Fate of degraded pollutants in waste gas biofiltration: An overview of carbon end-points.

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Abstract

The fate of the carbon from degraded pollutants in biofiltration is not well understood. The issue of missing carbon needs to be addressed quantitatively to better understand and model biofilter performance. Elucidating the various carbon end-points in various phases should contribute to the fundamental understanding of the degradation kinetics and metabolic pathways as a function of various environmental parameters. This article reviews the implications of key environmental parameters on the carbon end-points. Various studies are evaluated reporting carbon recovery over a multitude of parameters and operational conditions with respect to the analytical measurements and reported distribution of the carbon end-points.

Keywords: Biofiltration, Carbon balance, Volatile organic carbon (VOC), Biofilms

1 Introduction

Biofiltration provides a clean, cost effective, and environmentally friendly technology using mass transfer and microbial oxidation to degrade organic pollutants (Devinny et al., 1999; Kennes, 2012). The biofiltration process is used effectively for treating large streams of air contaminated with low concentrations (<1000 ppm) of pollutants (Iranpour et al., 2005). Biofilters are packed bed bioreactors degrading pollutants through a complex and mixed culture of microorganisms forming a pollutant-degrading biofilm on the porous bed medium. It has been successfully applied to treat a wide spectrum of organic and inorganic pollutants as well as a means to abate odours (Gallastegui et al., 2011; Girard et al., 2011; Mudliar et al., 2010; Ryu et al., 2009).

Biofilms are often growth restricted (e.g. - nutrient limited, etc.) especially in soil and various industrial processes such as biofiltration but possess the inherent ability to break down organic pollutants (Jorio et al., 2000a; Li et al., 2002; Xi et al., 2006). Biofilms proliferating in these dynamic environmental conditions are commonly unsaturated, operating at the air/solid interface. Many attempts have been made to close the carbon balance in these systems; however 10-50% of the degraded carbon often remains untracked (Avalos Ramirez et al., 2008; Cox et al., 2001; Deshusses, 1997b; Girard et al., 2011; Morales, 1998; Song and Kinney, 2000). In spite of the importance of these growth restricted, unsaturated biofilm processes in engineered systems, certain aspects of their activity/metabolism remain unclear, particularly the ultimate fate of carbon entering these systems.

Commonly assumed carbon end-points for organic carbon substrates are CO_2, active biomass and extracellular polymeric substances (EPS) .Other plausible carbon end-points include soluble microbial products (Jiang et al., 2010; Meng et al., 2009; Ni and Yu, 2011), soluble metabolites (Díaz et al., 2008), internal storage polymers (Reis et al., 2003) and volatile substances such as carbon monoxide (Haarstad et al., 2006). A common assumption is that the untracked carbon is utilised for microbial growth (biomass) but carbon extraction studies have not corroborated this hypothesis (Fürer and Deshusses, 2000; Song and Kinney, 2000; Vance et al., 1987). Accumulation of missing carbon within the system as biomass could clog up the reactor bed which is contrary to reports in non-growth systems (Deshusses, 1997b; Singh et al., 2006). Whilst microbes undoubtedly convert a portion of the organic substrates into soluble microbial products and other metabolites, their identities and relation to biodegradation of substrates remain to be fully investigated (Díaz et al., 2008; Kim et al., 2005b; Magbanua and Bowers, 2006). In the gaseous effluents, no other compounds other than CO_2 and untreated substrates are normally reported. There are limited reports of carbon monoxide reported in the off gas of some biodegradation processes (Haarstad et al., 2006; Hellebrand and Schade, 2008), and the possibilities of other unreported biogenic emissions cannot be ruled out. Thus, the carbon balance in these systems is yet to be closed conclusively and the identity of the unaccounted carbon remains elusive. This review presents a compilation of the various investigations tracking carbon and presents a link to the critical environmental parameters influencing the conversion to different degradation end-points.

2 Carbon balance and fate of pollutants

The biofilms in oxidative microbial processes in the waste gas treatment industry degrade waste organic compounds (C_xH_y) to CO_2, biomass and other metabolites (Deshusses, 1997a). The particular biochemical reaction catalyzed by the microorganisms proceeds via different pathways depending on the pollutant and nutrient availability. Under nutrient-limited conditions, a typical oxidation reaction for a hydrocarbon leads to the production of CO_2, water and heat which can be represented as follows:

$$C_xH_y + bO_2 \rightarrow x\,CO_2 + c\,H_2O + \text{Heat} \quad (1)$$

However, in the presence of sufficient nutrients, pollutant oxidation results in the formation of biomass along with other degradation products (Delhomenie et al., 2005) :

$$aC_xH_y + bO_2 + cNH_3 \rightarrow CH_{1.8}N_{0.2}O_{0.5} + dH_2O + \text{Heat} + eCO_2 \quad (2)$$

Where, $CH_{1.8}N_{0.2}O_{0.5}$ represents a generic formula for biomass.

CO_2 production is often a good indicator of the biological activity of the microbes, and it complements the tracking of pollutant degradation for the evaluation of a biofilter's performance efficacy (Bester et al., 2011; García-Peña et al., 2008). So it is common practice to monitor CO_2 production but limited success has been achieved in exhaustively pinning down the carbon flux through the system to its final end-points in different phases. Usually CO_2 measurement is for optimizing operating parameters to improve stability and process efficacy. Attempts to close the carbon balance is uneven, with 10 - 50 % of the degraded carbon missing

(Avalos Ramirez et al., 2008; Cox et al., 2001; Deshusses, 1997b; Girard et al., 2011; Morales, 1998; Song and Kinney, 2000).

A major portion of the degraded organic carbon is released as CO_2 (Jiménez et al., 2016; Jorio et al., 2000a; Li et al., 2002; Wang et al., 2012; Xi et al., 2006). From the CO_2 measurements, the remaining carbon fraction is often assumed to be biomass and is estimated based on the difference between the degraded pollutant and the CO_2 produced. This is because biomass measurements in operating biofilters are difficult. Researchers have estimated the carbon tied up in biomass directly through whole bed measurements combined with assumptions about the water content of wet biomass, representative sampling of the bed combined with the carbon content of cells, yield on nitrogen and chemical oxygen demand (COD)/carbon conversion etc. (Bester et al., 2011; Cox and Deshusses, 1999; Elmrini et al., 2004; Kroukamp and Wolfaardt, 2009). Therefore, the estimate of the carbon content of the biomass involves experimental uncertainties and assumptions, and the carbon mass balance closure in these highly complex systems remains difficult. Hence, there is a pressing need to track the unaccounted carbon in these biofilm processes through a holistic approach.

Most biofilter research performs a molecular balance on the pollutant (e.g. toluene, methane) and explicitly focusses on the *Consumption* term (e.g. elimination capacity) as a function of a variety of system inputs. As there is rarely any generation term for the pollutant, the mass balance for the pollutant simplifies to:

$$Consumption = Input - Output \quad (3)$$

Measuring the CO_2 allows an estimate of the accumulation of carbon in a biofilter by comparing the molar rate of CO_2 production to the molar rate of carbon degraded for the pollutant (i.e. – a carbon balance). This assumes no carbon is leaving the biofilter in the liquid phase or in the gas phase in a compound other than the pollutant or CO_2.

$$Carbon\ accumulation = x[a(C)_{in} - b(C)_{out}] - xc(CO_2) \quad (4)$$

$a(C)_{in}$ = molar flow rate of the pollutant entering the biofilter

$b(C)_{out}$ = molar flow rate of the pollutant exiting the biofilter

$c(CO_2)$ = molar flow rate of CO_2 exiting the reactor (corrected for any CO_2 present in the feed stream).

x = the number of carbon atoms in the molecular structure of the pollutant (1 in the case of CO_2)

It is this type of balance that is often used for estimates of biomass accumulation as compared to direct measurements. Tracking the carbon fraction in all three phases should account for the carbon end-points in the system encompassing the degradation products as a whole. An illustration of how the carbon entering the system exits or accumulates within the system in the solid, gas and liquid phase is presented in Fig. 1.

Figure 1: Flow chart identifying plausible carbon end-points in the system after toluene degradation.

2.1 Gas phase end-points

In the biofiltration process, the exiting gas stream is often analysed for CO_2 and un-reacted pollutants. The commonly used methods to analyse effluent gas streams includes gas chromatography with various detectors (TCD, FID) and CO_2 analysers. A few studies have attempted to analyse gas phase components by mass spectrometry but have seldom reported anything other than CO_2 and un-degraded organic pollutants (Domeño et al., 2010; Kastner and Das, 2005; Matteau and Ramsay, 1997; Møller et al., 1996).

CO_2 recoveries from various studies have ranged from 40-90% as a function of the mode of operation (nutrient-limited or nutrient-addition) and variable operational parameters (Deshusses, 1997b; Grove et al., 2009; Jorio et al., 2005; Wang et al., 2012). Cox et al. (2001) reported higher mineralization of ethanol to CO_2 at thermophilic conditions (60%) than for a mesophilic biofilter (46%). Carbon recovery as CO_2 was 58% for the biofiltration of binary mixtures of BTEX compounds compared to degradation of single BTEX compounds which ranged from 31-53% (García-Peña et al., 2008). Competitive inhibition for these closely related molecules could potentially impact the catabolic/anabolic pathways. Hence, the CO_2 production pattern is an important component in defining the product ratios of degraded carbon end-points. However, the possibility of other unreported biogenic emissions in these systems cannot be ruled out.

The effluent gas stream could possibly contain C-containing intermediates and dissolved. Carbon monoxide formation during solid organic waste degradation has been reported (Haarstad et al., 2006; Hellebrand and Schade, 2008). Normal mass spectrometry in biofiltration would easily miss this compound due to the similar molecular weight as N_2.

2.2 Solid Phase end-points

In biofiltration, the pollutants enter the biofilm and are utilized by the acclimatized microbial community as a carbon and/or energy source (Cabrol et al., 2012). The carbon substrate, apart from being mineralized to CO_2 and water for energy production, is partially diverted towards microbial growth and some non-growth associated products (Leson and Winer, 1991). These constituents form the solid phase accumulation in the system.

Studies delving into a carbon balance often assume the unaccounted carbon from the system is incorporated into the biomass or associated polymers and polysaccharides without robust quantification. But if the missing carbon reservoir were solely biomass or polysaccharides, this would cause clogging of the reactor beds which is not typically reported in growth-limited systems (Deshusses, 1997b; Singh et al., 2006). In nutrient-limited conditions, maintenance metabolism assumes significance, which means no net increase in active biomass (Cherry and Thompson, 1997). In actively growing systems with nutrient addition, bioreactor clogging is common and has been extensively covered in the literature (Delhoménie et al., 2003; Dorado et al., 2012; Maestre et al., 2007; Weber and Hartmans, 1996; Xi et al., 2006; Yang et al., 2010). However, limited clogging is occasionally reported indicating possible biological equilibrium between primary and secondary degraders (Diks et al., 1994). Although, surprisingly little quantitative knowledge exists on the composition of the biofilm components proliferating in these bioreactor systems.

Biomass yield forms an important parameter in model development which can be quantified from carbon recovery estimates (Bordel et al., 2008; Grove et al., 2009). Various studies which assumed the fraction of degraded pollutant not appearing as CO_2 was going to biomass reported biomass yields in the range of 0.17 – 0.43 g biomass per g pollutant (Deshusses, 1997b; Grove et al., 2009; Jorio et al., 2000b; Singh et al., 2006). However, there is no exhaustive quantification and characterization of these carbon end-points.

