Environmental Science & Technology

Article

pubs.acs.org/est

Identification of Preferential Paths of Fossil Carbon within Water Resource Recovery Facilities via Radiocarbon Analysis

Linda Y. Tseng,[*,†] Alice K. Robinson,[‡] Xiaying Zhang,[‡] Xiaomei Xu,[§] John Southon,[§] Andrew J. Hamilton,[∥] Reza Sobhani,[‡,#] Michael K. Stenstrom,[⊥] and Diego Rosso[‡,#]

[†]Environmental Studies Program & Department of Physics and Astronomy, Colgate University, 13 Oak Drive, Hamilton, New York 13346, United States

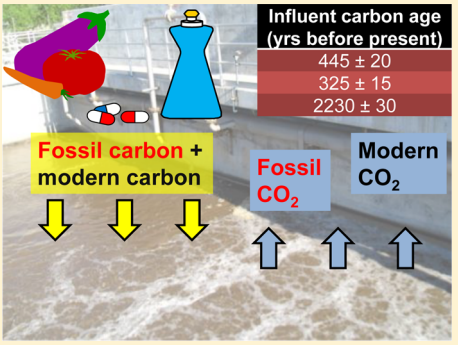
[‡]Civil and Environmental Engineering Department, [§]Earth System Science Department, and [#]Water-Energy Nexus Center, University of California, Irvine, California 92697-2175, United States

[∥]Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Dookie College, VIC 3647, Australia

[⊥]Civil and Environmental Engineering Department, University of California, Los Angeles, California 90095-1593, United States

Supporting Information

ABSTRACT: The Intergovernmental Panel on Climate Change (IPCC) reported that all carbon dioxide (CO_2) emissions generated by water resource recovery facilities (WRRFs) during treatment are modern, based on available literature. Therefore, such emissions were omitted from IPCC's greenhouse gas (GHG) accounting procedures. However, a fraction of wastewater's carbon is fossil in origin. We hypothesized that since the fossil carbon entering municipal WRRFs is mostly from soaps and detergents as dissolved organic matter, its fate can be selectively determined during the universally applied separation treatment processes. Analyzing radiocarbon at different treatment points within municipal WRRFs, we verified that the fossil content could amount to 28% in primary influent and showed varying distribution leaving different unit operations. We recorded the highest proportion of fossil carbon leaving the secondary treatment as off-gas and as solid sludge (averaged 2.08 kg fossil-CO_2-emission-potential m^{-3} wastewater treated). By including fossil CO_2, total GHG emission in municipal WRRFs increased 13%, and 23% if an on-site energy recovery system exists although much of the postdigestion fossil carbon remained in biosolids rather than in biogas, offering yet another carbon sequestration opportunity during biosolids handling. In comparison, fossil carbon contribution to GHG emission can span from negligible to substantial in different types of industrial WRRFs. With such a considerable impact, CO_2 should be analyzed for each WRRF and not omitted from GHG accounting.



INTRODUCTION

In recent years, an increase in the interest for quantifying greenhouse gas (GHG) emissions from wastewater treatment processes has been paralleled by numerous efforts to monitor and model such emissions.[1−6] The procedures published by the Intergovernmental Panel on Climate Change (IPCC)[7] are arguably the most widely applied for estimating the GHG emissions generated by water resource recovery facilities (WRRFs), due to their consistency across sites and geographic areas. The IPCC method assumes that all carbon dioxide (CO_2) emissions in the wastewater treatment process are modern (consistent with the background unpolluted atmosphere) and biogenic and thus should not be included in GHG inventory.[8] The rationale behind this assumption is that wastewater treatment processes involve the conversion of the modern carbon, derived from food and human waste, to CO_2, which is then quickly recycled through photosynthetic uptake.[9]

Modern carbon (as opposed to fossil or "old" carbon) is not originated from fossil fuels and consequently is associated with higher carbon-14 (^{14}C) abundance. However, WRRFs, even those receiving strictly municipal wastewater, are known to receive a variety of household[10] and personal care products with their influent,[11] many of which are derived from petrochemicals; hence, the assumption that nonbiogenic CO_2 is negligible is likely invalid.[12,13] In fact, it has long been known that synthetic detergents enter the WRRFs.[14] Griffith et al. (2009) conducted radiocarbon analysis of both particulate and dissolved carbon from the effluent of 12 WRRFs in the United States and found that fossil carbon (i.e., ^{14}C-free carbon) amounted on average to 14% of the particulate organic carbon and to 25% of the dissolved organic carbon. Nara et al. (2010) also found fossil carbon in the dissolved organic carbon of both the influent and effluent of a WRRF; domestic sewage, influent, and effluent of the WRRF had approximately 40−51%, 16−27%, and 27%, respectively.[15] The most extensive radiocarbon study of wastewater treatment

Received: June 1, 2016
Revised: September 4, 2016
Accepted: October 7, 2016
Published: November 2, 2016

ACS Publications © 2016 American Chemical Society

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

facilities to date was conducted by Law et al. (2013). The authors collected samples throughout the process train of four municipal WRRFs in Australia and used radiocarbon analyses to quantify the carbon mass balance. Their findings were that fossil carbon was present throughout the treatment processes of all four plants and that some likely was oxidized to CO_2 and emitted in the activated sludge basin and some left the plant via sludge, with an estimated addition of 2−12% to the direct GHG emissions (also referred to as Scope I emissions) from the treatment plants they studied. The presence of fossil carbon in both municipal and industrial wastewater suggests that GHG emissions from wastewater treatment may be underestimated.[13]

After the raw wastewater enters the WRRFs, the carbon at different processes could have distinct isotopic signature in the dissolved organic carbon (DOC), as suggested by Raymond and Bauer (2001) due to the microbial preference to use modern carbon for assimilation.[16] Although Nara et al. (2010) did not find a distinct difference in ^{14}C abundance between the DOC in wastewater influent and treated wastewater effluent,[15] in Law et al. (2013) the ^{14}C in the DOC generally became enriched in the effluent, when compared to the influent.[13]

In comparison to the reported fossil carbon in the municipal wastewater streams, the prevalence of fossil carbon in industrial waste streams is expected to be significantly different. Although to our knowledge, no radiocarbon studies of industrial wastewater have been published, fossil carbon was observed in sediments and natural waters downstream of industrial outfalls.[17−19] Given the origin of the carbon in certain industrial processes, the petrochemical industries, for example, are expected to have an almost exclusively fossil carbon balance throughout their wastewater treatment plants. Conversely, wastewater from the dairy processing industries would be expected to have opposite carbon balance (i.e., almost exclusively modern). In sum, a systematic study of the different industrial segments is needed to provide data for comprehensive models that transcend the overall assumption that all carbon in wastewater is modern.

Radiocarbon analysis provides a quantification of the relative prevalence of modern vs fossil carbon via measurement of the ^{14}C-to-^{12}C ratio.[12,13,17−22] Here, we hypothesize that although there may be a combination of modern and fossil carbon in municipal wastewater, the treatment processes can selectively determine the fate of carbon fractions (i.e., modern vs fossil) since petrochemicals are generally dissolved in nature (i.e., soluble chemical oxygen demand, or sCOD) while food and human waste are mostly particulate in nature (i.e., particulate COD, or pCOD).

