base solutions; we are not aware of previous studies which investigated regeneration of Polonite in this way. Chemical regeneration of Polonite, even if incomplete, may be beneficial under some circumstances, e.g., to extend the service life of large filter beds between scheduled maintenance/replacement events, or for situations where phosphate recovery is highly desirable.

A significant limitation of the current study is the lack of long-term performance data with our OWTS prototype, which is ideally obtained through field testing. However, other studies have shown that both clinoptilolite and Polonite are effective during long-term deployment. Renman and Renman reported an average of 98% PO$_4^{3-}$ removal across 92 weeks of testing, treating a total of 70 m$^3$ of domestic wastewater with 560 kg of Polonite [35]. While the percent removal of PO$_4^{3-}$ was likely higher in that study due to the lower concentration of PO$_4^{3-}$ in the influent ($4.9 \pm 1.9$ mg L$^{-1}$), the authors observed similar high pH $> 9$ of their effluent. Ultimately, we decided not to pursue long-term field testing of Polonite due to (1) the high effluent pH at loadings sufficient for giving $>80$% PO$_4^{3-}$ removal from blackwater and (2) the low regeneration ability of the media (i.e., only a minor fraction of binding sites can be regenerated and reused for multiple sorption cycles). Nevertheless, our results indicate that Polonite is an effective P sorption material, provided that high effluent pH and single-use filter media are acceptable for the application context (including local regulatory standards). Additionally, implementing Polonite as a single-use media requires a larger filter footprint than a material
which can be easily regenerated and reused, so space availability and media replacement frequency should also be taken into consideration. Recently, clinoptilolite was evaluated in a 1.5-year field testing study as a N-removal process subsequent to an anaerobic membrane bioreactor (AnMBR) [80, 81]. The results of this work are similar to what we observed; namely, that clinoptilolite can achieve high ammonium removal with real OWTS wastewater without compromising other treatment performance metrics. Castro et al. showed that large clinoptilolite beds (350 kg total clinoptilolite in two tanks) could be successfully regenerated using ~1 M NaCl and required regeneration every ~6 months [80]. Here, we have shown that NaCl, HCl, and KCl are all effective at regenerating clinoptilolite, and 1 M KCl shows the best recovery of sorbed ammonium at 2 h contact time. Regeneration with KCl could expand possibilities for beneficial reuse of the regeneration solution, particularly for direct reuse in agricultural applications where low sodium levels are desirable. The neutral pH of KCl also makes it easier to handle and transport than acidic HCl. We intend to report on extended testing of small clinoptilolite filters (≤ 25 kg), including using KCl solutions for media regeneration and N recovery, in a future publication.

In a broader context, there is unlikely to be a one-size-fits all solution to nutrient removal and recovery in OWTS due to the complex interplay among economic, cultural, geographic, and regulatory factors for any given context. This complexity motivates the development of new technologies and adaptation of existing technologies to new use-cases, but choosing appropriate nutrient removal methods for a particular context is not always straightforward. While biological nutrient remediation is commonplace in municipal-scale wastewater treatment plants, many biological processes are likely to be ineffective when scaled down [82], due in part to greater susceptibility to system shocks, climate, or seasonal variations. Some of the current state-of-the-art small-scale OWTS also struggle to meet strict discharge standards without increased technical complexity or requiring changes to the user interface or user behavior. For example, Reynaert et al. recently demonstrated a biologically activated membrane bioreactor (BAMBi) system where wastewater was treated on-site and recycled for toilet flushing and hand washing [61]. The authors note that in the case of toilet-flushing water, true water recycling was only possible due to separation of nearly all urine (via a urine-diverting toilet) and the majority of fecal material from the flush water prior to treatment. While this provided lower nutrient loadings in the wastewater and optimized the nutrient/carbon ratio for the BAMBi, additional separation, containment, and treatment methods are ultimately required for the separated urine and feces waste streams. The authors also report robust removal of COD (99.7%), total N (98.5%), and total P (99.9%) when treating hand washing water. However, a custom “nutrient-supplemented” soap was required to maintain the necessary nutrient/carbon ratio required for the biological treatment processes. The WHO has reported that rural households with limited hygiene services were more likely to have water and be without soap, rather than to have soap without water [10]. The requirement to use non-standard soaps, while feasible during field testing, may therefore not be practicable in many rural contexts due to limited long-term availability of these materials.