When a reactor is running on maintenance requirements under nutrient-limited conditions, a complete conversion of substrate into CO_2 is expected (Weber and Hartmans, 1996). However, the CO_2 fraction is invariably less than the theoretical estimate and carbon may be assimilated by the biomass in some form. Bacteria produce extracellular polymeric substances (EPS) which make up a major fraction of biofilms and play a very important part in biofilm structure, activity and performance (Sutherland, 2001). The major EPS components are comprised of polysaccharides and proteins in varying fractions but also include nucleic acids and lipids (Flemming and Wingender, 2010). EPS are secreted by the cells to enhance adhesion to substrates, contribute to the biofilm structure and influence microbial activity.

Biofilms as dynamic systems respond to environmental conditions physiologically which leads to variations in EPS composition (Schmitt et al., 1995). The origins and composition of EPS are very complex. Therefore a number of factors may affect the EPS composition and quantity, such as the type of limiting substrate (electron donor and acceptor), nitrogen and phosphorous limitation, and desiccation (Nielsen et al., 1997). The C/N ratio of the influent also influences the composition of EPS in terms of carbohydrates and proteins (Durmaz and Sanin, 2003). Thus EPS has been related to the macro-scale characteristics of biofilms describing its microbial and structural properties (Ras et al., 2011) and its production is also linked to microbial growth and substrate utilization (Laspidou and Rittmann, 2002). Moreover EPS can be degraded by bacteria as a source of carbon and energy under substrate-limited conditions (Kommedal et al., 2001). However, carbon extraction studies of microbial biomass in these systems are limited but seldom show significant carbon accumulation in the biofilms (Fürer and Deshusses, 2000; Song and Kinney, 2000; Vance et al., 1987). In addition, microbes also accumulates internal storage polymers as cellular reserves often driven by environmental conditions (Poblete-Castro et al., 2012; Reis et al., 2003; Xavier and Foster, 2007). Nutrient-limited systems rarely plug up which begs the question of other possible carbon sinks for biofilms in stationary phase degrading pollutants.

2.3 Liquid phase end-points

In addition to making active biomass and EPS, bacteria also convert a fraction of the organic substrate into soluble microbial products (SMPs) (de Silva and Rittmann, 2000; Namkung and Rittmann, 1986). SMPs are defined as soluble organic matter resulting from intermediates or end-products of substrate degradation and endogenous cell decomposition (Barker and Stuckey, 1999; Boero et al., 1991; Magbanua and Bowers, 2006). They have a wide molecular weight distribution, structure and function (Barker and Stuckey, 1999; Magbanua and Bowers, 2006; Rosenberger et al., 2006). A fractionation study by Jiang et al. (2010) studying SMPs in an activated sludge membrane system found proteins and carbohydrates as the major components of SMPs. These SMPs are important because they are ubiquitously present and contribute to the soluble organic matter in biological treatment system effluent (de Silva and Rittmann, 2000; Rosenberger et al., 2006).

178 The majority of SMP research has been done with pure cultures or wastewater treatment systems. A few waste
179 gas biofiltration studies which attempted closing the carbon balance have also reported inorganic and organic
180 carbon in the effluent liquid of the reactor, albeit at a variable percentage (3-39 %) depending on the mode of
181 operation (growth and nutrient limited) (Bester et al., 2011; Cox et al., 1998; Girard et al., 2011; Kim et al.,
182 2005b). However, their identities and the relationship between substrate biodegradation and SMPs are yet to be
183 determined conclusively in biofiltration. The accumulation of metabolic intermediates during volatile organic
184 carbon (VOC) treatment can inflict a detrimental effect on the process culture and in some cases results in a
185 more toxic form then the parent VOC being treated (Bordel et al., 2007). Duetz et al. (1994) described the
186 toluene-catabolic (TOL) pathway for toluene in strains with the pWWO plasmids that results in toluene being
187 first methyl-oxidized into benzyl alcohol which then leads to benzaldehyde, benzoic acid and catechol, these are
188 then further cleaved at the meta-position. These metabolites have the potential to effect performance efficacy as
189 they can be toxic to microbial communities (Ren and Frymier, 2002). Previously benzyl alcohol has been
190 reported of having mutagenic effects on *Pseudomonas putida* 54G resulting in loss of toluene degradation
191 capacity (Mirpuri et al., 1997).

192 Furthermore, oxygen limitation within the biofilm can shift metabolism, leading to products other than CO_2
193 (Kim et al., 2005b; Wilshusen et al., 2004; Yang et al., 2002). Oxygen limitations in overloaded biofilms can
194 lead to partially oxidized by-products such as carboxylic acids (Devinny and Hodge, 1995). Metabolic by-
195 products during anaerobic degradation of toluene have also been demonstrated but further studies are warranted
196 in aerobic biofilters in identifying transient intermediates (Beller et al., 1992). CO_2 can also be retained in the
197 liquid phase as carbonate (Gallastegui et al., 2011; Morales, 1998; Singh et al., 2006). However, the identities of
198 the carbon fractions in the liquid phase of the reactor are yet to be ascertained quantitatively in a controlled
199 situation, and therefore could be a significant sink for the degraded carbon in engineered systems.

200 Thus, it is evident from the literature thus far, for carbon balances conducted on biofilters, a variable percentage
201 of carbon remains unaccounted for in the system. Usually the emphasis has been largely on process optimization
202 and this fundamental question has met with limited success in the sporadic attempts made in the literature. Table
203 1 presents a compilation of the literature encompassing biofiltration of various VOCs, where the carbon mass
204 balance has received attention.

205

206 **Table 1**: Compilation of the literature encompassing carbon mass balance studies in biofiltration of various pollutants.

207

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
1.	Methyl ethyl ketone (MEK)	Biofilter: Non-growth	Compost + redwood chips + horse manure	Indigenous		C-CO_2: 82 ± 10 %	Gas Phase: GC FID, CO_2: Chemosorb column with TCD.	(Deshusses, 1997b)
2.	Toluene	Biotrickling: Growth	Pall rings	*P.corrugata , T. pyriformis , Vorticella microstoma, Klebsiella pneumoniae*		C- CO_2: 68 %, Biomass: 21 % Liquid: 6 %	Gas Phase: GC FID & TCD, Biomass: Weighing of wet packing + elemental balance, Liquid: TOC	(Cox and Deshusses, 1999)
3.	Toluene	Biofilter: Growth	Peat enriched with nutrients	*Acinetobacter lwoffi, Pseudomonas fluorescens, Pseudomonas putida, and Cla vibacter michigenense*	Toluene loads, ammonia addition	C-CO_2: 44.5 %, Carbonates: 14.3 %, Polymers: 32 %, Biomass: 9.2 %	Gas Phase: GC TCD, Biodegradable fractions were analysed through a digestion protocol.	(Morales, 1998)
4.	Toluene	Biofilter: Non-growth	Compost + bark and lava rocks	Inoculated with recycled liquid from a toluene degrading biotrickling filter		C- CO_2: 70 %	C^{14} toluene: scintillation, Gas Phase: GC FID &TCD, infrared CO_2 analyser	(Fürer and Deshusses, 2000)
5.	Toluene	Vapour phase Bioreactor (VPB): Growth	Porous silicate pellets	Heterotrophic microbial population adapted to toluene	Air flow: Unidirectional (UD), Directionally switching (DS)	C- CO_2: 63-66 %, Biomass: 34-37 % Liquid : >1 %	Gas Phase: GC-FID and CO_2 analyser. Biofilm analysis: COD	(Song and Kinney, 2000)
6.	Toluene, Benzene	Biofilter: Non-growth	Cylindrical activated carbon (CAC)	Heterotrophic population: bacilli, spore bacilli, fungi	Inlet load (IL) and gas flow rate	Toluene - CO_2: 64 % Benzene- CO_2: 51 % Assumption: Biomass and solute	Gas Phase: GC FID & HPLC, CO_2 analyser and bacterial counts	(Li et al., 2002)

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
7.	Ethanol	Biofilter: Growth	Polypropylene pall rings	Mixed microbial consortia from active green waste and food compost.	Temperature	C-CO_2: 60 % C-biomass: 14 % Unaccounted: 26 %	Gas Phase: GC FID & TCD, Biomass: dry weight, TOC	(Cox et al., 2001)
8.	Toluene and acetone	Trickle bed air biofilter (TBAB): Growth	Coal particles	Activated sludge	Inlet load (IL) and Gas flow rate	C- CO_2: 90 % Biomass: 10 %	Gas Phase: GC/FID, THC, and CO_2 analyzer Biomass: SCOD	(Chang and Lu, 2003)
9.	Ethanol	Biofilter: Growth	Sugarcane bagasse	*Candida utilis*	Inlet load (IL) and Gas flow	C- CO_2 : 16-76.3 % C-biomass: 2.8-5.7 % Acetaldehyde:1-7.8 % Ethyl acetate: 14-20 %	CO_2 : GC with TCD Cell # for biomass calculation	(Christen et al., 2002)
10.	Xylene	Biofilter: Growth	Spherical peat	Microbial activated consortium	Inlet load (IL) and Gas flow	C-CO_2: 82% Unaccounted: Assumed as biomass and solute	Gas Phase: THA and CO_2 analyser	(Elmrini et al., 2004)
11.	Styrene	Biofilter: Growth	Peat and Ceramic	*Pseudomonas sp.* SR-5	Inlet load (IL) and Gas flow	CO_2 and other degradation products: 90.4 % Biomass: 9.2 %	Gas Phase: GC/MS and FID, Biomass: Viable cell count and elemental analysis of carbon content	(Jang et al., 2004)
12.	Toluene	TBAB: Growth	Inorganic	Aerobic microbial culture sourced from activated sludge	Non-use /backwashing	C-CO_2: 63.2 % C-Liquid :15.5 % Unaccounted: 20.9 %	Gas Phase: GC FID and TOC	(Kim et al., 2005a)

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
13.	Toluene, styrene, methyl ethyl ketone and methyl isobutyl ketone	TBAB: Growth.	Pelletized diatomaceous Earth	Indigenous	Interchanging VOC's	C_CO_2: 63 % C-Liquid: 20 % Unaccounted: 15 %	Gas Phase: GC FID and TCD. Liquid: TOC	(Kim et al., 2005b)
14.	Toluene	Biofilter: Growth	Wood chips + propylene spheres	Activated sludge	Inlet load (IL) and Gas flow	CO_2: 83% approx. Explicit balance not attempted	Gas Phase: GC FID and TCD, Leachate: TOC	(Xi et al., 2006)
15.	Octane	Biofilter: Growth	Compost and perlite 50/50(v/v)	Mixed consortia adapted to Octane	Inlet concentration plus a shutdown period	CO_2 recovery: 25 % Remaining carbon assumed as biomass.	Gas Phase: GC FID and CO_2 analyzer	(Grove et al., 2009)
16.	Methane	Biotrickling: Growth	Inorganic packing	NA*	CH_4 and nitrate	CO_2 recovery: 82 % Biomass: 15 %	Gas Phase: THC and CO_2 analyzer Lixiviate: Ion chromatograph, UV detector, TOC	(Girard et al., 2011)
17.	Toluene and p-xylene	Biofilter	Inert material	NA*	Inlet load (IL)	p-xylene - CO_2: 89 % Toluene - CO_2: 91 % Accumulation based on conversion of an empirical biomass formula to carbon accumulation rate: 5-8 %	Gas Phase: GC FID and total hydrocarbon analyzer CO_2: NDIR CO_2 analyzer, Leachate: TOC analyzer	(Gallastegui et al., 2011)
18.	Toluene	Biotrickling: Growth	Granular activated carbon (GAC)	Activated sludge	Concentration, gas flow rate and temperature (55 ° C and ambient)	C in CO_2: 69 % C in biomass: 30.5 %	Gas Phase: GC FID and CO_2 analyzer. Leachate: TOC analyzer Fluorescence spectroscopy	(Wang et al., 2012)

