Comparison of the relative efficacies of granulated activated carbon and biochar to reduce chlorpyrifos and imidacloprid loading and toxicity using laboratory bench scale experiments

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Abstract

Pesticide loads and associated toxicity can be significantly reduced using integrated vegetated treatment systems. The major components of these systems remove moderately soluble and hydrophobic pesticides, but these systems need a strong sorbent material to remove more soluble pesticides, such as the neonicotinoid imidacloprid. Imidacloprid, and other neonicotinoids, are some of the most widely used insecticides in the world, are acutely toxic, and have been linked to a range of ecological effects.

Laboratory experiments were conducted to test the sorptive capacity of granulated activated carbon and biochar for removing imidacloprid and the organophosphate pesticide chlorpyrifos in a scaled-down treatment system. Simulated irrigation water spiked with individual pesticides was treated with a bench-top system designed to mimic a 600 L carbon installation receiving 108,000 L of flow per day for sixteen days.

Biochar reduced concentrations of chlorpyrifos (average concentration 1,187 ng/L) and imidacloprid (average concentration 4,135 ng/L) to less than detectable levels. Granulated activated carbon reduced chlorpyrifos to less than detectable concentrations, but allowed increasing concentrations of imidacloprid to break through. The breakthrough concentration of imidacloprid after one week of treatment was 22 ng/L, but after four weeks of treatment the breakthrough concentration was 73 ng/L.

Biochar and activated carbon both treated environmentally relevant concentrations of pesticides in a volume of water that represented a single growing cycle for four to six typical lettuce fields (~60 acres). Results indicate that these media would likely last an entire growing season, if used properly as a post-vegetation polishing step under conditions with reduced particle loads.

Introduction

Integrated vegetated treatment systems have been shown to be effective at removing up to 100% of pesticide loads in agriculture and urban runoff (Anderson et al. 2011; Anderson et al. 2016; Phillips et al. 2017). These systems include basins for the settling of suspended sediment, and vegetation for the adsorption and uptake of contaminants. They are particularly effective for low to moderately soluble pesticides such as the organophosphate chlorpyrifos and the pyrethroid bifenthrin. More soluble pesticides, such as the neonicotinoid imidacloprid, require additional sorption steps to reduce pesticide loading and concentrations to non-toxic levels.

Sorption of organic pollutants has been studied extensively (Sophia and Lima 2018), particularly the use of activated carbon (Dias et al. 2007), which has been described as the most widely used sorption medium. Activated carbon is usually a dense material, sometimes derived from coal or coconut charcoal. Most commercially available activated carbon products are manufactured by a few established chemical companies and optimized for specific adsorption characteristics. Granulated activated carbon (GAC) has been shown to be a useful component of integrated field treatment systems for agriculture, and is used as a polishing step for reducing loading of water soluble pesticides not treated by vegetative treatment systems (Phillips et al. 2017).

Although activated carbon is used extensively, it can be cost prohibitive for some applications. A number of reviews have discussed low-cost alternatives for activated carbon for various applications, including agricultural wastes, and of biochar (Ahmed et al. 2014; Bhatnagar and Sillanpaa 2010; Cha et al. 2016; Mohan et al. 2014). Biochar, a more recent collective term for carbon products produced by heating biomass in a closed system with little or no air (Lehmann and Joseph 2009), may provide a promising low-cost alternative to activated carbon. These substances are traditionally used as soil amendments, and can be prepared from agricultural waste materials, such as rice straw and corn stover (Taha et al. 2014). Biochar is produced at temperatures <700 °C, whereas activated carbon are biochar-type materials that have been activated with chemicals or temperatures >700 °C (Lehmann and Joseph 2009).

Biochar has been used successfully as remediation or treatment with contaminated soils (Jin et al. 2016; Yu et al. 2009), and drinking water (Gwenzi et al. 2017; Kearns et al. 2014), and some recent research has been conducted applying biochar to treat pesticides in simulated agricultural runoff (Cederlund et al. 2017; Taha et al. 2014). Recent research demonstrated the removal of chlorpyrifos by activated carbon in simulated agricultural runoff (Phillips et al. 2017), and a laboratory study showed similar success with imidacloprid removal (Voorhees et al. 2017). No studies have demonstrated the long-term efficacy of activated carbon or biochar in a field setting. Potential limitations to practical applications of these substances include cost, carbon disposal, and longevity, which is affected by reductions of contaminant active binding sites under real-world flow conditions. Binding sites can be blocked by particulate and organic matter and natural organic compounds.