The goal of the present study was to compare and estimate the potential GHG emission with the fossil carbon content of the wastewater at different points of the treatment process. We also included boundary conditions of fully modern vs fully fossil carbon with results from a pulp/paper mill and a petrochemical refinery wastewater treatment plant, respectively. Here we present the results of our study on the quantification of fossil carbon in municipal and industrial wastewaters at various points throughout their treatment.

MATERIALS AND METHODS

Site Description. Our study sites consisted of three municipal WRRFs and an industrial petrochemical site in Southern California, waste stabilization ponds in Australia, and a pulp/paper mill wastewater treatment plant in Canada (Figure 1).

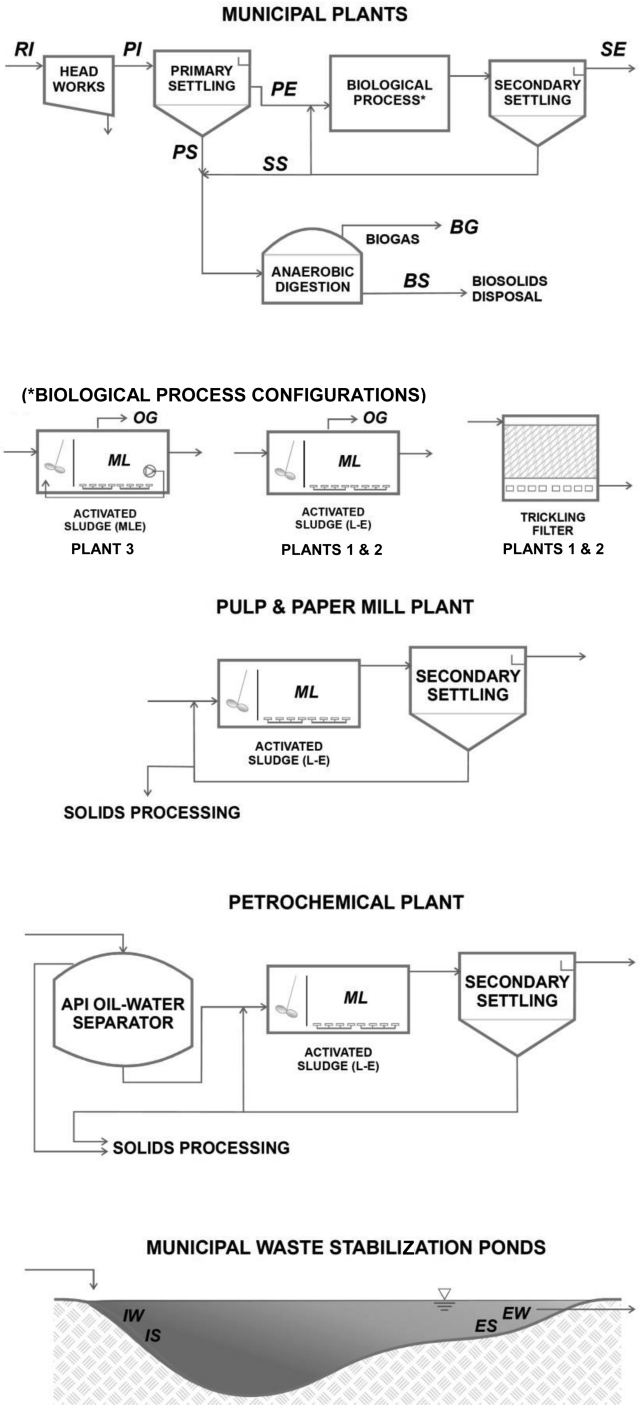


Figure 1. Our study sites included municipal water resource recovery facilities (WRRFs) in the United States, waste stabilization ponds in Australia, a pulp/paper mill wastewater treatment plant in Canada, and an industrial petrochemical site in the United States. Plant 1 was an urban water reclamation plant (341 000 m^3 d^{-1}) receiving both residential and industrial wastewater (about 10%). Plant 2 was located in a suburban setting and has a Ludzack−Ettinger (L−E) layout (28 000 m^3 d^{-1}) with less than 5% industrial contribution. Both featured primary treatment, a secondary treatment via activated sludge process (ASP) and trickling filter, operating in parallel, and on-site anaerobic digestion of sludge. Plant 3 was a WRRF with a modified Ludzack−Ettinger (MLE) configuration (60 000 m^3 d^{-1}) featuring primary treatment and secondary treatment by ASP with only some industrial influent. All three municipal WRRFs received food waste from both household garbage disposals and human waste. The petrochemical plant had an

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

Figure 1. continued

API oil−water separator and a dissolved air flotation unit. The pulp/paper mill wastewater was subjected to no pretreatment before the biological treatment process. The waste stabilization ponds received wastewater, and most of the influent solids settle in the beginning of the treatment. Key: RI, raw influent; PI, primary influent; PE, primary effluent; PS, primary sludge; ML, mixed liquor; SS, suspended solids; SE, secondary effluent; BS, biosolids; BG, biogas; OG, off-gas; IW, influent wastewater; IS, influent solids; EW, effluent water; ES, effluent solids.

Plant 1 was an urban water reclamation plant treating approximately 341 000 m^3 d^{-1} of both residential and industrial wastewater (about 10%). Plant 2 was located in a suburban setting, had a Ludzack−Ettinger (L−E) layout treating approximately 28 000 m^3 d^{-1}, and served a primarily residential area with less than 5% industrial contribution. Both Plants 1 and 2 featured primary treatment, a secondary treatment via activated sludge process (ASP) and trickling filter, operating in parallel, and an on-site anaerobic digestion of sludge for energy recovery (Figure 1). Plant 3 was an urban WRRF with a modified Ludzack−Ettinger (MLE) configuration that treats 60 000 m^3 d^{-1} and featured primary treatment and secondary treatment by ASP only. Plant 3 received primarily residential wastewater, though there was a portion of the influent industrial in nature. Note that for this plant, sludge digestion and digester gas production occurred off-site, so on-site data were only available for primary and secondary treatment. All three municipal WRRFs sampled in this study received food waste from household garbage disposals and human waste, as is common for WRRFs in the U.S.[23] Operating conditions at all three plants are summarized in Supporting Information Table S-1.

To demonstrate the range of radiocarbon signatures represented in WRRFs, samples were also collected from two industrial WRRFs. Samples of influent and effluent from a Canadian WRRF treating pulp/paper mill wastewater, and of the influent to the ASP of a WRRF treating oil refinery wastewater located in the U.S., were collected for this study. The refinery samples were collected at a point downstream of an American Petroleum Institute (API) oil−water separator and a dissolved air flotation unit that would have removed large quantities of oil and suspended solids; the ^{14}C results presented from this facility refer only to the carbon subjected to biological treatment. The pulp/paper mill wastewater was subjected to no pretreatment before the biological treatment process.

