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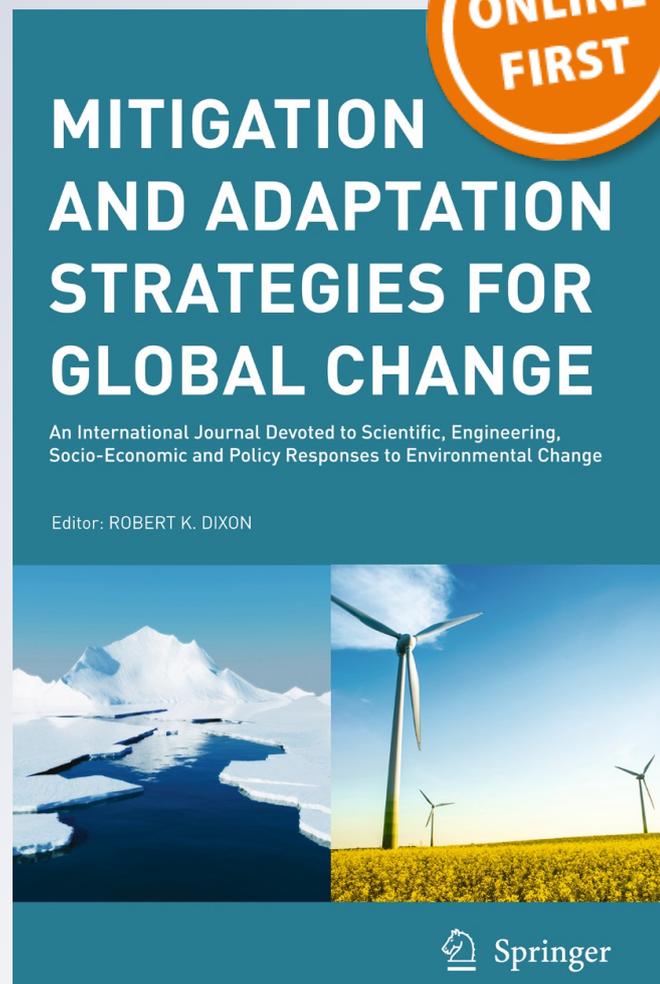
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Using activated biochar for greenhouse gas mitigation and industrial water treatment

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Abstract This study explored the feasibility of using residual biomass to both mitigate greenhouse gas (GHG) emissions and remediate water contaminated by hydrocarbons. Using produced (process-affected) water from Canada's oil sands operations as a case study, activated biochar (ACB) was found to have a higher affinity to organics than activated coal and removed 75 % of total organic carbon (TOC) from produced water in steam-assisted gravity drainage (SAGD) operations or 90 % of the TOC from synthetic tailings (ST) water sample. Up to 6 Tg dry biomass year⁻¹ would be required to treat the waters associated with the 93×10^6 -m³ of bitumen recovered per year. Landfilling the spent ACB and flaring any biogas produced were estimated to provide a greater GHG benefit than the combustion of the biochar + organics for heat to offset natural gas demand. Net costs for the ACB were about 13.84\$m⁻³ bitumen for SAGD operations and 1.76\$m⁻³ bitumen for mining operations. The values for mining operations justify further work to create a value chain that will integrate bioprocesses into the fossil fuel industry.

Keywords Activated biochar · Biochar · Lignocellulosic biomass · Oil sands · Organics · Produced water

1 Introduction

The world's fossil fuel-based energy systems not only contribute to climate change but also use and contaminate large volumes of water (Waughray 2011). The greenhouse gas (GHG) and water footprints tend to be higher for the unconventional resource development (e.g., oil sands, shale gas, and oil) that is rapidly growing around the world. Certainly, cost-effective mitigation efforts are needed to reduce GHG emissions and remove hydrocarbons from water.

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The pyrolysis of lignocellulosic biomass (e.g., wood, straw) to create biochar (Ronsse et al. 2013; Veksha et al. 2014a, b) has been proposed as either a renewable energy feedstock to displace coal (Gaunt and Lehmann 2008; Abdullah and Wu 2009) or a resilient form of carbon to provide a long-term sink for fossil carbon emissions (Lehmann et al. 2006). Biochar, like coal, can also be activated through chemical or physical means (Iranmanesh et al. 2014; Ahmad et al. 2014) to enhance its surface area properties so that it will adsorb organics that are found in air or water. Such activated carbons, typically made from coal, are commercially available and widely used to remove contaminants from water and air.

In this paper, Canada's oil sands operations provide a case study to explore the feasibility of converting residual biomass into an activated biochar (ACB) to remediate simultaneously, both air and water impacts. Steam-assisted gravity drainage (SAGD) is an oil recovery technology used for deep oil sands deposits (>400+m) that produces about $119 \times 10^3 \text{ m}^3$ bitumen day^{-1} in Alberta, Canada. Steam is injected into a horizontal well in the bitumen reservoir, reducing the viscosity of the bitumen that then flows to a second horizontal well located below the first where it is pumped to the surface along with the condensed water (Alberta Government 2013). Typically, 3 m^3 of water must be converted to steam to recover each cubic meter (m^3) of bitumen, and about 90 % (approx. 2.7 m^3 water m^{-3} bitumen) of the organic and salt-enriched water is recovered and reused within the process. The organics in the produced water contribute to both the corrosion and fouling of the boiler, making it necessary to shut down the system for maintenance more frequently than desired. Consequently, removal of the organics from the produced water should reduce the operational cost and increase the efficiency of the oil sand recovery process.

For oil sands deposits near the surface, mining operations coupled with hot water extraction are used to separate the bitumen from the sand. In 2012, this process recovered about $135 \times 10^3 \text{ m}^3 \text{ day}^{-1}$ in Alberta. Approximately, 3 m^3 water are sent to tailings ponds for every m^3 of bitumen recovered (Kasperski and Mikula 2011; Alberta Energy 2013), and of this amount, all but about 0.5 m^3 of water are reused in the process. The primary purpose of the tailings ponds is to remove fine particulates. However, the high levels of organic compounds (predominantly naphthenic acids (NA) (Fedorak et al. 2003) in the water are metabolized by anaerobic microbes, producing methane, a potent GHG (Holowenko et al. 2000; Siddique et al. 2006, 2008) that has about 25 times the global warming potential of carbon dioxide (CO_2) (Forster et al. 2007). Removal of the organics would reduce both the methane emissions and the toxicity of the tailings water.