This project was designed to determine the relative capacities of GAC and biochar to remove current-use pesticides from simulated runoff over extended simulated irrigation regimes under controlled laboratory conditions. The study also evaluated the media in sequence to determine whether a greater mass of pesticide could be removed when the treatments were used together. The removal efficiencies were tested using two representative pesticides, the organophosphate insecticide chlorpyrifos, and the neonicotinoid insecticide imidacloprid. Both pesticides are commonly used in California, and are linked to surface water toxicity (Anderson et al. 2018). The treatment systems were simulated in the laboratory using glass columns filled with the media (after Voorhees et al. 2017). Column breakthrough was determined with a combination of pesticide analysis and toxicity testing. The relative efficacies were compared in terms of loading capacity, toxicity reduction, relative cost, and potential for recycling the two carbon media. These results are intended to provide growers and resource managers a comparative analysis for consideration of on-farm implementation of carbon treatment as part of integrated runoff treatment systems.

Methods

Test Chemicals Selection

Chlorpyrifos and imidacloprid were the focus of a recent study of pesticide use, regulation and effects in Monterey and Imperial Counties (Anderson et al. 2018). These two counties were studied because they have different agricultural monitoring programs for water quality, and different pesticide use patterns. Chlorpyrifos makes up 2.6% of the total pounds of pesticide applied in Imperial County, but only 0.13% of total pounds applied in Monterey County. On a percentage basis, use of imidacloprid is more similar between the counties (0.23% and 0.38% for Monterey and Imperial Counties, respectively).

Both chlorpyrifos and imidacloprid are routinely detected in agricultural runoff at toxic concentrations to aquatic organisms (Anderson et al. 2018). These chemicals cause toxicity at low concentrations, particularly to organisms at the base of the food chain, such as aquatic stages of insects. Terrestrial flying insects often have larval aquatic stages, and world-wide declines in flying insects have been linked to current-use pesticides, including neonicotinoids, through impacts to aquatic insect larvae (Dirzo et al. 2014; Morrissey et al. 2015). Dirzo et al. (2014) reports a global decline of up to 35% of Lepidopteran species abundance over the last 40 years, although this decline has not been linked to individual pesticides.

Chlorpyrifos toxicity thresholds are typically in the low parts-per-trillion range for aquatic invertebrates such as the daphnid *Ceriodaphnia dubia* and the amphipod *Hyalella azteca*, whereas toxicity thresholds for imidacloprid are in the low parts-per-billion range. These pesticides are not the most toxic, but were chosen to represent a range of different pesticide uses, toxicity, and solubilities. Chlorpyrifos also has proven to elicit human nervous system and neurodevelopmental effects, which led to a ban on its use by homeowners in 2001 (Lovasi et al. 2011). Imidacloprid has had significant effects on pollinators with potential secondary effects on the human food supply (Simon-Delso et al. 2015; van der Sluijs et al. 2013).

Laboratory Experiments

Chlorpyrifos and imidacloprid stock solutions were pumped through separate 50 mL glass columns containing GAC, biochar and a combination of both materials. Activated carbon was sourced from Evoqua Water Technologies (Benicia, CA), and biochar was sourced from the Leland Agriculture Group (Fairfield, CA). Aquacarb® NS is a reactivated coal/coconut shell charcoal combination GAC, and is an economic alternative to virgin activated carbon products. Evergreen Biocarbon® was derived from organic sustainably-grown yellow pine wood. The average mass of GAC in each column was approximately 28g and the average mass of biochar was approximately 15g.

Each experiment proceeded for four weeks, and simulated sixteen irrigation events. Experiments evaluated treatment at laboratory-scaled flow rates comparable to field flow rates of 10 L/s (lab flow rate = 50 mL/min) and a total irrigation flow of approximately 108,000 L per event. The chosen flow rate was based on measured flow rates in agricultural practices and was greater than flow rates tested by Phillips et al. (2017). Flow rates were the same as those tested by Voorhees et al. (2017). Stock solutions were prepared by adding certified reagent-grade chlorpyrifos and imidacloprid (AccuStandard, New Haven CT) to 30 L of laboratory well water. Stock solutions were pumped through the three columns using a positive pressure peristaltic pump. Columns were packed with material at a volume scaled to be equivalent to a field installation of 600 L GAC or biochar.