Sample Collection and Processing. The ^{14}C content was measured throughout the treatment process for three municipal WRRFs (Plants 1, 2, and 3) in the U.S., and for one situated in Canada that treats pulp/paper mill wastewater and one that treats oil refinery wastewater in the U.S. Liquid or sludge samples were collected from each treatment process in acid-washed, 550 °C-baked glass vials, and ASP off-gas and digester gas samples were collected in evacuated, stainless steel 2-L canisters. To obtain off-gas samples, a floating plastic hood was placed in the ASP basin and off-gas was collected through a PVC tube attached to the hood. Tubing was flushed with off-gas for approximately 2 min before sample collection to remove atmospheric air.[24,25] Industrial wastewater samples were lyophilized and homogenized. Liquid and sludge samples of the municipal WRRFs were dried at 80 °C in a vented oven. An examination of the wastewater sludge samples demonstrated that lyophilizing and oven-drying yield comparable ^{14}C results (Supporting Information Figure S-1). For Plant 2 samples, aliquots of each sample were dried in preweighed aluminum dishes to determine sample dry weight per volume for carbon balance purposes. Volatile compounds, if present, may have been lost in the drying; however, such compounds are unlikely to make up a significant fraction of the carbon load.[26,27]

Waste stabilization pond samples[28] were obtained from three treatment plants in Victoria, Australia in 2013. All plants received municipal sewage from their respective town with no major industrial contribution. Each sample was collected and stored in a 10 mL borosilicate vial with a silicone septum prior to analysis. A total of 12 locations were sampled and 4 types of samples were collected: influent water, influent sludge, effluent water, and effluent sludge (in Figure 1: IW, IS, EW, ES, respectively).

Radiocarbon Measurements: Liquid/Solid Samples. Small portions of each sample were measured and placed in quartz tubes with 60−80 mg of CuO as an oxygen source and a piece of silver wire (length of about 0.5 cm) to remove trace sulfur. For samples suspected to have high total dissolved solids (TDS) content, including primary and secondary effluent samples, an additional outer quartz tube was added. Samples were sealed under vacuum and combusted to CO_2 at 900 °C for 3 h. The CO_2 generated in the combustion process was then purified in a vacuum line: water vapor was removed using a −80 °C cold trap, and then CO_2 was frozen in a liquid nitrogen cold trap while noncondensable trace gases were pumped away. The remaining CO_2 was transferred to a known volume and its size measured using a calibrated pressure gauge.[29] CO_2 was then converted to graphite according to the procedure described in Beverly et al. (2010).[30]

Radiocarbon Measurements: Gas Samples. CO_2 and methane (CH_4) in gas samples were separated cryogenically in a low-pressure vacuum line using ultrazero air as carrier gas. For digester gas samples, CH_4 was combusted to CO_2 through an online CuO furnace at 975 °C, and CO_2 and CH_4-derived CO_2 were reduced to graphite and analyzed separately, as described in Pack et al. (2015).[29] For off-gas samples, only CO_2 from the sample was analyzed because of our preliminary results that showed the low quantities of CH_4 present in these samples.

Radiocarbon data are reported in terms of fraction modern (Fm), normalized to an oxalic acid standard OX1 (the activity of the first radiocarbon standard, a 1890 grown wood, is 0.95 of OX1, prior to the Industrial Revolution), following the conventions of Stuiver and Polach (1977).[31−33] Results were corrected for mass-dependent fractionation to a common ^{13}C value of −25‰ using online accelerator mass spectrometer (AMS) $\delta^{13}C$ measurements (eq 2 and 3) at the W. M. Keck Carbon Cycle Accelerated Mass Spectrometry Laboratory (University of California, Irvine[58]). Isotopic analyses of ^{13}C and ^{14}C content are both relative measurements of their ratios, i.e., ^{13}C to ^{12}C ratios in a sample are compared to a standard. Thus, $\delta^{13}C > 0$ means ^{13}C is more enriched in the sample than in the standard. An Fm value of 1 means that the sample ^{14}C to ^{12}C ratio is the same as that of the absolute radiocarbon standard, and a value >1 means ^{14}C is more enriched in the sample than in the standard, usually due to bomb ^{14}C or tracer ^{14}C addition.

$$\mathrm{Fm} = \left[\frac{\left(\frac{^{14}C}{^{12}C}\right)_{\mathrm{sample},-25‰}}{0.95 \times \left(\frac{^{14}C}{^{12}C}\right)_{\mathrm{OX1},-19}} \right] \quad (1)$$

where

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

Table 1. 14C Results[a]