This paper compares the ability of ACB and activated coal (ACC) to remove organics from SAGD-produced waters and from an aqueous solution of NA mimicking the composition of oil sands tailings water (Holowenko et al. 2000; Siddique et al. 2006). The results are used to carry out a critical assessment of the potential scale and feasibility for integrating ACB into oil sands operations, both to clean process water and to provide a GHG benefit.

2 Materials and methods

2.1 Source of activated carbons and physical characterization

Steam-ACB made from hardwood and commercially available as ColorSorb G5 was obtained from Jacobi Carbons Inc. (Columbus, Ohio, U.S.). As a control, steam-activated carbon made from lignite coal (ACC) and commercially available as HydroDARCO-C was obtained from Norit Americas Inc. (Texas, U.S.). Both of these activated carbons are sold for use in water treatment.

Surface area and pore size distribution determination A sample of about 100 mg of each adsorbent was weighed into a sampling tube and then degassed under nitrogen flow at 300 °C for 3 h. The sample tube was then connected to a TriStar II (Micromeritics Instrument Corporation, Georgia, U.S.) for nitrogen adsorption at 77 K. The surface area was determined using Brunauer-Emmett-Teller (BET) adsorption isotherm. Pore size distribution was obtained from the adsorption cumulative pore area data generated by this instrument using the Barrett-Joyner-Halenda (BJH) method. A summary of these physical characteristics is given in Table 1.

2.2 Selection and preparation of organic-rich waters

Two water samples were used for these studies:

SAGD water was collected into a 20-L container from the process stream of an industrial SAGD facility (Athabasca region, Alberta, Canada) immediately following the water softening stage but prior to entering the boiler. This 80 °C water had a pH of 9.8, total organic carbon (TOC) content of 760 to 930 g C m⁻³, and total dissolved solids (TDS) corresponding to an electrical conductivity between 0.8 and 0.9 S m⁻¹. The container was completely filled and sealed. After the water inside was allowed to cool to room temperature, the container was then shipped to a laboratory at the University of Calgary, Alberta 660 km away, where it was stored at 4 °C. When water was drawn from the vessel for experimental use over the subsequent 6 months, the headspace was replaced with nitrogen (N₂) gas.

Simulated tailings (ST) water: Since the organics in tailings water decompose rapidly, it was not possible to access tailings water that could be preserved for use over many months. Hence, ST water was prepared that had a NA concentration of 45 to 60 g C m⁻³, similar to that reported in tailings water (Fedorak et al. 2002; Quagraine et al. 2005; Allen 2008). We used a practical grade NA standard (item #1338-24-5, Fisher Scientific, ON, Canada) that was a mixture of cyclic and acyclic NAs with carbon lengths from 11 to 18 (est. 73 % (w/w) C content). Stock solutions of this ST water were stored at 0–4 °C in 500-cm³ volumes.

2.3 Batch assay

In a batch adsorption assay, either 10 cm³ (SAGD water) or 20 cm³ (ST water) was placed into a 30-cm³ glass vial and the vial taken to temperature (25 °C for SAGD and ST water; 80 °C for

Table 1 Physical characteristics of adsorbents considered in this study

	Activated coal	Activated biochar
Surface area (m ² /g)	740	2,374
Pore area distribution (%)		
Macro-pore	0.4	1.4
Meso-pore	74.4	54.6
Micro-pore	25.2	44.1
Pore volume distribution (mL/g)		
Macro-pore	0.5	0.4
Meso-pore	8.6	1.7
Micro-pore	3.7	2.1

SAGD water only) before adding either 0.1 g (SAGD water) or 0.02 g (ST water) of adsorbent (ACB or ACC) to each (Note: These are typical operating temperatures for field operations and thus the rationale for the temperature choices). The mixtures were then shaken at 175 rpm for 18–24 h before analysis. After settling for 2–3 min, the supernatant (5–7 cm³) was drawn with a syringe and filtered through a 0.45- μ m nylon membrane filter (VWR International, Alberta, Canada). The filtrate was analyzed for TOC (Model TOC-VE, Shimadzu Corporation, Kyoto, Japan), calibrated against reagent grade potassium hydrogen phthalate. Three replicates of each adsorbent were prepared for both SAGD and ST waters, so mean values could be presented \pm standard errors (SE) and values compared using Student's *T* test in excel spreadsheet (Microsoft Excel 2010).

2.4 Flow-through assay

Samples (0.4 g) of ACB or ACC were packed into a stainless steel metal tube having an internal diameter of 0.8 cm, resulting in respective column heights of 3.1 and 2.4 cm, column volumes of 1.68 and 1.33 cm³, and packing densities of 0.24 and 0.30 g cm⁻³, respectively. Quartz wool was placed at the bottom and top of the columns to keep the adsorbent in place during the study. A silicon rubber thermolyne heating tape (1.27-cm wide and 183-cm long, Barnstead/Thermolyne, Iowa, U.S.) was coiled around the feed tube from the pump to the activated carbon column and maintained at either 25 or 80 °C using a thermocouple and PID temperature controller (Model 68900-01, Digi-Sense).

The water samples were pumped through the column using a pump (MasterFlex L/S, Cole-Parmer Instrument Company, Quebec, Canada) at a flow rate of 10 cm³ min⁻¹ to give residence times of approximately 0.13 and 0.17 min for the ACB and ACC, respectively. The column effluent was analyzed every 1–2 min (10 to 20 cm³ effluent) for TOC as described in the batch experiments.

2.5 Calculation of the GHG and economic costs and benefits

The adsorption measurements were used to calculate the adsorption capacity (units of mg TOC removed per g adsorbent) when either 75 % (SAGD water) or 90 % (ST water) of the organics had been removed. The values for ACB were then used to estimate the biomass demand for treating water produced from Canada's oil sands operations.

