Factors influencing nitrification in point-of-use BioSand filters

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ABSTRACT

The BioSand filter (BSF) is a point-of-use treatment technology used in developing countries to improve drinking water quality. Studies on the BSF to date have mainly focused on bacterial, protozoan and virus reduction and less on the filter’s effect on chemical contaminants that may also affect human health. This study explored the potential for nitrification in field-scale trials of four BSFs treating water from a covered drilled well in rural Cambodia. The effect of raw water ammonia concentration (0.4 to 18 mg-N/L) and filter idle time (2 and 24 h) were investigated. Incomplete nitrification was observed in both control and test BSFs as inferred from nitrite and nitrate measurements. At the highest ammonia loading (18 mg-N/L), the sum of ratios of nitrite and nitrate in BSF effluent exceeded the World Health Organization’s limit by as much as 40%, but only due to the presence of 1.5 mg-N/L nitrate in the influent. Three methods for minimizing nitrite and nitrate in filtered water were evaluated, including wasting certain fractions of filtered water that may have higher concentrations, cleaning the BSFs and allowing filtered water to aerate for a period of time. None of these methods were deemed to sufficiently counteract potential nitrification.

INTRODUCTION

Point-of-use treatment options in developing countries have been recognized as an appropriate solution to reduce the number of people that still lack access to safe drinking water (Sobsey et al. 2008). The BioSand filter (BSF) is one such treatment technology that is currently used in several countries across the globe. Recent attention has been given to the chemical processes that could occur within the BSF, including nitrification (Murphy et al. 2010a, b). Ammonia is converted into nitrite and nitrate during the process of nitrification. The process of nitrification requires oxygen as enzymes or microorganisms first oxidize ammonia into nitrite and then nitrite is oxidized into nitrate. The World Health Organization (WHO) drinking water quality guideline for nitrite is 3 mg/L (equivalent to 0.9 mg-N/L), the guideline for nitrate is 50 mg/L (equivalent to 11 mg-N/L) and the sum of the ratios of the concentrations of each compound relative to their individual maximum cannot exceed 1.0 (WHO 2011). The stricter WHO guideline on nitrite relative to nitrate is due to its ability to lead to methaemoglobinemia at low concentrations, to which infants are susceptible.

Murphy et al. (2010a, b) reported apparent production of nitrite and nitrate in 20 point-of-use BSFs installed in villages in Cambodia, with samples collected every 2 weeks for 6 months. The extent of the reported nitrification was such that 17 of 20 filters on average did not meet the 3.0 mg/L nitrite guideline and the combined nitrite–nitrate guideline ratio of 1.0 (Murphy et al. 2010b). Murphy et al. (2010b) reported source water concentrations for nitrite ranging from 0 to 28.3 mg/L (as nitrite) with an average of 3.3 mg/L. Nitrate concentrations in source waters were in the range of 0 to 37.7 mg/L (as nitrate) with an average of 2.1 mg/L. On average, 10 of 20 source waters surpassed a concentration of 3.0 mg/L for nitrite (before filtration). No source water exceeded the guideline value of 50 mg/L for nitrate. The source waters considered by Murphy...
et al. (2010b) contained relatively high concentrations of nitrite and nitrate, at least in part, because the study sites were located in a largely agricultural community where rice farming with fertilizer application took place twice during the study period. In addition to fertilizers, the surface water was impacted by human and animal waste. The potential health importance of nitrification in BSFs prompted this follow-up study to those findings reported by Murphy et al. to confirm the occurrence of nitrification under more controlled conditions and to test simple BSF operation strategies to counteract nitrification.

**MATERIALS AND METHODS**

**BioSand filter**

The experiments were conducted in Phnom Penh, Cambodia. Four version 8 concrete BSFs were specially constructed and installed by Clear Cambodia staff, based on guidelines in the Samaritan's Purse BSF Technical Manual (SPC 2008). A diagram of a BSF is given in Figure 1, with additional details available in Liang et al. (2010) and Murphy et al. (2010b). The BSFs were identical in design to those used by typical households in Cambodia. Filter media were sifted using a screen with 1.0 mm nominal pore size and washed for silt removal. The result was a filter with an effective size of 0.16 mm, a uniformity coefficient of 3.4, and silt content (<0.1 mm) of 2%. The maximum flow rate at installation was approximately 650 mL/min. The filters were acclimated for 5 weeks prior to the experiment by filtering 20 L of water each day, which is representative of household use.