location	sample type	sample date	Fm_b	Fm_s	^{14}C age (years before present)[b]
municipal plant 1	biogas CH_4	May 2011	1.0457[c]	1.4365 ± 0.0021	>modern
municipal plant 1	biogas CH_4	May 2011	1.0457[c]	1.4397 ± 0.0026	>modern
municipal plant 1	digester sludge eff	June 2011	1.0411[c]	1.961 ± 0.0051	>modern
municipal plant 1	primary eff	Oct 2011	1.0403[c]	1.6534 ± 0.0028	>modern
municipal plant 1	mixed liquor	Oct 2011	1.0403[c]	2.5102 ± 0.0047	>modern
municipal plant 1	sec sludge	Oct 2011	1.0403[c]	2.2154 ± 0.0053	>modern
municipal plant 1	raw influent	Aug 2013	1.04	0.9463 ± 0.0019	445 ± 20
municipal plant 1	primary influent	Aug 2013	1.04	0.9605 ± 0.0017	325 ± 15
municipal plant 1	primary sludge	Aug 2013	1.04	1.0306 ± 0.0022	−235 ± 20
municipal plant 1	primary eff	Aug 2013	1.04	0.9985 ± 0.0016	10 ± 15
municipal plant 1	mixed liquor	Aug 2013	1.04	1.4532 ± 0.003	>modern
municipal plant 1	TF sec sludge	Aug 2013	1.04	1.2494 ± 0.0022	>modern
municipal plant 1	TF eff	Aug 2013	1.04	2.1299 ± 0.0251	>modern
municipal plant 1	biosolids	Aug 2013	1.04	1.3015 ± 0.0023	>modern
municipal plant 2	ASP off-gas	Nov 2013	1.04	0.944 ± 0.0019	465 ± 20
municipal plant 2	ASP off-gas CH_4	Nov 2013	1.04	1.0144 ± 0.0019	modern
municipal plant 2	ASP off-gas CO_2	Nov 2013	1.04	1.0122 ± 0.002	modern
municipal plant 2	primary influent	Nov 2013	1.05	0.7574 ± 0.0027	2230 ± 30
municipal plant 2	mixed liquor	Nov 2013	1.05	0.8807 ± 0.0016	1020 ± 20
municipal plant 2	sec sludge	Nov 2013	1.05	0.8861 ± 0.0017	970 ± 20
municipal plant 2	sec eff	Nov 2013	1.05	0.8327 ± 0.0023	1470 ± 25
municipal plant 2	TF eff	Nov 2013	1.05	0.9218 ± 0.0019	655 ± 20
municipal plant 2	TF sec sludge	Nov 2013	1.05	0.8713 ± 0.0016	1105 ± 20
municipal plant 2	biosolids	Nov 2013	1.05	0.887 ± 0.0019	965 ± 20
municipal plant 2	primary sludge	Nov 2013	1.05	0.9951 ± 0.0023	40 ± 20
municipal plant 2	primary eff	Nov 2013	1.05	0.8867 ± 0.0021	965 ± 20
municipal plant 3	primary sludge	June 2011	1.0411[c]	1.0354 ± 0.0019	−275 ± 15
municipal plant 3	primary influent	June 2011	1.0411[c]	1.0449 ± 0.0021	−350 ± 20
municipal plant 3	primary influent	June 2011	1.0411[c]	1.0197 ± 0.0019	−150 ± 15
municipal plant 3	primary eff	June 2011	1.0411[c]	0.8412 ± 0.0023	1390 ± 25
municipal plant 3	primary eff	June 2011	1.0411[c]	0.9851 ± 0.0029	120 ± 25
municipal plant 3	sec eff	June 2011	1.0411[c]	0.8229 ± 0.006	1570 ± 60
municipal plant 3	sec eff	June 2011	1.0411[c]	0.5358 ± 0.0059	5010 ± 90
municipal plant 3	sec sludge	June 2011	1.0411[c]	0.8926 ± 0.002	915 ± 20
municipal plant 3	sec sludge	Nov 2010	1.0502[c]	0.8796 ± 0.0019	1030 ± 20
municipal plant 3	sec sludge	Nov 2010	1.0502[c]	0.8782 ± 0.0015	1045 ± 15
petrochemical plant	sec eff	Nov 2012	1.0411[c]	0.018 ± 0.0005	32270 ± 240
petrochemical plant	sec eff	Nov 2012	1.0411[c]	0.0175 ± 0.0005	32490 ± 250
petrochemical plant	sec eff	Nov 2012	1.0411[c]	0.0169 ± 0.0005	32800 ± 260
petrochemical plant	sec eff	Nov 2012	1.0411[c]	0.0178 ± 0.0005	32360 ± 240
pulp/paper mill plant	influent	Nov 2013	1.04	0.9586 ± 0.0018	–
pulp/paper mill plant	eff	Nov 2013	1.04	1.073 ± 0.0021	–
UC Irvine laboratory	tap water	Nov 2012	1.05	0.8251 ± 0.003	75 ± 15
UC Irvine laboratory	tap water	June 2011	1.0411[c]	0.9325 ± 0.0049	150 ± 15
UC Irvine laboratory	tap water	Nov 2010	1.0502[c]	1.1608 ± 0.0025	490 ± 15
UC Irvine laboratory	tap water	Oct 2011	1.0403[c]	0.9718 ± 0.002	190 ± 15
Southern California Home	tap water	May 2011	1.0457[c]	0.8772 ± 0.0015	520 ± 20
Southern California well	groundwater	May 2011	1.0457[c]	0.9434 ± 0.0036	110 ± 15
Southern California well	groundwater	May 2011	1.0457[c]	0.9731 ± 0.002	390 ± 20
Southern California well	groundwater	May 2011	1.0457[c]	0.7302 ± 0.0013	115 ± 15
Southern California well	groundwater	May 2011	1.0457[c]	0.6441 ± 0.0056	275 ± 20
waste stabilization pond	influent WW	Dec 2013	1.04	0.9941 ± 0.0015	60 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	0.9884 ± 0.0015	795 ± 30
waste stabilization pond	eff	Dec 2013	1.04	0.9928 ± 0.0019	0 ± 15
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9907 ± 0.0015	515 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	0.9816 ± 0.0015	100 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	0.9406 ± 0.0015	−135 ± 15
waste stabilization pond	eff	Dec 2013	1.04	0.9765 ± 0.0017	−235 ± 15
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9376 ± 0.0018	−250 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	0.9861 ± 0.0017	205 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	0.9525 ± 0.0022	270 ± 15

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

Table 1. continued

location	sample type	sample date	Fm_b	Fm_s	^{14}C age (years before present)[b]
waste stabilization pond	eff	Dec 2013	1.04	0.9861 ± 0.0018	200 ± 20
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9664 ± 0.0023	145 ± 20
waste stabilization pond	influent WW	Dec 2013	1.04	0.9925 ± 0.0018	130 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	0.9059 ± 0.0034	155 ± 15
waste stabilization pond	eff	Dec 2013	1.04	1.0007 ± 0.0016	120 ± 15
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9381 ± 0.0017	25 ± 20
waste stabilization pond	influent WW	Dec 2013	1.04	0.9874 ± 0.0016	−60 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	1.0177 ± 0.0017	45 ± 15
waste stabilization pond	eff	Dec 2013	1.04	1.0303 ± 0.0017	60 ± 15
waste stabilization pond	eff sludge	Dec 2013	1.04	1.032 ± 0.0017	125 ± 20
waste stabilization pond	influent WW	Dec 2013	1.04	0.9746 ± 0.0017	−5 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	0.9669 ± 0.0017	−505 ± 15
waste stabilization pond	eff	Dec 2013	1.04	0.9755 ± 0.0021	−105 ± 15
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9823 ± 0.002	−120 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	0.9836 ± 0.0016	−130 ± 15
waste stabilization pond	eff	Dec 2013	1.04	0.9812 ± 0.0016	−75 ± 20
waste stabilization pond	influent WW	Dec 2013	1.04	0.9852 ± 0.0017	185 ± 30
waste stabilization pond	influent sludge	Dec 2013	1.04	0.9967 ± 0.0021	−165 ± 15
waste stabilization pond	eff	Dec 2013	1.04	1.0078 ± 0.0018	2145 ± 15
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9947 ± 0.0017	−205 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	0.9928 ± 0.0017	−225 ± 20
waste stabilization pond	eff	Dec 2013	1.04	0.9848 ± 0.0021	75 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	1.0011 ± 0.0017	150 ± 15
waste stabilization pond	influent sludge	Dec 2013	1.04	1.0652 ± 0.0018	490 ± 15
waste stabilization pond	eff	Dec 2013	1.04	1.0137 ± 0.0017	190 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	1.0155 ± 0.0017	520 ± 20
waste stabilization pond	influent sludge	Dec 2013	1.04	1.0167 ± 0.0018	110 ± 15
waste stabilization pond	eff	Dec 2013	1.04	1.0098 ± 0.002	390 ± 20
waste stabilization pond	eff sludge	Dec 2013	1.04	0.9771 ± 0.003	115 ± 15
waste stabilization pond	influent WW	Dec 2013	1.04	1.0212 ± 0.0019	275 ± 20
waste stabilization pond	influent sludge	Dec 2013	1.04	0.7656 ± 0.0013	60 ± 15
waste stabilization pond	eff	Dec 2013	1.04	1.0267 ± 0.0017	795 ± 30
waste stabilization pond	eff eludge	Dec 2013	1.04	1.0292 ± 0.0021	0 ± 15

[a]Key: eff = effluent; sec = secondary; WW = wastewater; TF = trickling filter; ASP = activated sludge process. [b]Negative values of years before present that were much less than −500 were replaced with " >modern". [c]Levin et al., 2013.[52]

$$\left[\frac{^{14}C}{^{12}C}\right]_{\text{sample}[-25‰]} = \left[\frac{^{14}C}{^{12}C}\right]_{\text{sample},\delta‰}\left[\frac{1+\frac{-25}{1000}}{1+\frac{\delta}{1000}}\right]^2 \quad (2)$$

and

$$\delta = \left[\frac{\left[\frac{^{13}C}{^{12}C}\right]_{\text{sample}}}{\left[\frac{^{13}C}{^{12}C}\right]_{\text{standard}}} - 1\right] \times 1000 \quad (3)$$

and $(^{14}C/^{12}C)_{OX1,-19}$ is $^{14}C/^{12}C$ ratio of OX1 at its actual ^{13}C value of −19‰ (i.e., not normalized to −25‰).