Breakthrough events were assessed using a combination of analytical chemistry and toxicity testing (described below), and were defined as the first detectable pesticide measured in the column effluent after the maximum mass of pesticide has been loaded on the column. Each column treatment had a paired treatment blank to quantify possible toxic effects from the carbon-packed columns. Un-spiked water was passed through these blank columns. Toxicity tests were conducted on the post-column effluent from treatment blanks.

Toxicity Testing

Experiments consisted of sixteen pumping events conducted during four consecutive weeks for each pesticide. Post-column effluent was tested for toxicity every fourth pumping event. Toxicity was determined using two invertebrates. The cladoceran *Ceriodaphnia dubia* was used as the toxicity indicator for chlorpyrifos experiments, and the midge *Chironomus dilutus* was used for imidacloprid experiments (U.S. EPA 2002). *Ceriodaphnia dubia* demonstrates greater relative sensitivity to chlorpyrifos and *C. dilutus* demonstrates greater sensitivity to imidacloprid. Briefly, tests with *C. dubia* consisted of five replicate chambers containing 15 mL of test solution and five organisms. Organisms were counted, and test solution was renewed daily for 96 hours with survival measured as the test endpoint. Tests with *C. dilutus* consisted of four replicate chambers containing 5 mL of sand, 200 mL of test solution and twelve organisms. Tests solutions were renewed every other day for 10 days. Survival and midge larval growth endpoints were determined at the end of the exposure. In addition to the column treatment blanks, negative controls with clean laboratory culture water were tested with each batch of column samples.

Chemical Analysis

Chlorpyrifos stock solution and post-column effluent concentrations were measured during each pumping event using enzyme-linked immunosorbent assays (ELISA, Modern Water, New Castle DE). ELISA level of detection was 50 ng/L. Because there is no ELISA method for imidacloprid, and therefore no instantaneous analysis method for this pesticide, daily determinations of pesticide breakthrough were not possible. Weekly toxicity tests and liquid chromatography/mass spectrometry (LC/MS) analysis of imidacloprid were conducted. LC/MS analyses was conducted under the direction of Dr. Thomas Young, UC Davis Department of Civil and Environmental Engineering.

Extraction and analysis methods for LC/MS were as follows. Approximately one liter of each water sample was passed through an Oasis HLB cartridge (Waters, Massachusetts, USA) in a vacuum setting. After all the samples passed through, sodium sulfate was added to the empty water bottles to absorb excess water. The bottle was rinsed three times with 4 mL methanol to recover residues remaining in the container. The solvent was transferred to a glass evaporation tube. The cartridges were dried for at least one hour prior to elution. Ten milliliter of methanol was used to elute the Oasis cartridges into evaporation tubes. Internal standard was added prior to injection into an Agilent 7890B GC coupled to an Agilent 7200B QTOF-MS for analysis. The methanol eluent was combined with the bottle rinse and evaporated to a final volume of 0.2 mL using Turbovap (Biotage) followed by addition of 0.8 mL milliQ water. Internal standard was added and the extract was injected into an Agilent 1260 Infinity HPLC coupled to an Agilent 6530 QTOF-MS for analysis. The imidacloprid level of detection was 1 ng/L.

Results

Quality Assurance

Survival in all control and treatment blanks exceeded test acceptability criteria of 90% survival for *C. dubia* and 80% survival for *C. dilutus*, and *C. dilutus* larvae showed adequate growth in control and blank solutions (data not shown). Chlorpyrifos standard reference material recovery was 122% for ELISA analysis, and imidacloprid recovery was 80% for LC/MS analysis. The first imidacloprid toxicity test with *C. dilutus* did not include a combination treatment post-column effluent sample due to loss of sample.

Column Effectiveness

Stock solution concentrations for chlorpyrifos ranged from 1,100 ng/L to 1,360 ng/L, and imidacloprid concentrations ranged from 4,130 ng/L to 4,145 ng/L (Table 1). These concentrations were high enough to cause significant mortality to both organisms and significantly reduce growth to midge larvae.

Biochar reduced concentrations of chlorpyrifos below the method detection limit of 50 mg/L (Table 1), and concentration of imidacloprid below the level of detection of 1 ng/L. GAC also reduced concentrations of chlorpyrifos below the MDL, but allowed increasing concentrations of imidacloprid through the column as the four-week experiment progressed. The combined treatment of biochar and GAC did not allow breakthrough of imidacloprid.