**Raw water**

Raw water was collected from a covered deep well in Popeal Kaye Village, 50 km south-east of Phnom Penh, Cambodia. BSF units in this area had previously been identified by Murphy et al. (2010b) as showing evidence of nitrification. Murphy et al. (2010b) noted that ammonia, nitrite and nitrate levels were high (and at times exceeded WHO guidelines) in source waters due to the application of fertilizers on nearby rice fields and a lack of human and animal waste management. Three times per week (Monday, Wednesday and Friday), 200 L of water was transported to the laboratory in Phnom Penh in ten 20 L plastic carboys completely filled and capped to minimize the addition of oxygen during transport. The water was then stored in the carboys in the shade until use, which was never more than 30 hours. Overnight storage of source water prior to filtration is not uncommon in rural Cambodia. One full carboy of water was poured into each BSF each day, except on Sundays. Ammonia, nitrite, nitrate and pH of the raw water were measured immediately before the water was poured through the BSFs. Temperature data were not collected; typical daily low and high temperatures were 24°C and 32°C.

The well water characteristics are summarized in Table 1. Two samples of water were collected as a baseline. One was taken during the dry season, on June 8, 2011, and the other was taken during the wet season, on August 5, 2011, roughly at the beginning and end of the study period. The presence of Escherichia coli in the well water suggests that the groundwater may be under the influence of surface water; however, this water has low particulate and microbial levels compared to typical surface water and dug wells in the area.

**Ammonia-spiked water**

For certain experiments, ammonia was added to the water samples in the form of urea [(CO(NH₂)₂], which is commonly used as a fertilizer by Cambodian farmers and is a common
source of ammonia pollution. The ammonia solution was created by adding 48 drams of urea solids (roughly 180 mL) to 300 mL of deionized water and shaking vigorously to ensure complete dissolution. Fifty millilitres of the spiking solution was then added to a 20 L carboy and gently stirred to mix the contents. The step change in influent water after spiking was an average 9.7 mg/L as ammonia-nitrogen, with measured values ranging from 5 to 18 mg-N/L. In this study, ‘adjusted BSFs’ are those filters that have been spiked with ammonia. The high spiking concentration of ammonia ensured that ammonia was not rate limiting. The urea solution itself resulted in a spike of about 1.5 mg-N/L nitrate and the reported nitrate formation is in addition to this background level.

Chemical analyses

The chemical analyses for nitrogen-containing species used a HACH® DR/890 portable colorimeter and corresponding HACH® reagents. Table 2 outlines the test methods used. The analysis for raw water characterization was performed, in part, by Research Development International’s laboratory outside Phnom Penh. To measure high concentrations of ammonia (up to 18 mg/L-N) samples were diluted with ammonia-free bottled water by a factor of 100. For samples out of range of HACH® methods 8153 and 8507 (0.35–2.0 mg/L-N) for detecting nitrite, a dilution was done with nitrite-free bottled water and then the low nitrite method (HACH® 8507) was used.

Baseline performance

Initially, the four BSFs were acclimated for 5 weeks using raw water to establish a representative microbial community in the filters. The BSFs were then operated in parallel under identical conditions without any adjustment for an additional 3 weeks, during which time the ammonia, nitrite and nitrate concentrations in both influent and effluent were sampled every Monday, Wednesday and Friday with duplicate analysis. Six days per week, 15 L of water was poured into the BSFs, resulting in samples being taken after a 24 hour batch residence time. BSFs are operated in a batch mode. Typically, BSF users will pour 15 to 30 L into the filter, which displaces the previous volume of water that has been stored within the filter since the last application. The time since the last application of water is the ‘batch residence time’. Water takes approximately 2 hours to pass through the filter when flowing. Idle time is defined as the time between applications of water, minus the 2 hours of flow. For the study, 15 L of water was poured into the BSFs to ensure that samples all had a 24 hour residence time within the filter. If less than 15 L was poured into the filter, the entire volume of water stored in the filter would not be replaced. One exception was the test examining the impact of different filter depths on nitrite and nitrate formation, when 20 L was poured into the BSFs. All nitrite measurements during the 3 week baseline testing period were less than the lower limit of detection of 2 mg-N/L for Hach Method 8153 (subsequent nitrite