Further analyses of the cost and benefit from both a GHG and economic perspective were carried out using the data from the ACB batch analysis experiments given both conservative and optimistic assumptions for key parameters where optimistic scenarios have the lower costs and greater benefits:

- GHG emissions associated with biomass processing to ACB were either 40 (optimistic) or 100 (conservative) kg carbon dioxide equivalent (CO₂e) Mg⁻¹ dry biomass (Roberts et al. 2010).
- Long-term storage associated with landfilling the spent ACB was either 90 % (optimistic (Lehmann et al. 2006)) or 80 % (conservative (Roberts et al. 2010)) of the carbon in the ACB.
- The carbon price within Alberta, Canada was either 40\$ (optimistic (Vanderklippe 2013)) or 15\$ (conservative (Alberta Energy 2013)) Mg⁻¹ CO₂e.
- The cost of producing the ACB from residual biomass was either 400 \$ (optimistic) or 600 \$ (conservative) Mg⁻¹ ACB.

These calculations provided an estimate of the net material cost of ACB production to clean oil sands produced water and expressed per m³ of bitumen recovered from current operations.

3 Results and discussion

3.1 Removal of organics from SAGD-produced water

In the batch assay, the ACB and ACC were both effective in removing organics from the SAGD water (Fig. 1, left panel). After 24 h of treatment, 71 to 78 % of the organic carbon was removed from the water. At 80 °C, the ACB removed significantly more organic C ($77.1\% \pm 0.5$; 71.6 ± 0.5 g C kg⁻¹ ACB) than did ACC ($71.3\% \pm 0.7$; 66.3 ± 0.6 g C kg⁻¹ ACC) (Fig. 1a, b). Control experiments using silica sand removed only 2 to 6 % of the TOC (data not shown), supporting the adsorbent properties of ACB and ACC.

In batch experiments with ACB and ACC, more than 95 % of the organic carbon was removed by the time of the first sample (30 min after adding adsorbent), although a treatment time of 18–24 h was used in these batch assays.

A flow-through assay was also carried out using the SAGD water (Fig. 2, left panel). Initially (first 25 cm³ g⁻¹ ACC or ACB), the activated carbons were able to remove 78 % (ACC) to 85 % (ACB) of the organic C. However, ACC failed to remove 75 % of C and it was challenged with after only 42 cm³ SAGD water g⁻¹ ACC, whereas ACB maintained more than 75 % C removal after 157 cm³ SAGD water g⁻¹ ACB (Fig. 2). At this volume, the adsorption capacity for ACB was calculated to be 90 g C kg⁻¹ ACB, 25 % higher than that obtained in the

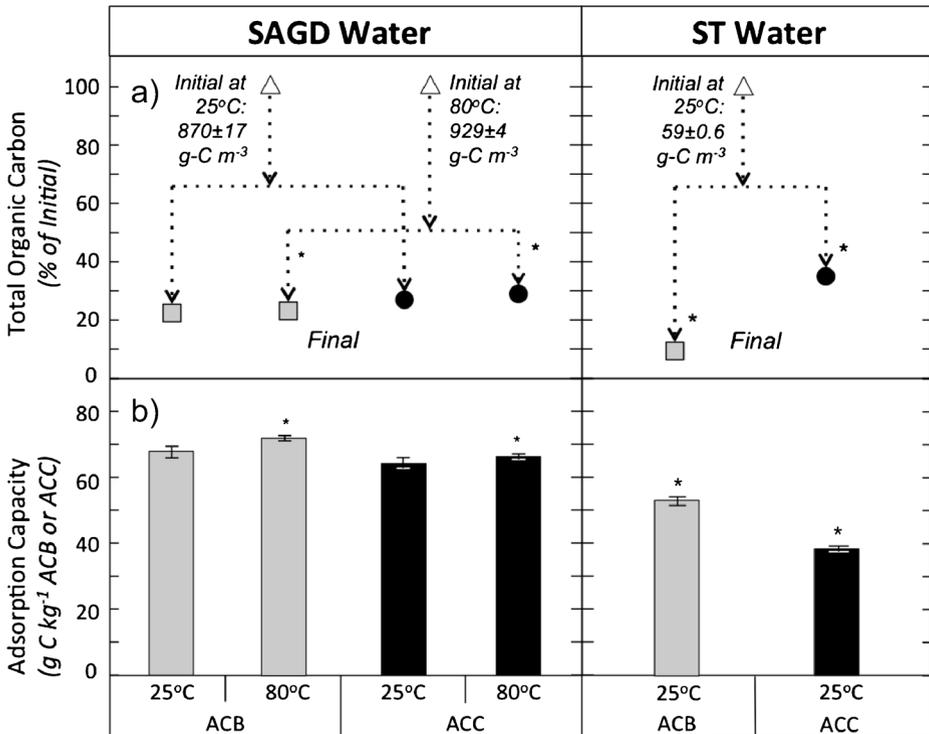


Fig. 1 Batch removal of organics from produced water by activated biochar (ACB, gray) or activated coal (ACC, black) at 25 and 80 °C (steam-assisted gravity drainage water only). Values are means (\pm standard error, $n=3$), error bars may be within symbols. The asterisk denotes treatments that were significantly different at $p \leq 0.05$