The ELISA MDL was close to the median lethal concentration (LC50) for *C. dubia* (53 ng/L (Bailey et al. 1997)), but no toxicity was observed in any of the post-column effluent samples. Although the GAC column had increasing breakthrough throughout the experiment, concentrations were well below the 96-hour LC50 for *C. dilutus* (11,800 ng/L (Raby et al. 2018)). No imidacloprid toxicity was observed in the post-column effluent samples (Table 1).

Table 1. Mean percent survival results for *C. dubia* and *C. dilutus*, and mean ash-free dry weight (AFDW) results for *C. dilutus* in spiked water and post-column effluents listed with stock solution concentrations and recovery concentrations in post-column effluents water for the three column types. CHL = chlorpyrifos, IMI = imidacloprid, GAC = granulated activated carbon, ND = non-detect, NA = not analyzed, SD = standard deviation, AFDW = ash-free dry weight.

Sample	1/22/2018 Mean % *C. dubia* Surv.	SD	Chlorpyrifos ng/L	1/29/2018 Mean % *C. dubia* Surv.	SD	Chlorpyrifos ng/L	2/5/2018 Mean % *C. dubia* Surv.	SD	Chlorpyrifos ng/L	2/12/2018 Mean % *C. dubia* Surv.	SD	Chlorpyrifos ng/L
Stock	0	0	1,100	0	0	1,360	0	0	1,157	0	0	1,131
CHL Biochar	100	0	ND	96	9	ND	88	18	ND	93	12	ND
CHL GAC	100	0	ND	100	0	ND	100	0	ND	100	0	ND
CHL Combo	100	0	ND	100	0	ND	100	0	ND	100	0	ND
Sample	5/14/2018 Mean % *C. dilutus* Surv.	SD	Imidacloprid ng/L	5/21/2018 Mean % *C. dilutus* Surv.	SD	Imidacloprid ng/L	5/29/2018 Mean % *C. dilutus* Surv.	SD	Imidacloprid ng/L	6/4/2018 Mean % *C. dilutus* Surv.	SD	Imidacloprid ng/L
Stock	2	4	4,130	0	0	4,145	6	4	4,135	73	14	4,130
IMI Biochar	96	8	ND	92	17	ND	98	4	ND	98	4	ND
IMI GAC	98	4	22	94	4	31	98	4	46	98	4	73
IMI Combo	NA	NA	ND	88	8	ND	100	0	ND	98	4	ND
Sample	Mean *C. dilutus* AFDW (g)	SD	Imidacloprid ng/L	Mean *C. dilutus* AFDW (g)	SD	Imidacloprid ng/L	Mean *C. dilutus* AFDW (g)	SD	Imidacloprid ng/L	Mean *C. dilutus* AFDW (g)	SD	Imidacloprid ng/L
Stock	NA	NA	4,130	NA	NA	4,145	0.17	0.06	4,135	0.19	0.02	4,130
IMI Biochar	5.44	1.08	ND	1.62	0.79	ND	3.00	1.80	ND	2.86	1.37	ND
IMI GAC	3.60	1.61	22	0.83	0.19	31	3.64	1.67	46	2.59	1.24	73
IMI Combo	NA	NA	ND	1.18	0.14	ND	1.93	0.86	ND	2.42	1.45	ND

Discussion

Recent studies have shown that soluble and moderately soluble pesticides are not sufficiently treated with traditional vegetated systems when the regulatory objective is elimination of toxicity in runoff (Hunt et al. 2008; Moore et al. 2014; Phillips et al. 2017). This is especially true in industrial-scale intensive agriculture situations where high volumes of irrigation runoff contain toxic concentrations of complex pesticide mixtures and elevated particulate loads. In these settings runoff residence times are on the order of hours, and toxic concentrations of pesticides can pass through the system. It is therefore necessary to include a form of carbon treatment as a polishing step to remove residual pesticides. Adding carbon filtration has proven effective in systems incorporating upstream sedimentation basins to remove particulate-bound pesticides, followed by vegetation to further sorb chemicals (Phillips et al. 2017). Use of carbon treatment will likely be most important with agrichemicals such as neonicotinoids, which do not readily adsorb to plant surfaces or sediments (Bonmatin et al. 2015), thus limiting the effectiveness of current treatment methods. Neonicotinoid use is on the rise in the U.S., and in some parts of California, imidacloprid use increased by 36% in as little as three years (Anderson et al. 2018). Voorhees et al. (2017) demonstrated that GAC successfully removed imidacloprid from simulated runoff. The current study was designed to assess the effectiveness of GAC for treatment of two current use pesticides under intermittent long-term flow regimes designed to mimic those in real-world irrigation run-off. Biochar was evaluated as an alternative carbon medium due to its lower cost and potential for re-use as a soil amendment.