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
19.	Formaldehyde	Biotrickling: Growth	Perlite	Leachate from previously degrading formaldehyde biofilter	Inlet load (IL) and ozone addition	CO_2: 27 % Leachate: 2.7 % Biomass: 2.2 %	Gas Phase: GC FID Liquid: TOC analyzer and GC/MS/SPME Solid: TOC analyzer	Maldonado-Diaz and Arriaga, 2015)
20.	Toluene	Biotrickling: Growth	Perlite	Activated sludge	Inlet load (IL)	CO_2 : 76.3 % Leachate: 1 % Biomass: 8.9 %	Gas Phase: GC FID & TC Liquid: TOC anlyzer Solid: Volatile solids combustion method (550°C)	(Jiménez et al., 2016)
21.	Cumene	Biotrickling: Growth	Loofa sponge	Indigenous soil microbes from petroleum site	Inlet load (IL)	CO_2 : 0.12 % Leachate: 70 % Biomass: 12.9 %	Gas Phase: GC FID Liquid: TOC analyzer and GC-MS Solid: TOC analyzer	(Shahi et al., 2016)
22.	Methane	Biotrickling: Growth	Inert packing	Activated sludge	Pseudo steady state, transient state (shock loads), and starvation conditions.	CO_2 : 66-88 %	Gas Phase: Hydrocarbon analyzer and CO_2 analyzer.	(Ferdowsi et al., 2016)
23.	Tricholorethylene (TCE) and Methanol	Biotrickling: Growth	Diatomaceous earth pellets	Fungi	Biofilter I- (70% methanol to 30% TCE) Biofilter II- (80% methanol to 20% TCE)	Carbon recovery: Biofilters I - 88.45% ± 4.63% Biofilters II 86.5% ± 4.35%	Gas Phase: GC FID and TC Liquid: TOC anlyzer Solid: Volatile solids combustion (Standard Methods 2540G)	(Chheda and Sorial, 2017)
24.	Toluene	Differential Biofilter: Non -growth	Soil and Biofilm	*Pseudomonas putida*, endogenous soil micromes	Bed configuration (Biofilm vs soil)	Biofilm: CO_2 : 79 ± 0.6 % Leachate: 10 ± 0.5% Biomass: 7.7 ± 1.5 % Soil: CO_2 : 81 ± 3 %	Gas Phase: GC FID Liquid: TOC analyzer Solid: TOC analyzer	(Bordoloi and Gostomski, 2018)

3 Influence of environmental parameters on carbon-endpoints

3.1 Temperature

Like any biological system, temperature is a critical operational parameter for the biofiltration process (Delhoménie and Heitz, 2005; Mudliar et al., 2010). Temperature is a defining factor for microbial activity both in terms of proliferation and biodegradation rates in engineered systems (Devinny et al., 1999; Jin et al., 2007; Vergara-Fernández et al., 2012). The majority of the biofiltration reports are in the 15-40 °C temperature range (Delhomenie et al., 2005; Jin et al., 2007; Shareefdeen et al., 2009; Vergara-Fernández et al., 2012). Thermophilic biofiltration, while less well studied, has reported higher activity over the 45-70 °C range (Luvsanjamba et al., 2007; Mohammad et al., 2007; Montes et al., 2014). As biofilters are often exposed to fluctuating temperatures, tracking the temperature-mediated impact on degradation end-products provides a vital link to the mechanistic understanding of the microorganism's physiological response.

3.1.1 Temperature mediated response on substrate utilization

Temperature variations in biofilters have a profound effect on the physical, biological and chemical aspects of biofiltration process parameters (Darlington et al., 2001; Veiga and Kennes, 2001). Temperatures below the optimal range inhibits microbial growth. It can structurally affect the lipids in the cell membrane hampering membrane transport machinery (D'Amico et al., 2003; Nedwell, 1999). Darlington et al. (2001) found a greater effect on substrate affinity than microbial activity at 20 °C. Higher temperatures can lead to drier conditions due to excess evaporation of bed moisture (Mohammad et al., 2007). Dry conditions can also favor fungal proliferation over bacteria (Nikolova and Nenov, 2005). Another potential problem is a temperature increase can decrease the solubility of pollutants and oxygen (Zhu et al., 2004). Zamir et al. (2014) reported a significant decrease in removal efficiency from 70-100% at 35 °C to 25% at 40 °C attributed to a decreased solubility of *n*-hexane at high temperature. High temperature can also induce protein denaturation and cell death as observed by Kong et al. (2013). However, limited knowledge exists on the effect of temperature on microbial community and metabolic pathways for biodegradation of volatile organic compounds. Most biofiltration research focuses on the impact of temperature on activity and performance without correlating it to the degradation product ratios.

Usually higher mineralization to CO_2 at increased temperatures may be coupled with maintenance requirements which are expected to take precedence in a nitrogen-limited system with the assumption of no active growth. The flow of electrons from the substrate leads to energy generation with a part of it dissipated as heat (Xiao and VanBriesen, 2006). In a nutrient-limited system with a continuous source of carbon/energy, the active population can be driven by the requisite energy for maintenance without any active growth. The performance of two reactors degrading ethanol at mesophilic and thermophilic temperature was monitored by Cox et al. (2001). Although the removal efficiencies were similar for both the reactors, there was marked difference in the amounts of CO_2 production and biomass accumulation. Higher temperature showed greater mineralization to CO_2 (60 %) as opposed to 46 % at ambient conditions. In another study treating toluene, 70% of the toluene was mineralized to CO_2 at an operating temperature of 55 °C, which was higher than the 53% observed at ambient temperatures (20-30 °C) (Wang et al., 2012).

Although temperature increases the metabolic activity of microbes, it can also simultaneously increase the maintenance requirements of the process culture (Cox et al., 2001). The microbes, as postulated to be in maintenance mode, must have sufficient energy to expend on maintenance requirements for the cells to survive through catabolic conversions. Without the supplement of nitrogen, the metabolic pathways are likely to be directed towards more energy generation unless there is an apparent advantage for the microbes to produce EPS. This is reflected in the higher CO_2 recovery at the highest temperatures.

Variation in mineralization pattern suggests microbial adaptation to different temperatures indicating a change in metabolic pathways which could affect the fate of carbon in the system. Tracking the temperature mediated response to degradation end-products could provide a vital link to the mechanistic understanding of the microorganism's physiological response. Temperatures not favourable to the degraders may result in decreased substrate affinity and/or impaired microbial activity putting stress on the microbes (Kong et al., 2013; Zamir et al., 2014). Various stress response for microbes have been elucidated which includes production of internal storage polymers like PHA's under nutrient limited conditions (Poblete-Castro et al., 2012). This could essentially alter the carbon endpoints in various phases. These difference in carbon recoveries as a function of temperature imply changing metabolic pathways for substrate utilization.

3.1.2 Link between temperature and community to degradation products.

In addition, variations in temperature can also affect the community structure evolution in a biofilter (Nadarajah et al., 2007; Wang et al., 2012) which can ultimately influence the various degradation end-products. Change in community structure after long term operations at different operating temperature has been reported (Mohammad et al., 2007). This suggests a significant effect of operating parameters such as temperature on microbial activity changes the dominant degrading community leading to temporal change in community structure. Kong et al. (2013) found differences in the microbial metabolic characteristics and microbial community between thermophilic and mesophilic biofilters degrading toluene. However, the dissimilarity decreased with time over longer-term operation of up to 296 days. It was suggested that long term exposure can help in the proliferation of an aptly adapted community. Estrada et al. (2013) reported variations in mineralization for bacterial and fungal biofilters degrading a VOC mixture at similar conditions. Bacteria had a higher fraction of mineralization (63 %) compared to fungi (43 %). This could translate into different specific degradation rates across communities which are also likely to influence the fate of degradation products.

Lu et al. (1999) found rod-shaped bacteria as the dominant community at 15 °C which changed to a predominance of bacilli and cocci at 50 °C in a biofilter treating BTEX vapors. Cox et al. (2001) found rod-shaped bacteria, yeasts and fungi in moderate concentration at the high temperature biofilter operating at 53 °C implying the presence of thermophilic ethanol degrading community. They also observed greater microbial diversity in the biofilters at ambient temperature than at higher temperatures. The biofilter mineralised 60% of the ethanol at 53 °C as opposed to 46% at ambient temperature. Gallastegui et al. (2013) attributed a two-fold higher mineralization to CO_2 for toluene than ethylbenzene to the dominant degrading community in the biofilter speculated to be fungi. However, the individual contribution of bacteria and fungi was not ascertained. They postulated a synergistic interaction between the bacteria and fungi which was previously reported to influence the mineralization of aromatic hydrocarbons (You-Qing et al., 2008). These adaptations to

temperature can influence a change in community structure with substrate degrading capability. Evolution of a different community would imply different metabolic pathways, which could affect the fate of carbon. Kong et al. (2013) found lower metabolic activities in thermophilic biofilters compared to mesophilic biofilters during the early phases but showed comparable values over long term operation (181 days). This study gave interesting insights on the temperature-microorganism dynamics in biofilters. These temperature-mediated attributes have illustrated a direct impact on the eventual degradation of the pollutants by the microbial adaptation to the changing temperature. The limited results available show that higher temperatures increase VOC mineralisation. This indicates a temperature-driven phenomenon of regulating the diversion of substrate degradation end-points. However, detailed knowledge on the intrinsic relationship of temperature with other environmental parameters on the fate of the degraded carbon is still limited.

3.2 Water

Sufficient water availability is required for all bioremediation including biofiltration (Coronado et al., 2014). In biofiltration, water availability in the bed can be measured using water potential (ψ). This is the energy status of the water in a system and is cumulatively comprised of osmotic potential (ψ_π), matric potential (ψ_m), gravitational potential (ψ_g), pressure potential (ψ_p) and overburden potential (ψ_Ω) (Papendick and Campbell, 1981). In biofiltration, matric potential tends to dominate at wet conditions but at low water contents osmotic potential can have an influence. Mobile water is held in the packing by capillary forces and gravitational forces. At saturation, the pores are completely filled with water resulting in zero matric potential (ψ_m) (Papendick and Campbell, 1981). As the water potential (ψ) decreases, water is drained out of the pores generating drier conditions and making it more difficult for the microorganism to utilize the water for their metabolic activity.

3.2.1 Transient water content dynamics in biofiltration

The water content of the packing material is critical to the microbial community and pollutant abatement in biofiltration. A change in water content in the packing materials is driven by both operational parameters and microbial kinetics. Both organic and inorganic packing materials have been used in biofiltration with varying hydrodynamic properties. Organic materials offers the advantage of residual inorganic nutrients and better water holding capacities whereas inorganic packing are more robust and possess higher surface areas (Dorado et al., 2010). Drying of the packing material can occur due to incomplete humidification of inlet air stream or microbial heat generation (Morales et al., 2003). Sakuma et al. (2009) reported drying at the inlet port of a biofilter reduced its performance. Microbial oxidation is an exothermic process; the metabolic heat generated from pollutant oxidation can increase the bed temperature thereby lowering the bed water content (Gostomski et al., 1997; Mysliwiec et al., 2001). Thus maintaining optimal water content is vital to the microbial process as water related stress can induce physiological responses that can be detrimental to process efficacy.