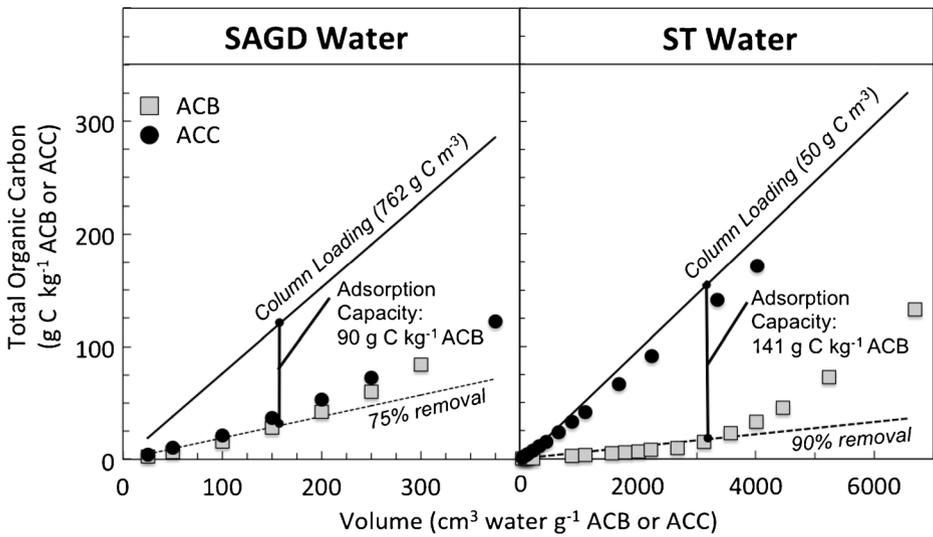


Fig. 2 Removal of organics from steam-assisted gravity drainage (SAGD) water at 80 °C or synthetic tailings (ST) water using a flow-through system. Activated biochar (ACB, gray); activated coal (ACC, black); solid lines, column loading rate; dashed lines, expected total organic carbon (TOC) removal of either 75 % TOC (SAGD water) or 90 % (ST water). The adsorption capacity at the maximum volume of water that the ACB was able to remove at either 75 % (SAGD water) or 90 % (ST water) of the organics is given in the figure. Values are plotted as mean \pm standard error, but the error bars are within the symbols

batch assay (71.6 ± 0.5 g C kg⁻¹ ACB, Fig. 1b) for which a similar removal level (75 %) of the organics was achieved.

3.2 Removal of organics in tailings water from oil sands mining operations

In batch studies with ST water (Fig. 1, right panel), the ACB was significantly more effective than ACC in removing NA, achieving 91 ± 1.3 % removal compared to only 66 % for ACC (Fig. 1a). The corresponding adsorption capacity for the ACB was calculated to be 53.5 ± 0.75 g C kg⁻¹ ACB compared to 38.5 ± 0.67 g C kg⁻¹ ACC (Fig. 1b).

With the flow-through assay (Fig. 2, right panel), ACC was ineffective in removing the NA from the ST water, while the ACB was highly effective. Initially (first 45 cm³ g⁻¹ ACC), the ACB was able to remove 95 % of the organics (Fig. 2). By the time the ACB's removal rate dropped below 90 %, over $3,100$ cm³ NA solution per gram ACB had been treated. Assuming a target of 90 % removal, the adsorption capacity of ACB was calculated as 141 g C kg⁻¹ ACB (Fig. 2). This value was 2.6-fold higher than that obtained from the batch assay with ST water in removing about 90 % of the NA. At the concentrations mimicking tailings water, it seems likely that the NA loading in the batch assay was significantly below that needed to saturate the ACB.

3.3 The opportunity and magnitude of the challenge

The data provided in the introduction on oil recovery and produced water needing treatment have been summarized in Table 2. Consequently, mining operations generate 148×10^6 m³ of water per year that could benefit from treatment, while SAGD operations generate an additional 118×10^6 m³ of water per year for a total of 266×10^6 m³/year (Table 2(C)).

Table 2 Estimation of the potential activated biochar (ACB) and biomass demands for treating water associated with steam-assisted gravity drainage (SAGD) and mining oil sands operations in Alberta, Canada

Item no.	Units	Oil sands technology					
		SAGD		Mining		Total	
Oil production in Alberta, Canada ^a	m ³ day ⁻¹	119,250		135,150		254,400	
Water use per m ³ oil recovered ^b	m ³ m ⁻³	2.7		3.0		-	
Water needing treatment annually ^c	10 ⁶ m ³ year ⁻¹	118		148		266	
Organic Carbon to be removed ^d	g C m ⁻³	641		49.5		-	
		Batch	Flow-through	Batch	Flow-through	Batch	Flow-through
Adsorption capacity ^e	g C kg ⁻¹ ACB	71.6	90	53.5	141	-	-
Activated biochar (ACB) demand ^f	Tg ACB year ⁻¹	1.05	0.84	0.14	0.05	1.19	0.89
Biomass demand ^g	Tg biomass year ⁻¹	5.26	4.19	0.68	0.26	5.95	4.45

^a From Canadian Association of Petroleum Producers (2011) assuming 0.159 m³/barrel of oil equivalent

^b From Alberta Energy (2013) and Kasperski and Mikula (2011)

^c Calculated as (item A × item B) × 365 days year⁻¹

^d Assumes 75 % of 855 g Carbon m⁻³ for SAGD water and 90 % of 55 g C m⁻³ for tailings water

^e Experimental data from Figs. 1 and 2

^f Assumes single use of ACB and calculated as (item C × item D) ÷ (item E × 1,000)

^g Assumes biomass conversion to ACB is 20 % by dry weight (Klass 1998)

The organic carbon level is about 10–15 times higher in SAGD water (760–950 g C m⁻³) (Kawaguchi et al. 2012), than in tailings water (50–100 g C m⁻³), and the reasons for reducing organic carbon levels differ with each oil sands technology. Table 2 takes these differences into consideration and provides an estimate of the magnitude of the opportunity/challenge in the current oil sands operations in Alberta.

SAGD operations While detailed studies have yet to be carried out to fully characterize the effect of organics removal on boiler fouling, we propose that removing 75 % of the organics from this water should significantly reduce or eliminate the depositions. Assuming an organic C content of 855 g C m⁻³ (average of the SAGD waters measured in this study), a 75 % reduction in organics would require a removal of 641 g C m⁻³ water (Table 2(D)). This was achieved with ACB using either batch or flow-through processing (Figs. 1 and 2), and given the adsorption capacities measured here (Table 2-E), 0.84 to 1.05 Tg of ACB would be required per year (Table 2-F). Producing this amount of ACB would require approximately five times its weight as dry biomass (4.2 to 5.3 Tg biomass year⁻¹; Table 2-G) since slow pyrolysis to make biochar would result in a 65–75 % loss of the original biomass (Klass 1998; Veksha et al. 2014a, b), and activation of the biochar would be expected to further reduce recovery to only about 20 % of the original feedstock mass. In the process, the C content would increase from 50 to 85 % C (Lehmann 2007), and the energy content would increase from 18 GJ Mg⁻¹ biomass to 30 GJ Mg⁻¹ ACB (Abdullah and Wu 2009).