These experiments were designed to saturate all active binding sites on the sorption media to the point of column breakthrough as a means to compare the relative binding capacities of GAC, biochar and the combination GAC/biochar treatment. The goal was to determine the practical life span of each filter media type. These results are intended to be used to inform growers on how long the filters can be left in the field before they are saturated and become ineffective. The experiment was conducted for four weeks and included sixteen simulated irrigation events. When scaled up to field conditions, the design was equivalent to treatment of 108,000 L of pesticide-laden water per event through a carbon installation containing 600 L of media. The total simulated flow in these experiments scales up to approximately 1.7 million liters of water. Conservative estimates indicate that approximately 60 acres of lettuce with 5% runoff could produce this amount of water during a crop cycle, but in most cases growers have only 1 to 2% runoff. Low breakthrough concentrations and absence of toxicity demonstrate that these media, when used correctly, have the potential to last in the field for an entire growing season, but results would vary depending on individual farming practices.

Biochar provides promising potential as an alternative to GAC because it may serve as a more sustainable method for treating pesticides. The Evergreen Biocarbon sourced from the Leland Agriculture Group was equally effective to GAC at removing chlorpyrifos, and more effective at removing imidacloprid, but both materials completely eliminated pesticide-related toxicity. Biochar has two attributes that may allow it to be a more cost-effective and sustainable sorption media. The biochar used in these experiment retails for <$1/pound versus $0.70-$2/pound for GAC. Biochar may also be less expensive to dispose of because it is currently used as a soil amendment in agriculture, and it may be possible to re-till it into farm soils or roads after it has been used to treat pesticides in irrigation runoff. Pesticides bound to the biochar will have the opportunity to degrade in place. Use of biochar as a soil amendment post-treatment would have a major cost advantage over bituminous GAC which requires disposal as hazardous waste after use.

There are numerous studies assessing the effectiveness of biochar as a soil amendment for water retention and infiltration, and the adsorption of pesticides (Jin et al. 2016; Yu et al. 2009). Few studies have assessed biochar filtration as a means for reducing pesticide concentrations in agricultural or urban runoff. Taha et al. (2014) demonstrated the ability of biochar to remove fifteen pesticides from spiked water, and Cederlund et al. (2017) looked at the reduction of chlorpyrifos, diuron, glyphosate and MCPA in sand columns amended with biochar. These studies demonstrated the effectiveness of biochar as a treatment medium, but did not discuss the practical application of biochar as a polishing step in field integrated treatment systems. Ulrich et al. (2017) used biochar to treat a number of spiked organic contaminants in simulated stormwater. Mohanty et al. (2018) discusses the use of biochar as a filtration medium in bioswales as a component of low impact development and reviewed other applications. These authors suggest biochar can be used in filter strips, vegetated ditches and wetlands, tree boxes and green roofs.

The current study builds on previous work with practical applications of GAC for treatment of agricultural runoff. Biochar and GAC both treated environmentally relevant concentrations of pesticides in a volume of water that represented a single growing cycle for four to six lettuce fields. The results indicate that these media would likely last an entire growing season, if used as a post-vegetation polishing step under conditions with reduced particle loads. Biochar had similar pesticide removal capacity to GAC, and has the potential to be more economical to install and dispose of. These results will inform resource managers currently working on development of implementation projects for pesticide reduction in coastal watersheds. This includes the California Regional Water Quality Control Boards, coastal Resource Conservation Districts (e.g., Santa Cruz and Monterey County RCDs), the University of California Cooperative Extension, the Central Coast Wetlands Group, and Moss Landing Marine Laboratory.

Future studies include a field comparison between GAC and biochar using simulated irrigation runoff spiked with imidacloprid and the pyrethroid pesticide permethrin. Carbon will be installed as a polishing step at the terminal end of a vegetated ditch. The first year of the study compares the efficacy of each carbon, whereas the second year will test the ability of the biochar to reduce pesticide concentrations in runoff from a cultivated test field.

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