Fossil Carbon Contribution. Since the sample Fm (Fm_s) is made up of background carbon signature and fossil carbon signature, and since fossil radiocarbon is ^{14}C-free (thus $Fm_f = 0$), knowing the Fm of the atmosphere around the time of sampling (i.e., background Fm or Fm_b), one can calculate the fossil contribution to the sample if Fm_s is lower than Fm_b. The fossil carbon contribution of a sample can be calculated using the isotopic mass balance[37]

$$Fm_s = x_b \cdot Fm_b + x_f \cdot Fm_f \quad (4)$$

$$x_b + x_f = 1 \quad (5)$$

where x_b is the fraction of sample containing background atmospheric radiocarbon Fm_b, x_f is the fossil radiocarbon contribution to sample, and Fm_f is the fossil radiocarbon signature. From the combination of eqs 4 and 5 the following equation can be derived:[13,20]

$$x_f = 1 - \frac{Fm_s}{Fm_b} \quad (6)$$

Fm_b, the ^{14}C signature of unpolluted background air (1.04–1.05 in this study, Table 1), has been decreasing with time after 1963 due to the exchange of bomb-^{14}C in the atmosphere with the carbon reservoirs in the ocean and land, and due to the Suess effect.[38] Besides the temporal variation, Fm_b also changes with latitude, controlled by the global atmospheric circulation. Its value in specific time and latitudinal zone can be found in literature that compiled data from either direction measurements or extrapolations.[39] Thus, the fossil carbon contribution of a sample, x_f, can be estimated from the measured values, Fm_s and the Fm_b, with respect to its location and time from the literature.[39]

CO_2-Equivalent Emission Potential. In this study, only carbonaceous matter was used to calculate the CO_2 equivalent emission potential ($mCO_{2,eq}$). For biogas, all was assumed to be combusted to CO_2 for energy recovery. The daily $CO_{2,eq}$

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

Table 2. Compilation of Fossil Carbon Contribution (x_f) in Each WRRF Processes from Literature

data source	this study	Griffith et al., 2009	O'Sullivan et al., 2010	Nara et al., 2010	Law et al., 2013	Schneider et al., 2015
groundwater	0.098					
	0.069					
	0.302					
	0.384					
tap water	0.214					
	0.104					
	−0.105[a]					
	0.161					
	0.066					
domestic sewage				0.401		
				0.517		
				0.395		
primary influent	−0.004			0.268	0.002	
	0.021			0.215	−0.433[a]	
	0.090			0.159	0.001	
	0.076				0.098	
	0.279				0.113	
					0.138	
					0.175	
					0.081	
					0.171	
					0.037	
					0.134	
					0.065	
					0.137	
primary sludge	0.005					
	0.009					
	0.052					
primary effluent	0.192	0.090				
	0.054	0.082				
	−0.589[a]	0.128				
	0.040	0.105				
	0.156					
mixed liquor	−1.413[a]				0.056	
	−0.397[a]				0.014	
	0.161					
ASP off-gas	0.092					0.103
	−0.247[a]					0.125
						0.153
						0.149
						0.123
						0.116
secondary sludge	0.143				0.075	
	0.162				0.077	
	0.164				0.137	
	−1.129[a]				0.135	
	0.156				0.076	
					0.071	
secondary effluent	0.210	0.208		0.268	−0.662[a]	
	0.485	0.241			−0.066	
	0.207	0.201			0.092	
		0.187			0.091	
		0.193			0.165	
		0.238			0.148	
		0.051			0.183	
		0.247			0.148	
		0.212			0.082	
		0.296			0.076	
		0.288			0.109	
		0.290			0.079	
		0.324				

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

Table 2. continued

data source	this study	Griffith et al., 2009	O'Sullivan et al., 2010	Nara et al., 2010	Law et al., 2013	Schneider et al., 2015
		0.234				
		0.273				
		0.505				
		0.151				
		0.178				
		0.132				
		0.055				
		0.109				
		0.117				
		0.146				
		0.200				
		0.122				
		0.458				
		0.674				
		0.115				
		0.108				
trickling filter sludge	−0.201[a]					
	0.170					
trickling filter effluent	−1.048[a]					
	0.122					
digester biogas	−0.374[a]		0.015		0.018	
	−0.377[a]		0.006		0.021	
	0.025		0.015		0.023	
	0.027		0.006		0.019	
	−0.069[a]				0.022	
	−0.132[a]					
digester biosolids	-0.251[a]				0.120	
	0.155				0.102	

[a]Negative x_f values were not included in the GHG analyses due to elevated input of ^{14}C.

production rate from CH_4 in the biogas ($mCO_{2,eq}|_{CH4}$) was calculated by converting the daily CH_4 production to $CO_{2,eq}$ using the stoichiometric conversion 2.75 kg_{CO2} kg_{CH4}^{-1}.[34]

$$mCO_{2,eq}|_{CH_4} = \left.\frac{dCO_{2,eq}}{dt}\right|_{CH_4}\left[\frac{kg_{CO_2}}{d}\right] = W_{BG}\left[\frac{m^3_{BG}}{d}\right]\cdot y_{CH_4,BG}\left[\frac{m^3_{CH_4}}{m^3_{BG}}\right]\cdot\rho_{CH_4}\left[\frac{kg_{CH_4}}{m^3_{CH_4}}\right]\cdot 2.75\left[\frac{kg_{CO_2}}{kg_{CH_4}}\right] \quad (7)$$

where ρ_{CH4} is the density of CH_4, $y_{CH4,BG}$ is the concentration of CH_4 in biogas (BG), and W_{BG} is the biogas production rate. The daily $CO_{2,eq}$ production rate from the CO_2 in the biogas ($mCO_{2,eq}|_{CO2}$) was calculated as

$$mCO_{2,eq}|_{CO_2} = \left.\frac{dCO_{2,eq}}{dt}\right|_{CO_2}\left[\frac{kg_{CO_2}}{d}\right] = W_{BG}\left[\frac{m^3_{BG}}{d}\right]\cdot y_{CO_2,BG}\left[\frac{m^3_{CO_2}}{m^3_{BG}}\right]\cdot\rho_{CO_2}\left[\frac{kg_{CO_2}}{m^3_{CO_2}}\right] \quad (8)$$

where $y_{CO2,BG}$ is the concentration of CO_2 in biogas and ρ_{CO2} is the density of CO_2. Hence, the total daily $CO_{2,eq}$ production rate from biogas $mCO_{2,eq}|_{BG}$ ($kg_{CO2,eq}$ d^{-1}):

$$mCO_{2,eq}|_{BG} = \left.\frac{dCO_{2,eq}}{dt}\right|_{BG} = mCO_{2,eq}|_{CH_4} + mCO_{2,eq}|_{CO_2} \quad (9)$$

was normalized to the wastewater flow Q_{ww} treated by the specific plant, to yield the $CO_{2,eq}$ emission intensity from biogas $\lambda CO_{2,eq}|_{BG}$:

$$\lambda CO_{2,eq}|_{BG} = \left.\frac{dCO_{2,eq}}{dV_{ww}}\right|_{BG}\left[\frac{kg_{CO_2}}{m^3_{ww}}\right] = \frac{\left.\frac{dCO_{2,eq}}{dt}\right|_{BG}\left[\frac{kg_{CO_2}}{d}\right]}{\frac{dV_{ww}}{dt}\left[\frac{m^3_{ww}}{d}\right]} = \frac{\left.\frac{dCO_{2,eq}}{dt}\right|_{BG}\left[\frac{kg_{CO_2}}{d}\right]}{Q_{ww}\left[\frac{m^3_{ww}}{d}\right]} \quad (10)$$

The output of eq 10 (i.e., $\lambda CO_{2,eq}|_{BG}$) represents the amount of CO_2-equivalent associated per unit wastewater capacity of the treatment plant, attributable to the biogas.