Table 1 | Dry and rainy season source water characterization results

<table>
<thead>
<tr>
<th>Test parameter</th>
<th>World Health Organization guideline</th>
<th>Dry season sample: June 8, 2011</th>
<th>Rainy season sample: August 5, 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity (mg/L as CaCO₃)</td>
<td>–</td>
<td>183</td>
<td>148</td>
</tr>
<tr>
<td>Ammonia (mg-N/L)</td>
<td>–</td>
<td>0.10</td>
<td>0.42</td>
</tr>
<tr>
<td>Nitrate (mg-N/L)</td>
<td>11</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>Nitrite (mg-N/L)</td>
<td>0.9</td>
<td>0.43</td>
<td>0.16</td>
</tr>
<tr>
<td>E. coli (cfu/100 mL)</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Total coliforms (cfu/100 mL)</td>
<td>0</td>
<td>60</td>
<td>301</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>5</td>
<td>0.58</td>
<td>1.95</td>
</tr>
<tr>
<td>pH</td>
<td>6.5–8.5</td>
<td>6.86</td>
<td>6.82</td>
</tr>
</tbody>
</table>

*Nitrate and nitrite measured using ion chromatography (Standard Method 4110; APHA 2005).

Table 2 | Summary of test methods used in study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method[^a]</th>
<th>Measurement range</th>
<th>Method precision[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Hach 8155</td>
<td>0 to 0.5 mg/L NH₃-N</td>
<td>14%</td>
</tr>
<tr>
<td>Nitrate</td>
<td>Hach 8039</td>
<td>0 to 30 mg/L NO₃-N</td>
<td>15%</td>
</tr>
<tr>
<td>Nitrite (High)</td>
<td>Hach 8153</td>
<td>2 to 150 mg/L NO₂-N</td>
<td>N/D[^c]</td>
</tr>
<tr>
<td>Nitrite (Low)</td>
<td>Hach 8507</td>
<td>0 to 0.35 mg/L NO₂-N</td>
<td>19%</td>
</tr>
</tbody>
</table>

[^b]Method precision (coefficient of variation) determined by quality control checks conducted prior to the study in source water spiked with a known concentration of ammonia, nitrite or nitrate.
[^c]Not determined.
measurements were conducted using Hach Method 8507, which had a lower detection limit of 0.005 mg-N/L).

**Impact of ammonia concentration on nitrite and nitrate formation**

Following the 5 weeks of acclimation and 3 weeks of baseline operation of the four BSFs, ammonia was added consistently to the source water for two of the filters at an average of 9.7 mg-N/L. The remaining two BSFs served as controls and continued to be fed unadjusted water (ammonia \( \approx 0.3 \) mg-N/L). The filters were operated under these conditions for 5 weeks, with effluent ammonia, nitrite and nitrate measured twice per week from each unit. Influent samples were taken prior to pouring the water into the BSFs rather than from the top of the diffuser basin. The effluent samples were then taken the following day, in 15 L composite samples, resulting in a water sample with a 24 hour batch residence time.

**Impact of cleaning filters on nitrite and nitrate formation**

The BSF flow rate decreases over time as the sand becomes clogged with biomass and non-degradable solids contained in the raw water. To restore the flow rate, users add 1 to 2 L of water to the top of the filter and manually clean the BSF by disturbing the upper layer of the sand with their fingers and removing the sediment that becomes suspended in the water with a cup or scoop (Singer 2011). The potential impact of this cleaning on nitrification was examined by recording the ammonia, nitrite and nitrate in the effluent from the two control and two ammonia-spiked BSFs over a 5 week period, with a single cleaning event occurring after week 3.

**Nitrite and nitrate formation at different depths within the filter bed**

The total volume of water in an idle BSF (v8) is approximately 15 L, of which approximately 10 L is pore volume within the filter media (sand), 2 L is water storage volume after the media in the gravel and 3 L is storage volume above the media (Figure 1). The hydraulics of the BSF is nearly plug-flow (Elliott et al. 2008). Therefore, when water is added to the filter, the first 2 L produced had been previously idle downstream of the filter media, the next 10 L would have been idle within the media and the next 8 L would be a blend of the old water that had been idle above the media mixed with the newly applied water. It was hypothesized that concentrations of nitrite and nitrate would be elevated in the water remaining in certain regions of the filter media during the idle time, and that one potential action to address partial nitrification could be to discard that portion of the filtered water. This hypothesis was tested by measuring nitrite and nitrate in water from an ammonia-spiked BSF in serial 2 L aliquots following a 24 hour residence time period. This experiment was only conducted once.

**Impact of filter idle time on nitrite and nitrate formation**

To evaluate the impact of idle time on nitrite and nitrate levels in the effluent, samples were analysed over the course of 4 successive days, with samples collected with batch residence times of 2, 4, 8 and 24 hours. Two ammonia-spiked BSFs were tested. To minimize any impact of filter bed depth on nitrification, a composite sample of 15 L of water was collected in a bucket and mixed.