3.2.2 Microbial response to water stress

Microbes exhibit an intricate set of physiological adaptions to transient hydration dynamics in unsaturated media like soil. Lower water potential can result is a drastic change to osmotic potential which directly affects the osmoregulation and cell turgor pressure. Cellular dehydration can also cause protein denaturation and structural damage to DNA. Drier conditions can also impair nutrient flux as water serves as a transport medium for nutrients to cells(Or et al., 2007a). Most bacteria produce extracellular polysaccharides (EPS) for their increased water holding capacity in low water content habitats (Holden et al., 1997; Van De Mortel and Halverson, 2004). Schimel et al. (2007) illustrated the microbial response via allocation of resources upon decreasing water potential. They proposed that during stressed conditions, microbes are compelled to produce protective molecules such as osmolytes and chaperones to maintain cellular integrity.

Various studies have linked water stress response to specific gene expressions. *Pseudomonas putida* induces alginate synthesis in response to an imposed water stress of -0.04 MPa along with genes responsible for trehalose biosynthesis (Gülez et al., 2012). Johnson et al. (2011) found that for *Sphingomonas wittichi* strain RW1 at a lower water potential (-0.25 MPa), the expression of genes involved with trehalose and exopolysaccharide biosynthesis increased and the expression of genes responsible for flagella biosynthesis decreased. They also found significant changes in membrane fatty acid components. Dmitrieva and Burg (2007) illustrated damage to the protein and DNA synthesis pathways as direct response to water stress.

Changing water potential influences the microbial community depending on the inherent acclimatization machinery at its disposal (Harris, 1981). Often water stress can shift the community structure with time. Sun et al. (2002) found an increase in bacterial population with increasing moisture content while the actinomycetes and moulds decreased. Lower surface colonization by *P. putida* KT2440 at negative water potentials was reported by Descene et al. (2008). They attributed this to limited bacterial motility due to shallow liquid films at the surface of the pores in the experimental system. Prenafeta-Boldú et al. (2012) reported sustained biofilter degradation by a mixed bacterial and fungal community in xerophilic conditions (water content was ~20%) dominated by fungi, especially *Exophiala oligosperma*. Fungi are known to thrive in low moisture conditions, which can influence the degradation end-products as the metabolic responses vary among different groups of microbial communities.

3.2.3 Effect of matric potential on degraded carbon end-points

Variation in CO_2 recovery fractions with changing matric potential implies changing metabolic pathways due to the imposed water stress. Lower matric potential brings in physical constraints like impaired solute diffusivity and microbial motility owing to reduction in hydrated pathways (Or et al., 2007b). This could render the process biologically limited due to reduced water availability for cellular function. At the optimal matric potential requisite cellular functions for maintenance can be easily met through catabolic energy generation process leading to higher pollutant mineralization to CO_2. This shift in substrate degradation products towards non-mineralized fractions as a function of matric potential could have immense significance in elucidating carbon-endpoints.

Water stress could potentially trigger a stress response maintaining intracellular osmolyte concentration to maintain cell turgor pressure (Van De Mortel and Halverson, 2004). Carbon from the substrate is required for production of osmolytes. The generation of osmolytes has been well documented as a mechanism induced in response to environmental stress. But at lower matric potential, the drier environment can drier conditions could cause a temporary surge in accumulation and osmolyte production (Kakumanu and Williams, 2014). In response to the drier environment, the microorganisms induce genes for producing important solutes like ectoine (LeBlanc et al., 2008), and protective proteins like chaperonin (Katoh et al., 2004).

Drier conditions at lower matric potentials can also facilitate fungal proliferation in biofilters because of their ability to thrive under such conditions (Gallastegui et al., 2013; Prenafeta-Boldú et al., 2008). It underlines the effect on microbial activity in response to transient gradients in water content in unsaturated surfaces commonly encountered in soils (Long and Or, 2009). However, the fate of degraded carbon is dependent on the dominant degrading community which dominates over time. Estrada et al. (2013) did a comparative study with a VOC mixture on bacterial and fungal biofiltration. They found higher VOC mineralization by bacteria (~63%) compared to fungi (~43%). Thus, the eventual fate of the degraded carbon was influenced by variations in matric potential and its associated effects on the microenvironment such as the microbial community.

3.3 Effect of substrate concentration on the fate of degraded carbon

Higher substrate concentrations can influence the active degrading community due to substrate toxicity(Song and Kinney, 2005). Kim et al. (2005b) found impaired degradation capability at higher inlet concentrations which can simultaneously alter microbial metabolism especially in a nutrient-limited system. Higher residual toluene can increase the stress on the process culture, which can lead to variation in degradation products from CO_2 recovery to other non-mineralized fractions. Various stress responses for microbes have been elucidated which includes production of internal storage polymers like PHAs under nutrient limited conditions (Poblete-Castro et al., 2012). Also, higher substrate concentrations might affect the non-degrading community if the concentrations are beyond the inhibitory range. Under favourable environmental conditions, they can contribute to increased mineralization by predation (Bhaskaran et al., 2008; Cox and Deshusses, 1999; Woertz et al., 2002).

Tracking the influence of interaction between environmental parameters on the fate of various degraded fractions can help to understand the process culture's metabolic response. Under nutrient-limited conditions, the assumption is there is no net biomass growth in biofilters (Cherry and Thompson, 1997). Since CO_2 recovery is never 100% as reported in the literature, it suggests a diversion of degraded carbon towards other products as influenced by the environmental parameters. For a nutrient-limited system, a plausible sink would be accumulation of EPS, storage polymers and soluble microbial products (SMP).

The C/N ratio of the influent also influences the composition of EPS in terms of carbohydrates and proteins (Durmaz and Sanin, 2003). Moreover EPS can be degraded by bacteria as a source of carbon and energy under substrate limited conditions (Kommedal et al., 2001). However, carbon extraction studies of microbial biomass in these systems are limited but seldom show significant carbon accumulation in the biofilms (Fürer and Deshusses, 2000; Song and Kinney, 2000; Vance et al., 1987). Nutrient limited systems rarely plug up which

begs the question of other possible carbon sinks for biofilms in stationary phase degrading pollutants using maintenance kinetics. There are also reports of microbes producing more EPS at lower temperatures (Le Bihan and Lessard, 2000). Less CO_2 recovery is an indication of the culture possibly producing EPS and other internal storage polymers for survival and associated benefits of nutrient pooling (Xavier and Foster, 2007). This further illustrates the interdependence and effect of multiple environmental parameters on the fate of degraded carbon in these engineered systems.

3.4 Physiological implications of non-mineralized fractions/biomass production

Maintenance metabolism assumes significance over active growth in a biofilters which are nutrient limited (Grove et al., 2009). Changing environmental conditions can significantly impact maintenance requirements which can increase under stress conditions. Several studies have reported lower biomass yields at higher temperatures, attributing it to increased cellular maintenance requirements with temperature (Cho et al., 2007; Cox et al., 2001; Luvsanjamba et al., 2007). Nasrin et al. (2011) reported that lower matric potential also impairs biomass yield and can initiate a change in microbial community structure. So these stress conditions may affect the metabolic pathways by either a reduction in the fraction of the active community or impaired activity itself at specific set of conditions. Simultaneously, there can be a shift in community structure with changes in environmental parameters (Bhaskaran et al., 2008; Cabrol et al., 2012; Kong et al., 2013; Wallenstein and Hall, 2012).

For both growth and maintenance, the bioenergetics in the cells is mediated through the catabolic and anabolic reactions which happen separately. But they are intricately coupled with the total energy expenditure which is partitioned into biomass and maintenance functions (Russell and Cook, 1995). However cells are not capable of utilizing all the energy for cellular functions. Xiao and VanBriesen (2006) estimated a 60% average energy capture efficiency. The rest of the energy is dissipated into the system as heat. But this energy capture efficiency is not constant and is subject to change with different substrates, strains and environmental conditions. (Von Stockar et al., 2006) suggested that for low growth systems, only a small amount of biomass is formed per substrate consumed as opposed to a high growth system where biomass formed per substrate consumed would be high. Zafar et al. (2014) correlated the variance in maintenance energy expenditure to changing specific growth rates and yields cumulatively comprising of biomass and PHB production.

Good empirical results identifying variance in biomass yields can also be interpreted through the energy dependent kinetics. At certain environmental conditions, more precisely at lower matric potential, higher substrate concentrations or higher temperature, the additional stress can increase the maintenance requirements. Without any driving force for biomass growth in the absence of nitrogen, resource allocation is most likely diverted towards metabolic pathways for production of storage polymers. So the variance in non-mineralized yield can be possibly attributed to the influence and interactions of environmental parameters which make it imperative for the microbial community to adapt to changing conditions. The observed yield changes can involve a shift in community structure with the predominance of a single community or co-existence of a diverse active community degrading toluene. Further metagenomics work is required to conclusively determine if there is a change in the active community fractions with changing conditions.

4 Conclusions

Knowledge of the carbon end-points could bridge the connection between functionalities, community structure and metabolic response if coupled with high throughput molecular biology techniques. It can be deduced from the literature that conclusive quantification of the fate across the range of pollutants is often lacking. Further review of the environmental parameters of the various studies provided a critical link to the variations in carbon end-points as a key component in regulating the degradation pathways. Robust empirical data on carbon recovery should serve as good framework for monitoring and deciding operating conditions based on the prior knowledge of factors influencing the end-points for stable and improved system efficacy. The influence of key parameters should reflect on the fate of the degradation products in response to the metabolic pathways of the active degrading community. So, unravelling the various facets of substrate utilization, carbon end-points in particular could lead to a better understanding of the fate of pollutants in the biofiltration of waste gases. In addition, insights on the interactions of various environmental parameters on substrate metabolism pertaining to various end products could help solve operational problems like clogging and start-up times.

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Fate of degraded pollutants in waste gas biofiltration: An overview of carbon end-points.

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Abstract

The fate of the carbon from degraded pollutants in biofiltration is not well understood. The issue of missing carbon needs to be addressed quantitatively to better understand and model biofilter performance. Elucidating the various carbon end-points in various phases should contribute to the fundamental understanding of the degradation kinetics and metabolic pathways as a function of various environmental parameters. This article reviews the implications of key environmental parameters on the carbon end-points. Various studies are evaluated reporting carbon recovery over a multitude of parameters and operational conditions with respect to the analytical measurements and reported distribution of the carbon end-points.

Keywords: Biofiltration, Carbon balance, Volatile organic carbon (VOC), Biofilms

1 Introduction

Biofiltration provides a clean, cost effective, and environmentally friendly technology using mass transfer and microbial oxidation to degrade organic pollutants (Devinny et al., 1999; Kennes, 2012). The biofiltration process is used effectively for treating large streams of air contaminated with low concentrations (<1000 ppm) of pollutants (Iranpour et al., 2005). Biofilters are packed bed bioreactors degrading pollutants through a complex and mixed culture of microorganisms forming a pollutant-degrading biofilm on the porous bed medium. It has been successfully applied to treat a wide spectrum of organic and inorganic pollutants as well as a means to abate odours (Gallastegui et al., 2011; Girard et al., 2011; Mudliar et al., 2010; Ryu et al., 2009).

Biofilms are often growth restricted (e.g. - nutrient limited, etc.) especially in soil and various industrial processes such as biofiltration but possess the inherent ability to break down organic pollutants (Jorio et al., 2000a; Li et al., 2002; Xi et al., 2006). Biofilms proliferating in these dynamic environmental conditions are commonly unsaturated, operating at the air/solid interface. Many attempts have been made to close the carbon balance in these systems; however 10-50% of the degraded carbon often remains untracked (Avalos Ramirez et al., 2008; Cox et al., 2001; Deshusses, 1997b; Girard et al., 2011; Morales, 1998; Song and Kinney, 2000). In spite of the importance of these growth restricted, unsaturated biofilm processes in engineered systems, certain aspects of their activity/metabolism remain unclear, particularly the ultimate fate of carbon entering these systems.