The stabilized digester sludge was assumed to become biosolids for land application and have no $\lambda CO_{2,eq}$ output from the top soil during the time scale of up to almost 200 years.[35] The $\lambda CO_{2,eq}$ of volatile suspended solids (VSS), for example from secondary waste activated sludge (WAS) (ex., $\lambda CO_{2,eq}|_{VSS,SS}$), was calculated by applying the conversion to COD 1.95 kg_{CO2} kg_{VSS}^{-1}.[34] The $\lambda CO_{2,eq}$ of the COD in the wastewater liquid, for example in the influent wastewater (ex., $\lambda CO_{2,eq}|_{COD,PI}$), was calculated by applying the conversion 0.99 kg_{CO2} kg_{COD}^{-1}.[36] The $\lambda CO_{2,eq}$ were normalized to the volume of wastewater treated in

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

the treatment plant using the WAS flow rate and the volume wastewater treated by the specific treatment plant.

$$\lambda CO_{2,eq}|_{VSS,SS}\left[\frac{kg_{CO_2}}{m^3_{ww}}\right] = \frac{dCO_{2,eq}}{dV_{ww}}\bigg|_{VSS,SS}\left[\frac{kg_{CO_2}}{m^3_{ww}}\right] = VSS\left[\frac{kg_{VSS}}{m^3_{ww}}\right]\cdot 1.95\left[\frac{kg_{CO_2}}{kg_{VSS}}\right] \quad (11)$$

$$\lambda CO_{2,eq}|_{COD,PI}\left[\frac{kg_{CO_2}}{m^3_{ww}}\right] = \frac{dCO_{2,eq}}{dV_{ww}}\bigg|_{COD,PI}\left[\frac{kg_{CO_2}}{m^3_{ww}}\right] = COD\left[\frac{kg_{COD}}{m^3_{ww}}\right]\cdot 0.99\left[\frac{kg_{CO_2}}{kg_{COD}}\right] \quad (12)$$

$$\Lambda CO_{2,eq}|_{VSS,SS}\left[\frac{kg_{CO_2}}{m^3_{WW}}\right] = \lambda CO_{2,eq}|_{VSS,SS}\cdot\frac{Q_{WAS}[m^3/d]}{Q_{WW}[m^3/d]} \quad (13)$$

where $\lambda CO_{2,eq}|_{COD,PI}$ is the plant wastewater capacity-normalized CO_2-equivalent from the primary influent, $\lambda CO_{2,eq}|_{VSS,SS}$ is the plant wastewater capacity-normalized CO_2-equivalent from the secondary sludge, and $\Lambda CO_{2,eq}|_{ww}$ is the plant wastewater capacity-normalized CO_2-equivalent while taking WAS production into consideration. The units of $\Lambda CO_{2,eq}|_{ww}$ come from $\lambda CO_{2,eq}|_{VSS,SS}$ (in WAS VSS concentration units of kg CO_2-equivalent from VSS m^{-3}_{WW}) multiplying Q_{WAS}, resulting in kg CO_2-equivalent from VSS generated d^{-1}. Then, dividing by the Q_{WW} results in kg CO_2-equivalent from VSS generated per m^3 wastewater flowing into the WRRF, thus normalizing the CO_2-equivalent emission potential to the wastewater treated by the WRRF.

RESULTS AND DISCUSSION

Radiocarbon Dating. *WRRFs.* The Fm and ^{14}C age for all samples are listed in Table 1, and their subsequent fossil contribution results are listed in Table 2. We could not apply our model (eq 6) to most of the samples from Plant 1 due to their Fm being much greater than Fm_b ($1.30 < Fm_s < 2.51$), giving extremely unusual corresponding negative values (years before present) as their carbon age (Table 1, detailed explanations in the next paragraph) and x_f values much less than zero. The extreme Fm values possibly resulted from having unknown amounts of ^{14}C inputs from industrial wastewater to Plant 1; however, known quantities of radiolabeled tracers in wastewater could be utilized to probe the fate and transport of a contaminant throughout the WRRFs. With data from other WRRFs having Fm_s around Fm_b or less than Fm_b indicating fossil carbon presence, giving corresponding x_f in the range of around or greater than zero, the primary influent to the WRRFs studied resulted in fossil carbon contribution $-0.004 < x_f < 0.279$ (Table 2), confirming that WRRFs receive both biogenic and petrochemical products. The influent contained particulate matter from the food refuse ground in sink disposals; thus, primary sludge also had low fossil carbon contribution (average $x_f = 0.022 \pm 0.026$, $N = 3$). Conversely, the oil refinery wastewater had the expected high fossil carbon contribution ($x_f = 0.983 \pm 0.0005$, $N = 4$; Table 1) given the almost exclusively fossil nature of its carbonaceous constituents. Since the oil refinery wastewater was exposed to atmospheric air, gas exchange may explain the slightly more modern radiocarbon signature in the wastewater. In contrast, the paper pulp wastewater showed a modern radiocarbon signature (average Fm 1.02, $x_f = 0.023$, $N = 2$) that resembled that of the ambient $^{14}CO_2$ background. Thus, different wastewaters contain varying radiocarbon signatures, and each wastewater process stream could have unique fossil GHG emission.

As mentioned above, most of the samples from Plant 1 had a radiocarbon signature that had Fm much greater than 1, having ^{14}C much more enriched in the samples than in the background atmosphere at the time of sampling (Table 1). Our investigation revealed that although Plant 1 is a municipal WRRF, it received approximately 10% of industrial wastewater; thus, it was likely that a source of ^{14}C other than the background atmosphere contributed a substantial amount of ^{14}C (albeit at legal levels) and skewed the radioisotopic signature of the wastewater influent. In fact, the radiolabeling facilities within Plant 1's collection service area may have contributed to the ^{14}C-enriched input. Since it was impossible to correct for the enriched ^{14}C from Plant 1 influent due to the unknown quantity of ^{14}C input, and since our model (eq 6) only accounted for two origins of carbon (background and fossil), we could not apply our model to the data from Plant 1. Subsequently, Plant 1 data having ^{14}C content much higher than the atmospheric background were not included in the GHG analyses below.[40]