The scale and nature of existing water treatment processes associated with SAGD operations and the need to maintain process water temperatures at or above 80 °C make a batch process the most feasible for potential use. For example, adding the adsorbent at the liming stage in water treatment may work well since a settling process is involved during which the spent ACB could be removed. Further work is needed to characterize the short-term kinetics of the organic removal at larger scales than that possible in the current study.

Mining operations In this study, we used ST water solution of 45–60 mg C as NA/L and achieved a 90 % reduction in organic C content with ACB in both batch and flow-through assays (Figs. 1 and 2). Assuming that a similar target could be achieved with actual tailings water, Alberta's current $135 \times 10^3 \text{ m}^3 \text{ days}^{-1}$ of oil produced from mining operations would require 50–140 Gg ACB per year (Table 2-F). Its production would require 260 to 680 Gg dry biomass per year (Table 2-G), a range of biomass demand that is considerably lower than that estimated above for treating SAGD water.

In mining operations, the ACB could be added directly to a tailings pond as a form of batch treatment, allowing it to settle, along with the bound organics, to the bottom of the pond. However, this strategy would not likely reduce methane emissions since microbes would still have access to the organics. With a flow-through design, the fine particulates would have to be removed from the produced water before contacting the ACB. While theoretically possible, the existing technologies for removing particulates are carried out after a month or longer in a tailings pond (Alberta Energy 2013) during which time the microbial degradation of organics to methane would have commenced. A third option could involve a batch treatment where the ACB is suspended in the tailings pond (for example, in a mesh) for a period of time to adsorb the organics and then removed for subsequent recycling, landfilling, or combustion as an energy resource.

At this stage, it is difficult to define how and when the ACB technology could be deployed. However, since the batch use of ACB seems to be the only feasible solution for treating produced water from both SAGD and mining operations, subsequent calculations of the GHG and economic implications were restricted to the results from the batch experiments.

While large, the magnitude of total biomass demand (4.5 to 6.0 Tg year⁻¹, Table 2-G) to supply ACB to treat all water from both SAGD and mining operations was estimated to be less than the volume of forest residues generated each year from the $100 \times 10^6 \text{ m}^3$ (about 47 Tg dry biomass) of round wood harvested per year in the provinces of British Columbia, Alberta, and Saskatchewan in Canada (National Forest Database (Canada) 2010).

3.4 GHG implications for batch processing of produced water

Large-scale incorporation of biomass into the recovery and processing of oil sands could decrease the GHG footprint associated with producing each m³ of bitumen. However, the production of ACB from residual biomass is not without an energy and GHG cost that must be subtracted from the overall carbon benefit associated with the use of a biomass product. Roberts et al. (2010) have carried out a detailed life cycle analysis of residual biomass (yard waste) to biochar conversion and estimated that CO₂e emissions were only about 20 kg CO₂e Mg⁻¹ of dry biomass feedstock, and this was mostly associated with the collection of the resource. Since the collection, processing, and transport of forest residue and ACB at the scale envisaged here would require large areas, our optimistic estimate was set at 40 kg CO₂e Mg⁻¹ dry biomass, and for a more conservative estimate, we used 100 kg CO₂e Mg⁻¹ dry biomass (Table 3-A1).

Table 3 Estimation of the costs and benefits in terms of GHG emissions and economics associated with the production of activated biochar (ACB), its batch use to treat produced waters from steam-assisted gravity drainage (SAGD) or mining oil sands operations and its ultimate use as either an energy resource or a carbon sink

Item no.	Units	Oil sands technology					
		SAGD		Mining		Total	
		Conservative	Optimistic	Conservative	Optimistic	Conservative	Optimistic
A. GHG costs and benefits associated with ACB production							
1. GHG emissions: residual biomass to ACB ^a	kg CO ₂ e Mg ⁻¹ dry	-100	-40	-100	-40	-	-
2. CO ₂ e emissions in ACB production ^b	Gg CO ₂ e year ⁻¹	-526	-211	-68.5	-27.4	-595	-238
3. Gross CO ₂ e embedded in ACB ^c	Gg CO ₂ e year ⁻¹	3,280	3,280	427	427	3,707	3,707
4. Net CO ₂ e embedded in ACB ^d	Gg CO ₂ e year ⁻¹	2,754	3,070	358	399	3,112	3,469
5. Net CO ₂ e benefit per t ACB ^e	kg CO ₂ e kg ⁻¹ ACB	2.62	2.92	2.62	2.92	-	-
B. GHG implications of landfilling spent ACB to sequester carbon							
1. Emissions from oxidation of bound organics ^f	Gg CO ₂ e year ⁻¹	-276	0	-276			
2. CO ₂ e benefit of landfilling spent ACB ^g	Gg CO ₂ e year ⁻¹	2,203	2,763	287	359	2,490	3,122
3. Net CO ₂ e benefit of landfilling spent ACB ^h	Gg CO ₂ e year ⁻¹	1,927	2,487	287	359	2,214	2,846
C. GHG implications of using spent ACB as a renewable energy resource							
1. Thermal energy in spent ACB ⁱ	PJ year ⁻¹	35.5	4.5	40.0			
2. Natural gas displacement ^j	PJ year ⁻¹	28.4	3.6	32.0			
3. CO ₂ e reduction from NG displacement ^k	Gg CO ₂ e year ⁻¹	1,402	177	1,579			
4. Net CO ₂ e benefit for spent ACB as energy ^l	Gg CO ₂ e year ⁻¹	600	915	109	150	708	1,065
D. GHG implications of avoiding CH₄ emissions from mine tailings							
1. Organic C removed by ACB ^m	Gg C year ⁻¹	-	7.33	7.33			
2. Avoided CH ₄ emissions ⁿ	Gg CH ₄ year ⁻¹	-	3.28	3.28			
3. Net CO ₂ e benefit of avoided CH ₄ emissions ^o	Gg CO ₂ e year ⁻¹	-	78.7	78.7			
E. Largest GHG emission benefit							
1. Total net CO ₂ e benefit ^p	Gg CO ₂ e year ⁻¹	1,927	2,487	365	438	2,292	2,925