Commonly assumed carbon end-points for organic carbon substrates are CO_2, active biomass and extracellular polymeric substances (EPS) .Other plausible carbon end-points include soluble microbial products (Jiang et al., 2010; Meng et al., 2009; Ni and Yu, 2011), soluble metabolites (Díaz et al., 2008), internal storage polymers (Reis et al., 2003) and volatile substances such as carbon monoxide (Haarstad et al., 2006). A common assumption is that the untracked carbon is utilised for microbial growth (biomass) but carbon extraction studies have not corroborated this hypothesis (Fürer and Deshusses, 2000; Song and Kinney, 2000; Vance et al., 1987). Accumulation of missing carbon within the system as biomass could clog up the reactor bed which is contrary to reports in non-growth systems (Deshusses, 1997b; Singh et al., 2006). Whilst microbes undoubtedly convert a portion of the organic substrates into soluble microbial products and other metabolites, their identities and relation to biodegradation of substrates remain to be fully investigated (Díaz et al., 2008; Kim et al., 2005b; Magbanua and Bowers, 2006). In the gaseous effluents, no other compounds other than CO_2 and untreated substrates are normally reported. There are limited reports of carbon monoxide reported in the off gas of some biodegradation processes (Haarstad et al., 2006; Hellebrand and Schade, 2008), and the possibilities of other unreported biogenic emissions cannot be ruled out. Thus, the carbon balance in these systems is yet to be closed conclusively and the identity of the unaccounted carbon remains elusive. This review presents a compilation of the various investigations tracking carbon and presents a link to the critical environmental parameters influencing the conversion to different degradation end-points.

2 Carbon balance and fate of pollutants

The biofilms in oxidative microbial processes in the waste gas treatment industry degrade waste organic compounds (C_xH_y) to CO_2, biomass and other metabolites (Deshusses, 1997a). The particular biochemical reaction catalyzed by the microorganisms proceeds via different pathways depending on the pollutant and nutrient availability. Under nutrient-limited conditions, a typical oxidation reaction for a hydrocarbon leads to the production of CO_2, water and heat which can be represented as follows:

$$C_xH_y + bO_2 \rightarrow x\,CO_2 + c\,H_2O + \text{Heat} \quad (1)$$

However, in the presence of sufficient nutrients, pollutant oxidation results in the formation of biomass along with other degradation products (Delhomenie et al., 2005) :

$$aC_xH_y + bO_2 + cNH_3 \rightarrow CH_{1.8}N_{0.2}O_{0.5} + dH_2O + \text{Heat} + eCO_2 \quad (2)$$

Where, $CH_{1.8}N_{0.2}O_{0.5}$ represents a generic formula for biomass.

CO_2 production is often a good indicator of the biological activity of the microbes, and it complements the tracking of pollutant degradation for the evaluation of a biofilter's performance efficacy (Bester et al., 2011; García-Peña et al., 2008). So it is common practice to monitor CO_2 production but limited success has been achieved in exhaustively pinning down the carbon flux through the system to its final end-points in different phases. Usually CO_2 measurement is for optimizing operating parameters to improve stability and process efficacy. Attempts to close the carbon balance is uneven, with 10 - 50 % of the degraded carbon missing

(Avalos Ramirez et al., 2008; Cox et al., 2001; Deshusses, 1997b; Girard et al., 2011; Morales, 1998; Song and Kinney, 2000).

A major portion of the degraded organic carbon is released as CO_2 (Jiménez et al., 2016; Jorio et al., 2000a; Li et al., 2002; Wang et al., 2012; Xi et al., 2006). From the CO_2 measurements, the remaining carbon fraction is often assumed to be biomass and is estimated based on the difference between the degraded pollutant and the CO_2 produced. This is because biomass measurements in operating biofilters are difficult. Researchers have estimated the carbon tied up in biomass directly through whole bed measurements combined with assumptions about the water content of wet biomass, representative sampling of the bed combined with the carbon content of cells, yield on nitrogen and chemical oxygen demand (COD)/carbon conversion etc. (Bester et al., 2011; Cox and Deshusses, 1999; Elmrini et al., 2004; Kroukamp and Wolfaardt, 2009). Therefore, the estimate of the carbon content of the biomass involves experimental uncertainties and assumptions, and the carbon mass balance closure in these highly complex systems remains difficult. Hence, there is a pressing need to track the unaccounted carbon in these biofilm processes through a holistic approach.

Most biofilter research performs a molecular balance on the pollutant (e.g. toluene, methane) and explicitly focusses on the *Consumption* term (e.g. elimination capacity) as a function of a variety of system inputs. As there is rarely any generation term for the pollutant, the mass balance for the pollutant simplifies to:

$$Consumption = Input - Output \quad (3)$$

Measuring the CO_2 allows an estimate of the accumulation of carbon in a biofilter by comparing the molar rate of CO_2 production to the molar rate of carbon degraded for the pollutant (i.e. – a carbon balance). This assumes no carbon is leaving the biofilter in the liquid phase or in the gas phase in a compound other than the pollutant or CO_2.

$$Carbon\ accumulation = x[a(C)_{in} - b(C)_{out}] - xc(CO_2) \quad (4)$$

$a(C)_{in}$ = molar flow rate of the pollutant entering the biofilter

$b(C)_{out}$ = molar flow rate of the pollutant exiting the biofilter

$c(CO_2)$ = molar flow rate of CO_2 exiting the reactor (corrected for any CO_2 present in the feed stream).

x = the number of carbon atoms in the molecular structure of the pollutant (1 in the case of CO_2)

It is this type of balance that is often used for estimates of biomass accumulation as compared to direct measurements. Tracking the carbon fraction in all three phases should account for the carbon end-points in the system encompassing the degradation products as a whole. An illustration of how the carbon entering the system exits or accumulates within the system in the solid, gas and liquid phase is presented in Fig. 1.

Figure 1: Flow chart identifying plausible carbon end-points in the system after toluene degradation.

106 **2.1 Gas phase end-points**

107 In the biofiltration process, the exiting gas stream is often analysed for CO_2 and un-reacted pollutants. The
108 commonly used methods to analyse effluent gas streams includes gas chromatography with various detectors
109 (TCD, FID) and CO_2 analysers. A few studies have attempted to analyse gas phase components by mass
110 spectrometry but have seldom reported anything other than CO_2 and un-degraded organic pollutants (Domeño et
111 al., 2010; Kastner and Das, 2005; Matteau and Ramsay, 1997; Møller et al., 1996).

112 CO_2 recoveries from various studies have ranged from 40-90% as a function of the mode of operation (nutrient-
113 limited or nutrient-addition) and variable operational parameters (Deshusses, 1997b; Grove et al., 2009; Jorio et
114 al., 2005; Wang et al., 2012). Cox et al. (2001) reported higher mineralization of ethanol to CO_2 at thermophilic
115 conditions (60%) than for a mesophilic biofilter (46%). Carbon recovery as CO_2 was 58% for the biofiltration of
116 binary mixtures of BTEX compounds compared to degradation of single BTEX compounds which ranged from
117 31-53% (García-Peña et al., 2008). Competitive inhibition for these closely related molecules could potentially
118 impact the catabolic/anabolic pathways. Hence, the CO_2 production pattern is an important component in
119 defining the product ratios of degraded carbon end-points. However, the possibility of other unreported biogenic
120 emissions in these systems cannot be ruled out.

121 The effluent gas stream could possibly contain C-containing intermediates and dissolved. Carbon monoxide
122 formation during solid organic waste degradation has been reported (Haarstad et al., 2006; Hellebrand and
123 Schade, 2008). Normal mass spectrometry in biofiltration would easily miss this compound due to the similar
124 molecular weight as N_2.

125 **2.2 Solid Phase end-points**

126 In biofiltration, the pollutants enter the biofilm and are utilized by the acclimatized microbial community as a
127 carbon and/or energy source (Cabrol et al., 2012). The carbon substrate, apart from being mineralized to CO_2
128 and water for energy production, is partially diverted towards microbial growth and some non-growth associated
129 products (Leson and Winer, 1991). These constituents form the solid phase accumulation in the system.

130 Studies delving into a carbon balance often assume the unaccounted carbon from the system is incorporated into
131 the biomass or associated polymers and polysaccharides without robust quantification. But if the missing carbon
132 reservoir were solely biomass or polysaccharides, this would cause clogging of the reactor beds which is not
133 typically reported in growth-limited systems (Deshusses, 1997b; Singh et al., 2006). In nutrient-limited
134 conditions, maintenance metabolism assumes significance, which means no net increase in active biomass
135 (Cherry and Thompson, 1997). In actively growing systems with nutrient addition, bioreactor clogging is
136 common and has been extensively covered in the literature (Delhoménie et al., 2003; Dorado et al., 2012;
137 Maestre et al., 2007; Weber and Hartmans, 1996; Xi et al., 2006; Yang et al., 2010). However, limited clogging
138 is occasionally reported indicating possible biological equilibrium between primary and secondary degraders
139 (Diks et al., 1994). Although, surprisingly little quantitative knowledge exists on the composition of the biofilm
140 components proliferating in these bioreactor systems.

Biomass yield forms an important parameter in model development which can be quantified from carbon recovery estimates (Bordel et al., 2008; Grove et al., 2009). Various studies which assumed the fraction of degraded pollutant not appearing as CO_2 was going to biomass reported biomass yields in the range of 0.17 – 0.43 g biomass per g pollutant (Deshusses, 1997b; Grove et al., 2009; Jorio et al., 2000b; Singh et al., 2006). However, there is no exhaustive quantification and characterization of these carbon end-points.

When a reactor is running on maintenance requirements under nutrient-limited conditions, a complete conversion of substrate into CO_2 is expected (Weber and Hartmans, 1996). However, the CO_2 fraction is invariably less than the theoretical estimate and carbon may be assimilated by the biomass in some form. Bacteria produce extracellular polymeric substances (EPS) which make up a major fraction of biofilms and play a very important part in biofilm structure, activity and performance (Sutherland, 2001). The major EPS components are comprised of polysaccharides and proteins in varying fractions but also include nucleic acids and lipids (Flemming and Wingender, 2010). EPS are secreted by the cells to enhance adhesion to substrates, contribute to the biofilm structure and influence microbial activity.

Biofilms as dynamic systems respond to environmental conditions physiologically which leads to variations in EPS composition (Schmitt et al., 1995). The origins and composition of EPS are very complex. Therefore a number of factors may affect the EPS composition and quantity, such as the type of limiting substrate (electron donor and acceptor), nitrogen and phosphorous limitation, and desiccation (Nielsen et al., 1997). The C/N ratio of the influent also influences the composition of EPS in terms of carbohydrates and proteins (Durmaz and Sanin, 2003). Thus EPS has been related to the macro-scale characteristics of biofilms describing its microbial and structural properties (Ras et al., 2011) and its production is also linked to microbial growth and substrate utilization (Laspidou and Rittmann, 2002). Moreover EPS can be degraded by bacteria as a source of carbon and energy under substrate-limited conditions (Kommedal et al., 2001). However, carbon extraction studies of microbial biomass in these systems are limited but seldom show significant carbon accumulation in the biofilms (Fürer and Deshusses, 2000; Song and Kinney, 2000; Vance et al., 1987). In addition, microbes also accumulates internal storage polymers as cellular reserves often driven by environmental conditions (Poblete-Castro et al., 2012; Reis et al., 2003; Xavier and Foster, 2007). Nutrient-limited systems rarely plug up which begs the question of other possible carbon sinks for biofilms in stationary phase degrading pollutants.