Elevated ^{14}C in wastewater has been reported in previous studies, though not at the high level observed here (Table 1). Griffith et al. (2009) and Law et al. (2013) have both attributed the elevated ^{14}C to biomedical tracer waste contamination.[12,13] Since the off-gas sample collected from ASP contained atmospheric CO_2 introduced into the treatment basin via aeration, and also CO_2 generated in the ASP through microbial respiration, the presence of excess ^{14}C in the off-gas sample (Table 1) suggests that ASP microorganisms are able to metabolize the ^{14}C-enriched substrate to CO_2. In addition, the high levels of ^{14}C in both the ASP and trickling filter effluents also imply that microorganisms may be able to assimilate ^{14}C-enriched substrate for biomass growth, leaving elevated ^{14}C microbial byproducts in both treatment effluents[10] (Table 1); alternatively, the elevated ^{14}C in sludge leaving both secondary treatment processes may suggest that the compounds containing ^{14}C have a chemical affinity for microbial flocs, since many manmade ^{14}C-labeled materials are in the form of organic compounds, such as amino acids. Based on the data collected here, the effluent of the tricking filter contains approximately 1.5×10^{-9} mg L^{-1}, or 7.1 μCi L^{-1} (natural levels are in the pCi L^{-1} range), of ^{14}C, while the ASP effluent contains approximately 1.0×10^{-9} mg L^{-1}, or 4.8 μCi L^{-1}. The presence of excess ^{14}C in WRRF effluent was also noted in a previous study by Davisson et al. (1999), who analyzed radiocarbon in the mixing and transport of injected recycled water in the groundwater basin and detected elevated levels of both ^{14}C and ^{3}H.[41]

Data from the anaerobic digester of Plant 1 also indicate ^{14}C enrichment in both the biosolids and digester biogas (Table 1). These values for CH_4 and CO_2 samples isolated from the anaerobic digester should be interpreted as indicative only of the ^{14}C content of the substrate and the microbial processes present

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

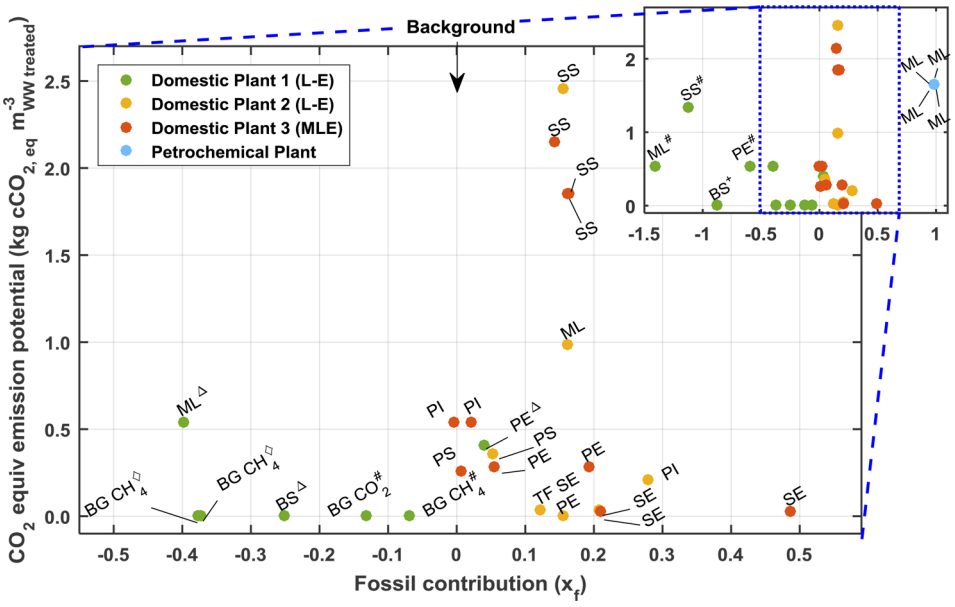


Figure 2. Fraction fossil carbon contribution (relative to background unpolluted atmosphere) of the samples collected from three water resource reclamation facilities (WRRFs) with their carbon dioxide emission equivalent from carbonaceous matter ($cCO_{2,eq}$). Secondary sludge (SS) had the highest CO_2 emission equivalent while having a relatively modern radiocarbon signature. In contrast, secondary effluent (SE) on average had a low CO_2 emission potential while having an older radiocarbon signature. Expectedly, petrochemical wastewater (WW) had the oldest carbon signature and a high CO_2 emission potential. A possible source may be contributing $_{14}C$ to Plant 1; thus, there were drastically different results at the same treatment locations on different days of sampling (denoted by ◇, + , #, and Δ for May 2011, June 2011, October 2011, and August 2013) having a Fm range of 0.95−2.51.[51] Key: PI, primary influent; PE, primary effluent; ML, mixed liquor; SE, secondary effluent; PS, primary sludge; TF, trickling filter; BS, biosolids; BG, biogas.

in the digester and not compared to atmospheric background ^{14}C levels, as CH_4 is synthesized on-site in airtight digesters.

The results for Plant 1 demonstrate the potential of radiocarbon tracer as a diagnostic tool for the fate of ^{14}C in different processes of WRRFs. Additionally, although the chemical forms of the ^{14}C-containing molecules present in Plant 1 were unknown, the results from this site present insights into the microbial biomass preferential partitioning to remove ^{14}C in a wastewater treatment plant, or insights into the diversity of molecules that are formed by the biomass during the treatment processes.[10] As such, a safe low-level radiolabeled tracer with known chemical properties could be utilized to probe the behavior of a particular contaminant of interest through the treatment process with little human health or environmental risk.

For Plants 2 and 3, the primary effluent on average had a slightly older carbon signature than primary influent, with x_f being 0.134 ± 0.0716 (N = 4) and 0.099 ± 0.156 (N = 5), respectively (Tables 1 and 2). The higher ^{14}C content (suggesting a lower fossil carbon contribution) in the influent settled from the influent as primary sludge (average x_f = 0.022 ± 0.026, N = 3; Tables 1 and 2) and was not transported to the secondary treatment in the effluent stream. Since primary effluent had more fossil carbon, it may indicate that fossil carbon entered WRRFs in the soluble form (i.e., sCOD), while influent modern carbon was particulate in nature (i.e., pCOD). The results suggest that food and human waste which are derived from modern carbon may be indeed be particulate and settle easily, and that the primary treatment process may selectively determine the fate of modern and fossil carbon fraction in the influent.

As the treatment progressed to ASP, an even older radiocarbon signature emerged from Plants 2 and 3, with x_f ranging from 0.122 to 0.485 (Tables 1 and 2). Generally, secondary sludge, mixed liquor, and secondary effluents from ASP and trickling filter had similar and consistent radiocarbon signature. The effluent of the ASP had significantly older radiocarbon signature than the primary effluent (N = 3 and 3, respectively; χ^2 test, p < 0.05), suggesting that ASP may remove and metabolize modern carbon more effectively than it does fossil carbon at Plants 2 and 3; inversely, the results may suggest that the biomass in ASP assimilates fossil carbon more effectively. Indeed, the off-gas from the ASP in Plant 2 had a more modern radiocarbon signature, with x_f of 0.092 (Tables 1 and 2). Thus, the results from Plants 2 and 3 did not show that microorganisms prefer to use modern carbon for carbon assimilation as suggested by Raymond and Bauer (2001).[16] Instead, our results might even suggest that microorganisms prefer assimilating the carbon forms of fossil origin. In general, the two plants had a similar distinct, older radiocarbon signature in the secondary treatment processes stream.