**Impact of effluent storage time on nitrite and nitrate levels**

A simple study was conducted to track nitrite and nitrate concentrations of ammonia-spiked BSF-filtered water during storage in uncapped 500 mL plastic bottles, for 4 to 72 hours. The bottles were kept outdoors under shade to simulate storage conditions in rural areas. This study was conducted on a single BSF-fed ammonia-spiked water with duplicate samples taken each time.

**RESULTS AND DISCUSSION**

**Baseline BSF performance**

The results showed that, in general, the four BSFs performed similarly (Figure 2).
There was considerable variability in measurements from week to week within each BSF (shown as the small dots in Figure 2, each of which represents duplicate analysis of a discrete sampling event). This is not unexpected, as over the 3 weeks of the baseline test the influent water quality changed (31% and 55% coefficient of variation for nitrate and ammonia influent samples, respectively), along with changes in microbial community characteristics and filtration rates with increasing headloss. Importantly, however, the average ammonia and nitrate leaving the four BSFs operated in parallel were similar (shown as the open symbols in Figure 2), demonstrating that the four BSFs were reasonable replicates for the experiment.

**Impact of ammonia concentration on nitrite and nitrate formation**

The two control BSFs (with no spiked ammonia) exhibited a small average increase in nitrate (0.18 and 0.11 mg/L as N) and a 0.003 and 0.005 mg/L as N increase in nitrite relative to the average influent concentrations over the 5 weeks of ammonia spiking (Figure 3). However, these values are not statistically significant due to the variability in the analytical methods. In contrast, the ammonia-spiked BSFs showed substantial increases in both nitrite and nitrate concentrations in the filtered water. The nitrite concentrations were approximately 0.5 mg-N/L higher than in the influent, with several measurements nearly reaching the WHO limit of 0.9 mg-N/L. The increase in nitrate across the two ammonia-spiked BSFs averaged about 1.0 mg-N/L, with up to 3 mg-N/L formation observed (recall from the ‘Materials and methods’ section that the urea solution itself resulted in a spike of about 1.5 mg-N/L nitrate and the reported nitrate formation is in addition to this background level).

The differences between effluent and influent concentrations in both nitrite and nitrate in the ammonia-spiked BSFs compared to the control BSFs were significant ($p < 0.01$) under conditions of high ammonia loading. These results provide further supporting evidence for the theory that nitrification can occur in BSFs. The presence of nitrite in the effluent suggests that conditions did not favour complete nitrification to nitrate. This is not unexpected, as warm temperatures and variable concentrations of ammonia are conditions that are more favourable to ammonia oxidizing bacteria relative to nitrite oxidizing bacteria, such that nitrite may tend to accumulate (Houweling et al. 2011).

The WHO guidelines specify that the sum of the ratios of nitrite to nitrate relative to their individual limits should not exceed 1.0 (i.e., if the nitrite concentration is 50% of its limit, then the nitrate cannot exceed 50% of its limit). In the two ammonia-spiked BSFs, approximately half of the 20 individual measurements over the 5 weeks exhibited ratios above 0.9, ranging from 0.9 to 1.4 (the two control BSFs had ratios remaining below 0.2 in all cases). In all cases, the ratios would have remained below 1.0 had
urea not been added which caused an increase of influent nitrate levels. Hence, additional formation of nitrite and nitrate within the BSFs when high levels of ammonia are present in BSF influent did not in itself cause the WHO ratio limit to be exceeded. Nevertheless, these results demonstrate a risk of nitrification within BSFs when high levels of ammonia are present in BSF influent which can cause effluent nitrite and nitrate to exceed the WHO limit. It should be emphasized, however, that the amount of ammonia applied (9.7 mg-N/L) can be considered ‘very high’ when compared to the influent ammonia concentrations of the 20 BSFs surveyed by Murphy et al. (2010b), which did not exceed 0.35 mg/L. The fact that under such extreme conditions the nitrite and nitrate only periodically slightly surpassed the WHO limit could be cause for some expectation that under more normal conditions (e.g., the two control BSFs), nitrite and nitrate concentrations would be well below the WHO limits.

Impact of cleaning filters on nitrite and nitrate formation

During the cleaning process, the top layer of the sand media is manually rinsed and particulates are removed to allow a return to faster filtration rates. It was hypothesized that this might remove some of the biomass that produces the nitrification, leading to less nitrite and nitrate in the treated water. No such consistent trend, however, was observed (data not shown).