2.3 Liquid phase end-points

In addition to making active biomass and EPS, bacteria also convert a fraction of the organic substrate into soluble microbial products (SMPs) (de Silva and Rittmann, 2000; Namkung and Rittmann, 1986). SMPs are defined as soluble organic matter resulting from intermediates or end-products of substrate degradation and endogenous cell decomposition (Barker and Stuckey, 1999; Boero et al., 1991; Magbanua and Bowers, 2006). They have a wide molecular weight distribution, structure and function (Barker and Stuckey, 1999; Magbanua and Bowers, 2006; Rosenberger et al., 2006). A fractionation study by Jiang et al. (2010) studying SMPs in an activated sludge membrane system found proteins and carbohydrates as the major components of SMPs. These SMPs are important because they are ubiquitously present and contribute to the soluble organic matter in biological treatment system effluent (de Silva and Rittmann, 2000; Rosenberger et al., 2006).

178 The majority of SMP research has been done with pure cultures or wastewater treatment systems. A few waste
179 gas biofiltration studies which attempted closing the carbon balance have also reported inorganic and organic
180 carbon in the effluent liquid of the reactor, albeit at a variable percentage (3-39 %) depending on the mode of
181 operation (growth and nutrient limited) (Bester et al., 2011; Cox et al., 1998; Girard et al., 2011; Kim et al.,
182 2005b). However, their identities and the relationship between substrate biodegradation and SMPs are yet to be
183 determined conclusively in biofiltration. The accumulation of metabolic intermediates during volatile organic
184 carbon (VOC) treatment can inflict a detrimental effect on the process culture and in some cases results in a
185 more toxic form then the parent VOC being treated (Bordel et al., 2007). Duetz et al. (1994) described the
186 toluene-catabolic (TOL) pathway for toluene in strains with the pWWO plasmids that results in toluene being
187 first methyl-oxidized into benzyl alcohol which then leads to benzaldehyde, benzoic acid and catechol, these are
188 then further cleaved at the meta-position. These metabolites have the potential to effect performance efficacy as
189 they can be toxic to microbial communities (Ren and Frymier, 2002). Previously benzyl alcohol has been
190 reported of having mutagenic effects on *Pseudomonas putida* 54G resulting in loss of toluene degradation
191 capacity (Mirpuri et al., 1997).

192 Furthermore, oxygen limitation within the biofilm can shift metabolism, leading to products other than CO_2
193 (Kim et al., 2005b; Wilshusen et al., 2004; Yang et al., 2002). Oxygen limitations in overloaded biofilms can
194 lead to partially oxidized by-products such as carboxylic acids (Devinny and Hodge, 1995). Metabolic by-
195 products during anaerobic degradation of toluene have also been demonstrated but further studies are warranted
196 in aerobic biofilters in identifying transient intermediates (Beller et al., 1992). CO_2 can also be retained in the
197 liquid phase as carbonate (Gallastegui et al., 2011; Morales, 1998; Singh et al., 2006). However, the identities of
198 the carbon fractions in the liquid phase of the reactor are yet to be ascertained quantitatively in a controlled
199 situation, and therefore could be a significant sink for the degraded carbon in engineered systems.

200 Thus, it is evident from the literature thus far, for carbon balances conducted on biofilters, a variable percentage
201 of carbon remains unaccounted for in the system. Usually the emphasis has been largely on process optimization
202 and this fundamental question has met with limited success in the sporadic attempts made in the literature. Table
203 1 presents a compilation of the literature encompassing biofiltration of various VOCs, where the carbon mass
204 balance has received attention.

205

206 **Table 1**: Compilation of the literature encompassing carbon mass balance studies in biofiltration of various pollutants.

207

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
1.	Methyl ethyl ketone (MEK)	Biofilter: Non-growth	Compost + redwood chips + horse manure	Indigenous		C-CO_2: 82 ± 10 %	Gas Phase: GC FID, CO_2: Chemosorb column with TCD.	(Deshusses, 1997b)
2.	Toluene	Biotrickling: Growth	Pall rings	*P.corrugata , T. pyriformis , Vorticella microstoma, Klebsiella pneumoniae*		C- CO_2: 68 %, Biomass: 21 % Liquid: 6 %	Gas Phase: GC FID & TCD, Biomass: Weighing of wet packing + elemental balance, Liquid: TOC	(Cox and Deshusses, 1999)
3.	Toluene	Biofilter: Growth	Peat enriched with nutrients	*Acinetobacter lwoffi, Pseudomonas fluorescens, Pseudomonas putida, and Cla vibacter michigenense*	Toluene loads, ammonia addition	C-CO_2: 44.5 %, Carbonates: 14.3 %, Polymers: 32 %, Biomass: 9.2 %	Gas Phase: GC TCD, Biodegradable fractions were analysed through a digestion protocol.	(Morales, 1998)
4.	Toluene	Biofilter: Non-growth	Compost + bark and lava rocks	Inoculated with recycled liquid from a toluene degrading biotrickling filter		C- CO_2: 70 %	C^{14} toluene: scintillation, Gas Phase: GC FID &TCD, infrared CO_2 analyser	(Fürer and Deshusses, 2000)
5.	Toluene	Vapour phase Bioreactor (VPB): Growth	Porous silicate pellets	Heterotrophic microbial population adapted to toluene	Air flow: Unidirectional (UD), Directionally switching (DS)	C- CO_2: 63-66 %, Biomass: 34-37 % Liquid : >1 %	Gas Phase: GC-FID and CO_2 analyser. Biofilm analysis: COD	(Song and Kinney, 2000)
6.	Toluene, Benzene	Biofilter: Non-growth	Cylindrical activated carbon (CAC)	Heterotrophic population: bacilli, spore bacilli, fungi	Inlet load (IL) and gas flow rate	Toluene - CO_2: 64 % Benzene- CO_2: 51 % Assumption: Biomass and solute	Gas Phase: GC FID & HPLC, CO_2 analyser and bacterial counts	(Li et al., 2002)

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
7.	Ethanol	Biofilter: Growth	Polypropylene pall rings	Mixed microbial consortia from active green waste and food compost.	Temperature	C-CO_2: 60 % C-biomass: 14 % Unaccounted: 26 %	Gas Phase: GC FID & TCD, Biomass: dry weight, TOC	(Cox et al., 2001)
8.	Toluene and acetone	Trickle bed air biofilter (TBAB): Growth	Coal particles	Activated sludge	Inlet load (IL) and Gas flow rate	C- CO_2: 90 % Biomass: 10 %	Gas Phase: GC/FID, THC, and CO_2 analyzer Biomass: SCOD	(Chang and Lu, 2003)
9.	Ethanol	Biofilter: Growth	Sugarcane bagasse	*Candida utilis*	Inlet load (IL) and Gas flow	C- CO_2 : 16-76.3 % C-biomass: 2.8-5.7 % Acetaldehyde:1-7.8 % Ethyl acetate: 14-20 %	CO_2 : GC with TCD Cell # for biomass calculation	(Christen et al., 2002)
10.	Xylene	Biofilter: Growth	Spherical peat	Microbial activated consortium	Inlet load (IL) and Gas flow	C-CO_2: 82% Unaccounted: Assumed as biomass and solute	Gas Phase: THA and CO_2 analyser	(Elmrini et al., 2004)
11.	Styrene	Biofilter: Growth	Peat and Ceramic	*Pseudomonas sp.* SR-5	Inlet load (IL) and Gas flow	CO_2 and other degradation products: 90.4 % Biomass: 9.2 %	Gas Phase: GC/MS and FID, Biomass: Viable cell count and elemental analysis of carbon content	(Jang et al., 2004)
12.	Toluene	TBAB: Growth	Inorganic	Aerobic microbial culture sourced from activated sludge	Non-use /backwashing	C-CO_2: 63.2 % C-Liquid :15.5 % Unaccounted: 20.9 %	Gas Phase: GC FID and TOC	(Kim et al., 2005a)

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
13.	Toluene, styrene, methyl ethyl ketone and methyl isobutyl ketone	TBAB: Growth.	Pelletized diatomaceous Earth	Indigenous	Interchanging VOC's	C_CO_2: 63 % C-Liquid: 20 % Unaccounted: 15 %	Gas Phase: GC FID and TCD. Liquid: TOC	(Kim et al., 2005b)
14.	Toluene	Biofilter: Growth	Wood chips + propylene spheres	Activated sludge	Inlet load (IL) and Gas flow	CO_2: 83% approx. Explicit balance not attempted	Gas Phase: GC FID and TCD, Leachate: TOC	(Xi et al., 2006)
15.	Octane	Biofilter: Growth	Compost and perlite 50/50(v/v)	Mixed consortia adapted to Octane	Inlet concentration plus a shutdown period	CO_2 recovery: 25 % Remaining carbon assumed as biomass.	Gas Phase: GC FID and CO_2 analyzer	(Grove et al., 2009)
16.	Methane	Biotrickling: Growth	Inorganic packing	NA*	CH_4 and nitrate	CO_2 recovery: 82 % Biomass: 15 %	Gas Phase: THC and CO_2 analyzer Lixiviate: Ion chromatograph, UV detector, TOC	(Girard et al., 2011)
17.	Toluene and p-xylene	Biofilter	Inert material	NA*	Inlet load (IL)	p-xylene - CO_2: 89 % Toluene - CO_2: 91 % Accumulation based on conversion of an empirical biomass formula to carbon accumulation rate: 5-8 %	Gas Phase: GC FID and total hydrocarbon analyzer CO_2: NDIR CO_2 analyzer, Leachate: TOC analyzer	(Gallastegui et al., 2011)
18.	Toluene	Biotrickling: Growth	Granular activated carbon (GAC)	Activated sludge	Concentration, gas flow rate and temperature (55 ° C and ambient)	C in CO_2: 69 % C in biomass: 30.5 %	Gas Phase: GC FID and CO_2 analyzer. Leachate: TOC analyzer Fluorescence spectroscopy	(Wang et al., 2012)

No	Pollutant	Biofiltration Mode	Packing	Microbes	Variables	Carbon Balance: Endpoints (gC)	Analytical Methods	Reference
19.	Formaldehyde	Biotrickling: Growth	Perlite	Leachate from previously degrading formaldehyde biofilter	Inlet load (IL) and ozone addition	CO_2: 27 % Leachate: 2.7 % Biomass: 2.2 %	Gas Phase: GC FID Liquid: TOC analyzer and GC/MS/SPME Solid: TOC analyzer	Maldonado-Diaz and Arriaga, 2015)
20.	Toluene	Biotrickling: Growth	Perlite	Activated sludge	Inlet load (IL)	CO_2 : 76.3 % Leachate: 1 % Biomass: 8.9 %	Gas Phase: GC FID & TC Liquid: TOC anlyzer Solid: Volatile solids combustion method (550°C)	(Jiménez et al., 2016)
21.	Cumene	Biotrickling: Growth	Loofa sponge	Indigenous soil microbes from petroleum site	Inlet load (IL)	CO_2 : 0.12 % Leachate: 70 % Biomass: 12.9 %	Gas Phase: GC FID Liquid: TOC analyzer and GC-MS Solid: TOC analyzer	(Shahi et al., 2016)
22.	Methane	Biotrickling: Growth	Inert packing	Activated sludge	Pseudo steady state, transient state (shock loads), and starvation conditions.	CO_2 : 66-88 %	Gas Phase: Hydrocarbon analyzer and CO_2 analyzer.	(Ferdowsi et al., 2016)
23.	Tricholorethylene (TCE) and Methanol	Biotrickling: Growth	Diatomaceous earth pellets	Fungi	Biofilter I- (70% methanol to 30% TCE) Biofilter II- (80% methanol to 20% TCE)	Carbon recovery: Biofilters I - 88.45% ± 4.63% Biofilters II 86.5% ± 4.35%	Gas Phase: GC FID and TC Liquid: TOC anlyzer Solid: Volatile solids combustion (Standard Methods 2540G)	(Chheda and Sorial, 2017)
24.	Toluene	Differential Biofilter: Non -growth	Soil and Biofilm	*Pseudomonas putida*, endogenous soil micromes	Bed configuration (Biofilm vs soil)	Biofilm: CO_2 : 79 ± 0.6 % Leachate: 10 ± 0.5% Biomass: 7.7 ± 1.5 % Soil: CO_2 : 81 ± 3 %	Gas Phase: GC FID Liquid: TOC analyzer Solid: TOC analyzer	(Bordoloi and Gostomski, 2018)