Table 3 (continued)

Item no.	Units	Oil sands technology					
		SAGD		Mining		Total	
		Conservative	Optimistic	Conservative	Optimistic	Conservative	Optimistic
2. ...expressed per m ³ of oil produced ^d	kg CO ₂ e m ⁻³	44.27	57.13	7.41	8.88	-	-
F. Economics associated with GHG benefit							
1. Assumed value of carbon ^r	US\$ Mg ⁻¹ CO ₂ e	\$15	\$40	\$15	\$40	-	-
2. Total GHG value ^s	10 ⁶ \$year ⁻¹	\$28.90	\$99.46	\$5.48	\$17.53	\$34	\$117
3. GHG value per m ³ of oil produced ^t	\$m ⁻³	\$0.66	\$2.29	\$0.13	\$0.40	-	-
G. Economics of ACB production							
1. ACB cost ^u	\$Mg ⁻¹ ACB	-\$600	-\$400	-\$600	-\$400	-	-
2. Total ACB cost ^v	10 ⁶ \$year ⁻¹	-\$632	-\$421	-\$82	-\$55	-\$714	-\$476
3. ACB cost per m ³ of oil produced ^w	\$m ⁻³	-\$14.51	-\$9.67	-\$1.89	-\$1.26	-	-
4. Net ACB cost per m ³ of oil produced ^x	\$m ⁻³	-\$13.84	-\$7.39	-\$1.76	-\$0.86	-	-
5. GHG value as a proportion of ACB cost ^y	%	4.6 %	23.6 %	6.7 %	32.0 %	-	-

^aFrom Roberts et al. (2010) for biomass to biochar [20 kg CO₂e Mg⁻¹ biomass × 2 (optimistic) or × 5 (conservative)] (see text)

^bCalculated as item A1 × Table 2G

^cCalculated as Table 2F × (85 % C in ACB) × 3.667 kg CO₂e kg⁻¹ C × 1,000 g kg⁻¹

^dCalculated as item A3 – item A2

^eCalculated as item A4 – Table 2F

^fAssumes the bound organics or their products of anaerobic digestion (see text) would be combusted to CO₂ and released to the air. While this represents a GHG reduction when compared with current practices in oil sands mining (see item D), in SAGD operations, the current fate of the organic C is less certain so we have calculated it as Table 2C × Table 2D × –3.667 kg CO₂e kg C⁻¹

^gAssumes 80 % (conservative) or 90 % (optimistic) of the C in ACB is retained in storage. Calculated as item A4 × (0.8 or 0.9)

^hCalculated as item B2 + item B1

ⁱ Assumes mass energy density of 30 GJ Mg⁻¹ for ACB (Abdullah and Wu 2009) and 38 GJ Mg⁻¹ for the adsorbed organic C (Pohamish 2004). Calculated as ((Table 2C × Table 2D) × 38 GJ Mg⁻¹ organics ÷ (73 % C in organics) ÷ 166 GJ PJ⁻¹) + Table 2F × 30 GJ Mg⁻¹ ACB)

^j Assumes heat recovery from spent ACB combustion = 80 % of that from natural gas, i.e., (item A1 × 0.8)

^k Calculated as item C2 ÷ 55.7 GJ Mg⁻¹ CH₄ × 2.75 Mg CO₂e Mg⁻¹ CH₄ × 1,000 Gg Tg⁻¹

^l Calculated at item C3 + item A2 + item B1

^m Calculated as Table 2C × Table 2D

ⁿ See text for details. Calculated as item D1 × 67.2 % CH₄ × 50 % released to atmosphere × 0.75 Mg C Mg⁻¹ CH₄

^o Calculated as item D2 × 25 Mg CO₂e Mg⁻¹ CH₄ (Forster et al. 2007)

^p The highest number (GHG benefit) between (item C4 and item B3) plus item D3 (for mine tailing only)

^q Calculated as item E1 / (Table 2A × 365 days/year)

^r Assumes 15 Mg⁻¹ CO₂e (conservative) or 40 Mg⁻¹ CO₂e (optimistic) (Vanderklippe 2013)

^s Calculated as item F1 × item E1 / 1,000

^t Calculated as (item F2 × 1e6) / (Table 2A × 365 days year⁻¹)

^u Assumes 400 Mg⁻¹ ACB (optimistic) or 600 Mg⁻¹ ACB (conservative)

^v Calculated as item G1 × Table 2F

^w Calculated as item G2 × 1e6 / (Table 2A × 365 days year⁻¹)

^x Calculated as item G3 + item F3

^y Calculated as item F3 / item G3

The slow pyrolysis of biomass to biochar is an exothermic reaction whereby approximately 29 % of the biomass energy is available for other processes (Roberts et al. 2010). We have assumed that this energy is sufficient to activate the biochar.

Given these assumptions, the emissions associated with collecting the biomass, converting it to ACB and transporting it to the oil sands operations were estimated to range from -238 (optimistic) to -595 (conservative) Gg CO₂e year⁻¹ (Table 3-A2). To balance these emissions, the carbon content of the ACB produced was estimated to be 3,707 Gg CO₂e year⁻¹ (Table 3-A3), resulting in a net GHG benefit embedded as carbon in the ACB of 3,112 (conservative) to 3,469 (optimistic) Gg CO₂e year⁻¹ (Table 3-A4). Expressed per kilogram ACB, the produced ACB was estimated to have a GHG carbon abatement value of 2.6 (conservative) to 2.9 (optimistic) kg CO₂e (Table 3-A5). While these values for kilogram CO₂e benefit per kilogram ACB were lower than those previously reported for biochar (Gaunt and Lehmann 2008; Roberts et al. 2010), such a result was expected for an ACB given its lower conversion efficiency and the transport distances envisaged in this study.