Nitrite and nitrate formation at different depths within the filter bed

Serial 2 L aliquots of water were withdrawn from a BSF to which water had been added 24 hours previously, to examine whether certain regions within the BSF were more responsible for nitrification than other regions. As shown in Figure 4, the nitrite concentration was lowest in the first 2 L of withdrawn water, which had remained idle in the region downstream of the media (in the gravel underdrain and the riser pipe). Since the gravel and riser pipe do not have the high surface area for nitrification that might be present in the filter bed, it is understandable that less nitrification might be observed. Subsequent aliquots of water withdrawn had been idle in the lower depths of the filter, followed by aliquots that had been idle in the upper depths. The final two aliquots were not idle in the filter, but were from the new batch of influent used to push the stored treated water out of the BSF. These samples all exhibited considerable increases in nitrite with a maximum somewhere near the middle depths of the filter media. The nitrate concentrations were more uniform, with a localized maximum occurring again somewhere near the middle depths of the filter.

The data suggest that minimal nitrite and nitrate levels might be achieved by using only water from the first 2 to 4 L of water withdrawn from the filter after new water is poured in. The effect here is that the water has no idle time in the filter media. The practicality of this approach is doubtful as there is no method using the current BSF design to limit users to drinking only this water. Furthermore, one of the benefits of the BSF system is that pathogen reduction is believed to be improved with idle time within the filter media (Elliott et al. 2008; Jenkins et al. 2011). Long idle times within the filter media may therefore be conducive to water that is safer in terms of pathogens, possibly offsetting any potential increased risk of nitrification.
Impact of filter idle time on nitrite and nitrate formation

It was expected that idle time could have an impact on nitrite and nitrate in the effluent water, since water could be in contact with the filter media and its nitrifying bacteria for times as short as approximately 25 min if more than one hydraulic volume of water were filtered at a time, or conversely, for more than 24 hours if water were withdrawn intermittently or not again until the next day. The mean of the results from the two BSFs studied are shown in Figure 5.

There was some variability in the results; for example, the 8 hour batch residence time had noticeably less nitrite than the other samples. Importantly, however, all the results show similar nitrite and nitrate concentrations after both 2 and 24 hour residence times, which suggests that limiting the residence time to 2 hours may not significantly minimize exposure to nitrite or nitrate. These results are similar to observations by Murphy et al. (2004), where estimated idle times of between 3 and 36 hours did not yield a significant difference in evidence of nitrification.

Impact of effluent storage time on nitrite and nitrate levels

Nitrite is more toxic to humans than nitrate on a per-mole basis, as reflected by the stricter WHO guideline. Nitrite is oxidized to nitrate, so a potential strategy to minimize risk from nitrite is to store effluent water in a vented container to allow oxidation of nitrite to nitrate by direct chemical oxidation, bacterially mediated oxidation, or volatilization of nitrous acid. A weakness of this strategy is the greater potential for contamination of the water during storage through unsanitary contact (Wright et al. 2004; Liang et al. 2010).

Nitrite and nitrate concentrations were largely unchanged over the 72 hour storage period, suggesting that such storage would be an ineffective strategy for oxidizing nitrite formed during BSF treatment, under the conditions tested (Figure 6).

CONCLUSIONS AND RECOMMENDATIONS

In 2010, Murphy et al. (2010a, b) reported evidence of nitrification in BSFs in Cambodia which caused concern among practitioners who oversee the installation of these devices. This study was an important follow-up to confirm the nitrification, to quantify it, and to try to identify methods to minimize the risk. While this study was limited, the factors that caused the limitations (working in a resource-limited country with rudimentary tools) are also, in a sense, a strength in that the study was undertaken under exact field conditions.

This study showed that nitrification in BSFs can occur; however, a very high concentration of ammonia was used...
(average 9.7 mg-N/L vs. 0.35 mg-N/L maximum reported by the Murphy et al. (2010a, b) studies) and for a long batch residence time (24 hours). Under these conditions, the combined concentration of nitrite and nitrate sometimes exceeded the WHO guidelines for the sum of the ratios of the two compounds by up to 40%, but none of the samples exceeded the individual nitrite and nitrate limits. Furthermore, the WHO guidelines would not have been exceeded if nitrate in the influent had not been increased through nitrate contamination (1.5 mg-N/L) in the ammonia spiking solution. As such, this study tends to suggest that the magnitude of the nitrification problem in BSFs may be minor, except under extreme cases, compared to the proven pathogen removal that BSFs can offer.

If it is not possible to redesign the BSF system to reduce nitrification, an alternative approach would be to restrict its use when waters contain a high concentration of ammonia. Unfortunately, it is difficult for communities such as those in Cambodia that participated in this study to identify waters that may contain elevated ammonia. Work to create better indicators of ammonia pollution would be beneficial. This study also reinforces the importance of source water protection as a key to public health in developing communities.

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