Despite the clear need for a multiplicity of approaches in providing on-site and non-sewered sanitation systems, recent regulatory standards have been somewhat narrow in addressing different water reuse contexts [83], particularly when it comes to nutrients. For example, the ISO 30500 standard for pre-fabricated non-sewered sanitation systems briefly mentions recovery of nutrients, and states that the nutrient concentration in the effluent “can be used to determine the reasonable reuse” of the effluent [18]. At the same time, ISO 30500 dictates minimum load reduction percentages of 70% for total nitrogen and 80% for total phosphorus in treated effluent. However, no distinction is made regarding nutrient load reductions for different end fates of the effluent, implying that these load reductions are to be met regardless of
whether the effluent is discharged directly to the environment. However, if effluent is to be reused directly for irrigation purposes, removal of nutrients essential for plant growth may be neither necessary nor necessarily preferred; in such a case, a standard based on a range of effluent nutrient concentrations appropriate for plant growth would be more applicable. Wastewater reuse for agricultural purposes is already widespread practice in many countries [84], and safe agricultural wastewater reuse is recognized by the WHO as playing a fundamental role in economic and social development [85]. The effluent from our OWTS prototype typically contains 50–150 mg L\(^{-1}\) NH\(_3\) and 41.6–48.2 mg L\(^{-1}\) PO\(_4^{3-}\), both of which are well within the range of typical fertilizer solutions. In setting performance goals for nutrient removal based on recent OWTS standards, our system requires additional nutrient-removal capabilities, which increases energy requirements, materials cost, and overall emissions of this technology, in order to recover nutrients which may eventually be re-diluted in clean water for reuse. We contend that regulatory standards for OWTS, much like the OWTS themselves, should be fit-for-purpose to accommodate specific water reuse applications and best enable efficient nutrient reuse.

4. Conclusions

The natural silicate-based minerals clinoptilolite and Polonite were implemented in our OWTS prototype as nutrient-removal media after identifying their optimal placement in the treatment system. We found that KCl was particularly effective at recovery of ammonium from clinoptilolite, and clinoptilolite showed robust performance after multiple regeneration cycles. We investigated for the first-time chemical regeneration of Polonite and found that a fraction of sorption sites could be regenerated with strong base solutions. While both materials were effective at removing their target nutrients with no start-up time or performance loss after long idle time, the contexts in which they are likely to be most practicable vary considerably, especially when taking into consideration their relative abilities to be regenerated and reused for multiple treatment cycles. In discussing the different contexts for implementation of these minerals, we question whether the regulatory standards likely to be applied to this OWTS inadvertently stifle its possible application for direct water reuse in agricultural applications. Nevertheless, agricultural water reuse is not economically viable or desirable in all contexts, and continued investigation of nutrient removal/recovery technologies for use in OWTS remains valuable in a broader context, where every OWTS must be designed for a specific use-case. We strongly suggest that regulatory standards for water reuse should keep step with new technologies and adapt to accommodate fit-for-purpose water reuse applications.

Supporting information

S1 Data. Supplementary tables and figures. (PDF)
S2 Data. Datasets 1 and 2 collected during operation of OWTS prototype. (XLSX)
S3 Data. Calculation of total N and total P for OWTS prototype dataset 2. (XLSX)
S4 Data. Additional underlying datasets. (XLSX)
S5 Data. Final report from field testing site. (PDF)
S6 Data. Calculations comparing nutrient content to commercially-available fertilizer.
(XLSX)

Acknowledgments
The authors thank Sarani Sasidharan, Prateek Kachoria, Claire M. Welling, and Sonia Grego supported by the India Engineering Field Testing Project for providing data on the field testing in India. We also thank Graham H. Miller for providing engineering support in the Duke Center for WaSH-AID laboratory.

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