The net GHG value of the ACB will depend on how it is used for water treatment and its ultimate destination as either an energy resource or a carbon sink. Three alternatives were considered:

1. *Spent ACB landfilled to sequester carbon:* The spent ACB could be landfilled to lock up the carbon and prevent it from returning to the atmosphere. We assumed that the bound organics on the biochar would either be removed before storage (using low level, waste heat from the industrial process), or the ACB would be stored in such a way as to ensure the complete oxidation of the bound organics to CO₂, thereby preventing any release of CH₄ to the atmosphere. For example, the landfill gases generated by anaerobic digestion of the organics could be collected and combusted, releasing only CO₂ to the atmosphere. In the case of current SAGD operations, this carbon would probably have been re-injected into the reservoir (with the steam or as a component in the boiler blow-down), so this CO₂ emission was calculated as an additional GHG emission (Table 3-B1). In the case of current mining operations, the organic C in tailings water ultimately ends up in the atmosphere and its GHG implications are considered below.

Unlike the bound organic C, the C in the biochar itself should be highly resistant to microbial degradation. Previous studies with biochar have calculated that 80 % (conservative (Roberts et al. 2010)) to 90 % (optimistic (Lehmann et al. 2006)) of the C would be retained for hundreds, if not thousands, of years (Table 3-B2). Consequently, the net GHG benefit was estimated to range from 2,214 to 2,846 Gg CO₂e year⁻¹ (Table 3-B3).

2. *Spent ACB used as an energy resource:* Oil sands recovery and processing technologies use a large amount of natural gas to generate the hot water (mining operations) or steam (SAGD operations) needed to separate the bitumen from the sand. The spent ACB and bound organics could be used as a source of energy to displace the use of natural gas and realize a system-level reduction in GHG emissions. To calculate the thermal energy value of the spent ACB, we assumed a mass energy density of 30 GJ Mg⁻¹ for the ACB (Abdullah and Wu 2009) and 38 GJ Mg⁻¹ for the bound organics (Pohanish 2004). Given the water volume being treated for organic carbon removal (Table 2-C, D), we calculated that the complete oxidation of the spent ACB could generate 40 PJ year⁻¹ (Table 3-C1).

To calculate the natural gas that could be displaced through combustion of the spent ACB, we assumed that heat recovery from spent biochar production would be 80 % of that from

natural gas (Table 3-C2). These values were used to calculate the CO₂e emissions from natural gas combustion that would be displaced as a result of the combustion of the spent ACB (Table 3-C3). Finally, the emissions associated with the production of the ACB were subtracted (Table 3-A2) along with those associated with combustion of the organics removed from the SAGD operations (Table 3-B1) to give a net GHG benefit that ranged from 708 to 1,065 Gg CO₂e year⁻¹ (Table 3-C4).

3. *Reducing emissions from mine tailings:* As noted previously, one driver for removing organics from tailings ponds may be to remove the organic substrates that lead to the atmospheric release of CH₄, a potent GHG. Unfortunately, there are no published reports of long-term CH₄ emission measurements from oil sands tailings ponds, and the studies that have been done (Fedorak et al. 2003; Holowenko et al. 2000; Siddique et al. 2008; Clearstone Engineering Ltd 2007) estimate rates that vary over 100-fold, from 60 to 8,000 cm³ m⁻³ water day⁻¹ (Siddique et al. 2008).

To calculate the total emissions likely to arise from anaerobic metabolism of the NA in the tailings water, we assumed that a methanogenic consortia of microbes generated CH₄ according to the following reaction (Heider et al. 1999):



in which values for *A* and *B* were set to be typical of NAs having carbon numbers (*A*) ranging from 7 to 22 (Grewer et al. 2010), and then, *X*, *Y*, and *Z* were calculated as $A - B/4 - 1$, $A/2 - B/8 + 0.5$, and $B/8 + A/2 - 0.5$, respectively.

When this equation was applied to more than 50 putative NA structures, the proportion of NA carbon ending up in CH₄ (i.e., $Z/(Y+Z)$) was estimated to be 67.2 ± 0.3 %. Given a target removal of 90 % of the organics in the tailings water, the use of ACB could remove 7.3 Gg C year⁻¹ of substrate for microbial metabolism (Table 3-D1). This would avoid 4.9 Gg C year⁻¹ of CH₄ emissions, but approximately 50 % of this (Bastviken et al. 2008; Saidi-Mehrabad et al. 2013) was likely to be oxidized to CO₂ by other microbes on its migration to the atmosphere, thereby reducing the estimate of avoided GHG emissions to 3.3 Gg CH₄ year⁻¹ (Table 3-D2). To calculate the net GHG benefit, the CH₄ emissions were multiplied by a global warming potential for CH₄ (24 kg CO₂e kg⁻¹ CH₄) to derive an estimate of 79 Gg CO₂e year⁻¹ (Table 3-D3). The value for global warming potential was reduced to 24 from 25 kg CO₂e kg⁻¹ CH₄ described previously since the end product (CO₂) was assumed to be released to the atmosphere.

Given the calculations presented in Table 3 (A to D), the use of the spent ACB as a carbon sink (Table 3-B3) should provide almost three times more GHG benefit than using it as an alternative source of energy (Table 3-C4). This fate for the spent ACB should also be less expensive than using it as an energy resource, especially considering the capital and operating costs of the latter option and the recent trend in North America towards a low price for natural gas. In the case of SAGD water treatment technologies, a net GHG benefit was predicted to be between 1,927 (conservative) and 2,487 (optimistic) Gg CO₂e year⁻¹ (Table 3-E1). Such values are equivalent to about 4–7 % of the upstream GHG emissions associated with SAGD operations in Alberta, Canada (Charpentier et al. 2009).

For the mining operations, the GHG benefit that was estimated to arise from the removal of the organic carbon from the tailings pond water (Table 3-D3) was added to the GHG benefit associated with sequestration (Table 3-B3), to give a net GHG benefit of between 365 (conservative) to 438 (optimistic) Gg CO₂e year⁻¹ (Table 3-E1). Therefore, even with this

additional GHG benefit associated with mining operations, the annual GHG benefit was estimated to be manifold higher in the SAGD operations than in the mining operations. This was not surprising since the ACB demand was calculated to be 8.7- to 18-fold higher per m^3 of bitumen produced in SAGD than in mining operations (Table 2-F, A).