3 Influence of environmental parameters on carbon-endpoints

3.1 Temperature

Like any biological system, temperature is a critical operational parameter for the biofiltration process (Delhoménie and Heitz, 2005; Mudliar et al., 2010). Temperature is a defining factor for microbial activity both in terms of proliferation and biodegradation rates in engineered systems (Devinny et al., 1999; Jin et al., 2007; Vergara-Fernández et al., 2012). The majority of the biofiltration reports are in the 15-40 °C temperature range (Delhomenie et al., 2005; Jin et al., 2007; Shareefdeen et al., 2009; Vergara-Fernández et al., 2012). Thermophilic biofiltration, while less well studied, has reported higher activity over the 45-70 °C range (Luvsanjamba et al., 2007; Mohammad et al., 2007; Montes et al., 2014). As biofilters are often exposed to fluctuating temperatures, tracking the temperature-mediated impact on degradation end-products provides a vital link to the mechanistic understanding of the microorganism's physiological response.

3.1.1 Temperature mediated response on substrate utilization

Temperature variations in biofilters have a profound effect on the physical, biological and chemical aspects of biofiltration process parameters (Darlington et al., 2001; Veiga and Kennes, 2001). Temperatures below the optimal range inhibits microbial growth. It can structurally affect the lipids in the cell membrane hampering membrane transport machinery (D'Amico et al., 2003; Nedwell, 1999). Darlington et al. (2001) found a greater effect on substrate affinity than microbial activity at 20 °C. Higher temperatures can lead to drier conditions due to excess evaporation of bed moisture (Mohammad et al., 2007). Dry conditions can also favor fungal proliferation over bacteria (Nikolova and Nenov, 2005). Another potential problem is a temperature increase can decrease the solubility of pollutants and oxygen (Zhu et al., 2004). Zamir et al. (2014) reported a significant decrease in removal efficiency from 70-100% at 35 °C to 25% at 40 °C attributed to a decreased solubility of *n*-hexane at high temperature. High temperature can also induce protein denaturation and cell death as observed by Kong et al. (2013). However, limited knowledge exists on the effect of temperature on microbial community and metabolic pathways for biodegradation of volatile organic compounds. Most biofiltration research focuses on the impact of temperature on activity and performance without correlating it to the degradation product ratios.

Usually higher mineralization to CO_2 at increased temperatures may be coupled with maintenance requirements which are expected to take precedence in a nitrogen-limited system with the assumption of no active growth. The flow of electrons from the substrate leads to energy generation with a part of it dissipated as heat (Xiao and VanBriesen, 2006). In a nutrient-limited system with a continuous source of carbon/energy, the active population can be driven by the requisite energy for maintenance without any active growth. The performance of two reactors degrading ethanol at mesophilic and thermophilic temperature was monitored by Cox et al. (2001). Although the removal efficiencies were similar for both the reactors, there was marked difference in the amounts of CO_2 production and biomass accumulation. Higher temperature showed greater mineralization to CO_2 (60 %) as opposed to 46 % at ambient conditions. In another study treating toluene, 70% of the toluene was mineralized to CO_2 at an operating temperature of 55 °C, which was higher than the 53% observed at ambient temperatures (20-30 °C) (Wang et al., 2012).

Although temperature increases the metabolic activity of microbes, it can also simultaneously increase the maintenance requirements of the process culture (Cox et al., 2001). The microbes, as postulated to be in maintenance mode, must have sufficient energy to expend on maintenance requirements for the cells to survive through catabolic conversions. Without the supplement of nitrogen, the metabolic pathways are likely to be directed towards more energy generation unless there is an apparent advantage for the microbes to produce EPS. This is reflected in the higher CO_2 recovery at the highest temperatures.

Variation in mineralization pattern suggests microbial adaptation to different temperatures indicating a change in metabolic pathways which could affect the fate of carbon in the system. Tracking the temperature mediated response to degradation end-products could provide a vital link to the mechanistic understanding of the microorganism's physiological response. Temperatures not favourable to the degraders may result in decreased substrate affinity and/or impaired microbial activity putting stress on the microbes (Kong et al., 2013; Zamir et al., 2014). Various stress response for microbes have been elucidated which includes production of internal storage polymers like PHA's under nutrient limited conditions (Poblete-Castro et al., 2012). This could essentially alter the carbon endpoints in various phases. These difference in carbon recoveries as a function of temperature imply changing metabolic pathways for substrate utilization.

3.1.2 Link between temperature and community to degradation products.

In addition, variations in temperature can also affect the community structure evolution in a biofilter (Nadarajah et al., 2007; Wang et al., 2012) which can ultimately influence the various degradation end-products. Change in community structure after long term operations at different operating temperature has been reported (Mohammad et al., 2007). This suggests a significant effect of operating parameters such as temperature on microbial activity changes the dominant degrading community leading to temporal change in community structure. Kong et al. (2013) found differences in the microbial metabolic characteristics and microbial community between thermophilic and mesophilic biofilters degrading toluene. However, the dissimilarity decreased with time over longer-term operation of up to 296 days. It was suggested that long term exposure can help in the proliferation of an aptly adapted community. Estrada et al. (2013) reported variations in mineralization for bacterial and fungal biofilters degrading a VOC mixture at similar conditions. Bacteria had a higher fraction of mineralization (63 %) compared to fungi (43 %). This could translate into different specific degradation rates across communities which are also likely to influence the fate of degradation products.

Lu et al. (1999) found rod-shaped bacteria as the dominant community at 15 °C which changed to a predominance of bacilli and cocci at 50 °C in a biofilter treating BTEX vapors. Cox et al. (2001) found rod-shaped bacteria, yeasts and fungi in moderate concentration at the high temperature biofilter operating at 53 °C implying the presence of thermophilic ethanol degrading community. They also observed greater microbial diversity in the biofilters at ambient temperature than at higher temperatures. The biofilter mineralised 60% of the ethanol at 53 °C as opposed to 46% at ambient temperature. Gallastegui et al. (2013) attributed a two-fold higher mineralization to CO_2 for toluene than ethylbenzene to the dominant degrading community in the biofilter speculated to be fungi. However, the individual contribution of bacteria and fungi was not ascertained. They postulated a synergistic interaction between the bacteria and fungi which was previously reported to influence the mineralization of aromatic hydrocarbons (You-Qing et al., 2008). These adaptations to

temperature can influence a change in community structure with substrate degrading capability. Evolution of a different community would imply different metabolic pathways, which could affect the fate of carbon. Kong et al. (2013) found lower metabolic activities in thermophilic biofilters compared to mesophilic biofilters during the early phases but showed comparable values over long term operation (181 days). This study gave interesting insights on the temperature-microorganism dynamics in biofilters. These temperature-mediated attributes have illustrated a direct impact on the eventual degradation of the pollutants by the microbial adaptation to the changing temperature. The limited results available show that higher temperatures increase VOC mineralisation. This indicates a temperature-driven phenomenon of regulating the diversion of substrate degradation end-points. However, detailed knowledge on the intrinsic relationship of temperature with other environmental parameters on the fate of the degraded carbon is still limited.

3.2 Water

Sufficient water availability is required for all bioremediation including biofiltration (Coronado et al., 2014). In biofiltration, water availability in the bed can be measured using water potential (ψ). This is the energy status of the water in a system and is cumulatively comprised of osmotic potential (ψ_π), matric potential (ψ_m), gravitational potential (ψ_g), pressure potential (ψ_p) and overburden potential (ψ_Ω) (Papendick and Campbell, 1981). In biofiltration, matric potential tends to dominate at wet conditions but at low water contents osmotic potential can have an influence. Mobile water is held in the packing by capillary forces and gravitational forces. At saturation, the pores are completely filled with water resulting in zero matric potential (ψ_m) (Papendick and Campbell, 1981). As the water potential (ψ) decreases, water is drained out of the pores generating drier conditions and making it more difficult for the microorganism to utilize the water for their metabolic activity.

3.2.1 Transient water content dynamics in biofiltration

The water content of the packing material is critical to the microbial community and pollutant abatement in biofiltration. A change in water content in the packing materials is driven by both operational parameters and microbial kinetics. Both organic and inorganic packing materials have been used in biofiltration with varying hydrodynamic properties. Organic materials offers the advantage of residual inorganic nutrients and better water holding capacities whereas inorganic packing are more robust and possess higher surface areas (Dorado et al., 2010). Drying of the packing material can occur due to incomplete humidification of inlet air stream or microbial heat generation (Morales et al., 2003). Sakuma et al. (2009) reported drying at the inlet port of a biofilter reduced its performance. Microbial oxidation is an exothermic process; the metabolic heat generated from pollutant oxidation can increase the bed temperature thereby lowering the bed water content (Gostomski et al., 1997; Mysliwiec et al., 2001). Thus maintaining optimal water content is vital to the microbial process as water related stress can induce physiological responses that can be detrimental to process efficacy.

3.2.2 Microbial response to water stress

Microbes exhibit an intricate set of physiological adaptions to transient hydration dynamics in unsaturated media like soil. Lower water potential can result is a drastic change to osmotic potential which directly affects the osmoregulation and cell turgor pressure. Cellular dehydration can also cause protein denaturation and structural damage to DNA. Drier conditions can also impair nutrient flux as water serves as a transport medium for nutrients to cells(Or et al., 2007a). Most bacteria produce extracellular polysaccharides (EPS) for their increased water holding capacity in low water content habitats (Holden et al., 1997; Van De Mortel and Halverson, 2004). Schimel et al. (2007) illustrated the microbial response via allocation of resources upon decreasing water potential. They proposed that during stressed conditions, microbes are compelled to produce protective molecules such as osmolytes and chaperones to maintain cellular integrity.

Various studies have linked water stress response to specific gene expressions. *Pseudomonas putida* induces alginate synthesis in response to an imposed water stress of -0.04 MPa along with genes responsible for trehalose biosynthesis (Gülez et al., 2012). Johnson et al. (2011) found that for *Sphingomonas wittichi* strain RW1 at a lower water potential (-0.25 MPa), the expression of genes involved with trehalose and exopolysaccharide biosynthesis increased and the expression of genes responsible for flagella biosynthesis decreased. They also found significant changes in membrane fatty acid components. Dmitrieva and Burg (2007) illustrated damage to the protein and DNA synthesis pathways as direct response to water stress.

Changing water potential influences the microbial community depending on the inherent acclimatization machinery at its disposal (Harris, 1981). Often water stress can shift the community structure with time. Sun et al. (2002) found an increase in bacterial population with increasing moisture content while the actinomycetes and moulds decreased. Lower surface colonization by *P. putida* KT2440 at negative water potentials was reported by Descene et al. (2008). They attributed this to limited bacterial motility due to shallow liquid films at the surface of the pores in the experimental system. Prenafeta-Boldú et al. (2012) reported sustained biofilter degradation by a mixed bacterial and fungal community in xerophilic conditions (water content was ~20%) dominated by fungi, especially *Exophiala oligosperma*. Fungi are known to thrive in low moisture conditions, which can influence the degradation end-products as the metabolic responses vary among different groups of microbial communities.