When expressed per m^3 bitumen produced, the GHG emissions benefit was estimated to be 7.4 to 8.9 $\text{kg CO}_2\text{e m}^{-3}$ for bitumen produced in mining operations and 44 to 57 $\text{kg CO}_2\text{e m}^{-3}$ for bitumen produced through SAGD (Table 3-E2). Assuming the ACB technologies were to be implemented in both SAGD and mining operations, the largest GHG benefit is calculated to range from 2.3 to 2.9 $\text{Tg CO}_2\text{e/year}$ (Table 3-E1). These values are equivalent to about 10 % of the GHG emissions expected from the recovery of oil sands product at the rates identified in Table 2 (28 $\text{Tg CO}_2\text{e/year}$; Bergerson et al. 2012). Additional GHG emissions are associated with the upgrading of the bitumen and its transportation, refining, and combustion of the refined petroleum products as a transportation fuel. Therefore, the maximum GHG benefit calculated here is <3 % of the “well to tank” GHG emissions and <1 % of the “well to wheels” GHG emissions associated with oil sands product.

3.5 The economics of using ACB in batch treatment of oil sands water treatment

There should be economic benefits associated with reducing the environmental footprint of oil sands operations. In Alberta, Canada, large final GHG emitters (including the oil sands companies) are required to demonstrate a 12 % reduction in GHG emissions per unit of production. If they fail to meet this target, they pay a tax of approximately $15\text{\$Mg}^{-1}\text{ CO}_2\text{e}$ into a technology fund (Alberta Energy 2013). This price was used for the conservative assessment. Discussions are ongoing to increase this “tax” to as much as $40\text{\$Mg}^{-1}\text{ CO}_2\text{e}$ on 40 % of emissions (Vanderklippe 2013), so a 40\$ value was used for the optimistic assessment (Table 3-F1).

Drawing on estimates for the total net GHG benefits (Table 3-E1), we calculated total annual GHG benefits as 34×10^6 to 117×10^6 \$ (Table 3-F2). When expressed per m^3 of oil, these GHG benefits could be worth as little as $0.13\text{\$m}^{-3}$ bitumen (conservative, mining operations) or as much as $2.29\text{\$m}^{-3}$ bitumen (optimistic, SAGD operations) (Table 3-F3).

The cost of ACB production and transport was conservatively set at $600\text{\$Mg}^{-1}$ ACB and optimistically set at $400\text{\$Mg}^{-1}$ ACB (Table 3-G1). The annual cost of providing the ACB was estimated to range from $476 \times 10^6\text{\$year}^{-1}$ (optimistic) to $714 \times 10^6\text{\$year}^{-1}$ (conservative) (Table 3-G2). When expressed per m^3 bitumen, the cost of the ACB ranged from 1.26\$ to 1.89 $\text{\$m}^{-3}$ for water from mine tailings to 9.67\$ to 14.51 $\text{\$m}^{-3}$ for water from the SAGD operations (Table 3-G3). When these costs were taken into account in the GHG benefits (Table 3-F3), the net cost dropped to 0.86\$ to 1.76 $\text{\$m}^{-3}$ bitumen for water from mine tailings to 7.39\$ to 13.84 $\text{\$m}^{-3}$ bitumen for water from the SAGD operations (Table 3-G4). These values include only the cost of the ACB and do not consider the capital and operational cost of implementing the treatments. The additional water treatment costs could be equal to or greater than the ACB costs presented here.

Recent prices for bitumen from Canada's oil sands have been over $500\text{\$m}^{-3}$ bitumen (approx. 80\$/“barrel”), a discount compared to world prices for oil in 2013. SAGD water treatment prices as high as 13.84 $\text{\$m}^{-3}$ bitumen may be too high for deployment to be feasible. It may be possible to further reduce the cost for water treatment by developing a more effective ACB or by recycling the ACB.

A lower price for treating tailings water from mining operations (up to 1.76 $\text{\$m}^{-3}$ bitumen) holds more promise as a viable technology, especially when one considers the potential environmental benefits and the poor public image associated with these ponds. While the

ACB demand to treat the $148 \times 10^6 \text{ m}^3$ of produced water per year was estimated to be 5 to 11 % of that needed to treat the SAGD water, it is important to note that an additional $925 \times 10^6 \text{ m}^3$ of legacy tailings ponds exist from past oil sands operations (Cryderman 2013), and there are pressures to reclaim this water and land (ERCB 2012). Use of ACB to remove the organics may not only have GHG benefits but may also be an important step to allow for the large-scale desalination of the tailings water so the water can be released back to the natural environment.

While the analysis presented here was focused on treatment of produced water from oil sands operations, the concept of creating and using the adsorbent properties of activated biochars should be applicable to other large-scale, practical applications involving oil and gas operations (e.g., flow-back water from hydraulic fracturing), municipalities, agricultural, food, or pharmaceutical industries. Activated biochars could also be created to remove volatile organic compounds from gas streams, including those associated with the energy sector (e.g., fugitive emissions from pipelines or shale gas production). As in the present analysis, the resulting spent ACBs should have value as either a renewable energy resource or as a carbon sink.

4 Conclusion

This study supports the proposal that the production and use of activated biochar have the potential to simultaneously mitigate GHG emissions and remediate water contamination associated with industrial scale activities. In regions of the world where little economic value is placed on mitigating GHG emissions, the water treatment benefits could improve the economic viability of biochar production and use. By strategically creating such value chains, it may be possible to not only reduce the environmental footprint associated with human activities but also create a new industry that adds value to residual biomass, a by-product of forestry and agricultural operations that can have additional adverse environmental impacts. Ideally, the activated biochar would be produced from locally grown biomass (Iranmanesh et al. (2014), using technologies that enhance yield to reduce costs (Veksha et al. 2014a, b).

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