3.2.3 Effect of matric potential on degraded carbon end-points

Variation in CO_2 recovery fractions with changing matric potential implies changing metabolic pathways due to the imposed water stress. Lower matric potential brings in physical constraints like impaired solute diffusivity and microbial motility owing to reduction in hydrated pathways (Or et al., 2007b). This could render the process biologically limited due to reduced water availability for cellular function. At the optimal matric potential requisite cellular functions for maintenance can be easily met through catabolic energy generation process leading to higher pollutant mineralization to CO_2. This shift in substrate degradation products towards non-mineralized fractions as a function of matric potential could have immense significance in elucidating carbon-endpoints.

Water stress could potentially trigger a stress response maintaining intracellular osmolyte concentration to maintain cell turgor pressure (Van De Mortel and Halverson, 2004). Carbon from the substrate is required for production of osmolytes. The generation of osmolytes has been well documented as a mechanism induced in response to environmental stress. But at lower matric potential, the drier environment can drier conditions could cause a temporary surge in accumulation and osmolyte production (Kakumanu and Williams, 2014). In response to the drier environment, the microorganisms induce genes for producing important solutes like ectoine (LeBlanc et al., 2008), and protective proteins like chaperonin (Katoh et al., 2004).

Drier conditions at lower matric potentials can also facilitate fungal proliferation in biofilters because of their ability to thrive under such conditions (Gallastegui et al., 2013; Prenafeta-Boldú et al., 2008). It underlines the effect on microbial activity in response to transient gradients in water content in unsaturated surfaces commonly encountered in soils (Long and Or, 2009). However, the fate of degraded carbon is dependent on the dominant degrading community which dominates over time. Estrada et al. (2013) did a comparative study with a VOC mixture on bacterial and fungal biofiltration. They found higher VOC mineralization by bacteria (~63%) compared to fungi (~43%). Thus, the eventual fate of the degraded carbon was influenced by variations in matric potential and its associated effects on the microenvironment such as the microbial community.

3.3 Effect of substrate concentration on the fate of degraded carbon

Higher substrate concentrations can influence the active degrading community due to substrate toxicity(Song and Kinney, 2005). Kim et al. (2005b) found impaired degradation capability at higher inlet concentrations which can simultaneously alter microbial metabolism especially in a nutrient-limited system. Higher residual toluene can increase the stress on the process culture, which can lead to variation in degradation products from CO_2 recovery to other non-mineralized fractions. Various stress responses for microbes have been elucidated which includes production of internal storage polymers like PHAs under nutrient limited conditions (Poblete-Castro et al., 2012). Also, higher substrate concentrations might affect the non-degrading community if the concentrations are beyond the inhibitory range. Under favourable environmental conditions, they can contribute to increased mineralization by predation (Bhaskaran et al., 2008; Cox and Deshusses, 1999; Woertz et al., 2002).

Tracking the influence of interaction between environmental parameters on the fate of various degraded fractions can help to understand the process culture's metabolic response. Under nutrient-limited conditions, the assumption is there is no net biomass growth in biofilters (Cherry and Thompson, 1997). Since CO_2 recovery is never 100% as reported in the literature, it suggests a diversion of degraded carbon towards other products as influenced by the environmental parameters. For a nutrient-limited system, a plausible sink would be accumulation of EPS, storage polymers and soluble microbial products (SMP).

The C/N ratio of the influent also influences the composition of EPS in terms of carbohydrates and proteins (Durmaz and Sanin, 2003). Moreover EPS can be degraded by bacteria as a source of carbon and energy under substrate limited conditions (Kommedal et al., 2001). However, carbon extraction studies of microbial biomass in these systems are limited but seldom show significant carbon accumulation in the biofilms (Fürer and Deshusses, 2000; Song and Kinney, 2000; Vance et al., 1987). Nutrient limited systems rarely plug up which

begs the question of other possible carbon sinks for biofilms in stationary phase degrading pollutants using maintenance kinetics. There are also reports of microbes producing more EPS at lower temperatures (Le Bihan and Lessard, 2000). Less CO_2 recovery is an indication of the culture possibly producing EPS and other internal storage polymers for survival and associated benefits of nutrient pooling (Xavier and Foster, 2007). This further illustrates the interdependence and effect of multiple environmental parameters on the fate of degraded carbon in these engineered systems.

3.4 Physiological implications of non-mineralized fractions/biomass production

Maintenance metabolism assumes significance over active growth in a biofilters which are nutrient limited (Grove et al., 2009). Changing environmental conditions can significantly impact maintenance requirements which can increase under stress conditions. Several studies have reported lower biomass yields at higher temperatures, attributing it to increased cellular maintenance requirements with temperature (Cho et al., 2007; Cox et al., 2001; Luvsanjamba et al., 2007). Nasrin et al. (2011) reported that lower matric potential also impairs biomass yield and can initiate a change in microbial community structure. So these stress conditions may affect the metabolic pathways by either a reduction in the fraction of the active community or impaired activity itself at specific set of conditions. Simultaneously, there can be a shift in community structure with changes in environmental parameters (Bhaskaran et al., 2008; Cabrol et al., 2012; Kong et al., 2013; Wallenstein and Hall, 2012).

For both growth and maintenance, the bioenergetics in the cells is mediated through the catabolic and anabolic reactions which happen separately. But they are intricately coupled with the total energy expenditure which is partitioned into biomass and maintenance functions (Russell and Cook, 1995). However cells are not capable of utilizing all the energy for cellular functions. Xiao and VanBriesen (2006) estimated a 60% average energy capture efficiency. The rest of the energy is dissipated into the system as heat. But this energy capture efficiency is not constant and is subject to change with different substrates, strains and environmental conditions. (Von Stockar et al., 2006) suggested that for low growth systems, only a small amount of biomass is formed per substrate consumed as opposed to a high growth system where biomass formed per substrate consumed would be high. Zafar et al. (2014) correlated the variance in maintenance energy expenditure to changing specific growth rates and yields cumulatively comprising of biomass and PHB production.

Good empirical results identifying variance in biomass yields can also be interpreted through the energy dependent kinetics. At certain environmental conditions, more precisely at lower matric potential, higher substrate concentrations or higher temperature, the additional stress can increase the maintenance requirements. Without any driving force for biomass growth in the absence of nitrogen, resource allocation is most likely diverted towards metabolic pathways for production of storage polymers. So the variance in non-mineralized yield can be possibly attributed to the influence and interactions of environmental parameters which make it imperative for the microbial community to adapt to changing conditions. The observed yield changes can involve a shift in community structure with the predominance of a single community or co-existence of a diverse active community degrading toluene. Further metagenomics work is required to conclusively determine if there is a change in the active community fractions with changing conditions.

4 Conclusions

Knowledge of the carbon end-points could bridge the connection between functionalities, community structure and metabolic response if coupled with high throughput molecular biology techniques. It can be deduced from the literature that conclusive quantification of the fate across the range of pollutants is often lacking. Further review of the environmental parameters of the various studies provided a critical link to the variations in carbon end-points as a key component in regulating the degradation pathways. Robust empirical data on carbon recovery should serve as good framework for monitoring and deciding operating conditions based on the prior knowledge of factors influencing the end-points for stable and improved system efficacy. The influence of key parameters should reflect on the fate of the degradation products in response to the metabolic pathways of the active degrading community. So, unravelling the various facets of substrate utilization, carbon end-points in particular could lead to a better understanding of the fate of pollutants in the biofiltration of waste gases. In addition, insights on the interactions of various environmental parameters on substrate metabolism pertaining to various end products could help solve operational problems like clogging and start-up times.

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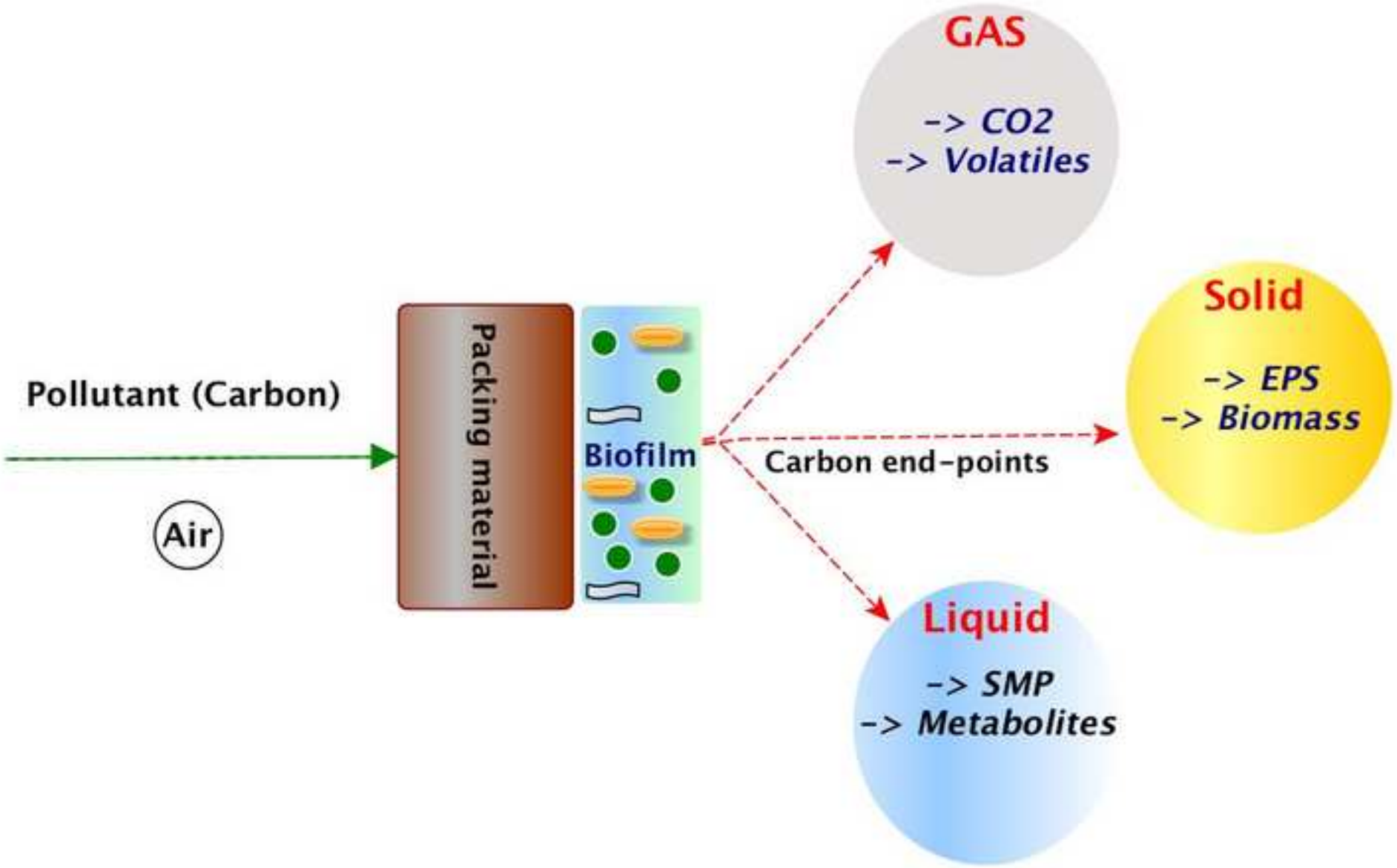
Figure 1


GAS
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