The anaerobic digester, receiving both primary and secondary sludge, produced biogas and biosolids with two distinct radiocarbon signatures in Plant 2. The biogas had a more modern radiocarbon signature compared to that of the ASP off-gas, with x_f of 0.025 in the CH_4 portion of the biogas and 0.027 in the CO_2 portion. The biogas fossil contribution was similar to that of the primary sludge (average x_f = 0.029, N = 2), while the fossil contribution of biosolids from Plant 2 (x_f = 0.155) was similar to that of the secondary sludge (x_f = 0.156 ± 0.001, N = 3; Table 2). This suggests that anaerobic digesters may also selectively determine the fate of modern and fossil carbon fraction, and that primary sludge may be more easily digested to biogas. Our results do not suggest that different microbial populations within the anaerobic digester utilize modern and fossil carbon differently from the ASP microbial population; rather, a more modern digester biogas than the digested biosolids

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

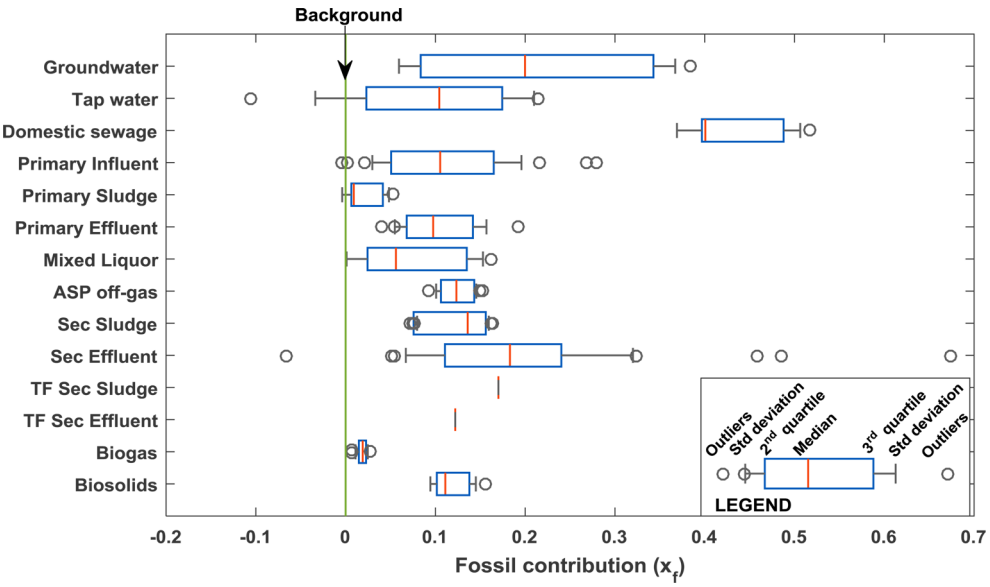


Figure 3. Compilation of wastewater radiocarbon data from this study and from literature.[12,13,15,45,46] This analysis shows that the presence of fossil carbon in the wastewater is prevalent in our study and literature studies, varying fossil carbon content during different wastewater treatment processes, and a strong agreement on the fossil content for some of the wastewater treatment process (i.e., primary effluent, ASP off-gas, biogas, and biosolids). $N_{groundwater}$ = 4, $N_{tap\ water}$ = 4, $N_{domestic\ sewage}$ = 3, $N_{primary\ influent}$ = 20, $N_{primmary\ sludge}$ = 3, $N_{primary\ effluent}$ = 8, $N_{mixed\ liquor}$ = 3, $N_{ASP\ off\text{-}gas}$ = 7, $N_{sec\ sludge}$ = 10, $N_{sec\ effluent}$ = 42, $N_{TF\ sec\ sludge}$ = 1, $N_{TF\ sec\ effluent}$ = 1, N_{biogas} = 11, and $N_{biosolids}$ = 3 (see Table 2). Key: ASP, activated sludge process; Sec, secondary; TF, trickling filter.

implies that modern carbon was preferentially utilized by the methanogenic microbial consortia inside the digester.

The results for the two industrial wastewaters sampled in this study (Table 1) illustrate the wide range of radiocarbon ages present in waste streams. Both types of industrial wastewater measurements may contain carbon from industrial waste and also from any organic chemicals, such as carbonate for pH adjustment or organic polymers for coagulation, added in the treatment process. The oil refinery wastewater with an average Fm of 0.018 ± 0.0005 (N = 4) indicates an origin almost entirely fossil (x_f = 0.983 ± 0.0005, N = 4). Nearly all the CO_2 generated by the oil refinery would be most accurately viewed as a net contribution of fossil GHG to the atmosphere.

The influent to the plant treating pulp/paper mill industrial wastewater was modern with x_f of only 0.078. After treatment, the effluent was found to have similar ^{14}C enrichment (Fm = 1.07, x_f = −0.031; Tables 1 and 2) as the background atmospheric radiocarbon signature due to exposure to ambient air. This industrial treatment plant represents the opposite end point to the refinery plant; its carbon load was primarily modern, and the IPCC's assumption of rapidly cycling, biogenic carbon is potentially valid for its emissions. Other major industries that involve processing of agricultural products, including beer and wine production, dairy, meat, and poultry processing, vegetable oil manufacturing, and sugar refining, may have a radiocarbon signature similar to that of pulp/paper production in the waste stream, suggesting IPCC's assumption potentially being valid for them as well.

Waste Stabilization Ponds. The radiocarbon signature of the four sample types in the waste stabilization ponds were not significantly independent of each other (Supporting Information Figure S-2), analyzed using the χ^2 test, with a narrow Fm average range from 0.96 to 1.00. All except one sample had fossil carbon contribution within the range of 0.008−0.264, which was within the range found in the primary treatment of Plants 2 and 3. The radiocarbon signature also did not appear to change through the waste stabilization pond treatment. Moreover, the results did not show any microbial preferences in carbon assimilation for radiocarbon during the treatment.

CO_2 Equivalent Potential Emission from WRRFs. The comparison of $\lambda CO_{2,eq}|_{ww}$ for WRRF samples to the fossil carbon contribution is presented graphically in Figure 2. Focusing on results from Plants 2 and 3 only, primary influent, effluent, and sludge have a more modern radiocarbon signature (x_f = 0.094 ± 0.103, N = 12) and a range of 0.00 < $\lambda CO_{2,eq}|_{ww}$ < 0.54 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$; secondary sludge had the highest $\lambda CO_{2,eq}|_{ww}$ (1.39−1.84 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$) with an older radiocarbon signature (x_f = 0.156 ± 0.010, N = 4); and secondary effluent on average had a low $\lambda CO_{2,eq}|_{ww}$ (0.03−0.04 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$) with an even older radiocarbon signature (x_f = 0.256 ± 0.158, N = 3). These translate to average potential fossil CO_2-equivalent emissions of 0.016, 0.294, and 0.010 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$ from primary treatment, secondary sludge, and secondary effluent, respectively. Our analysis of fossil $\lambda CO_{2,eq}|_{ww}$ indicates that although secondary effluent had the oldest carbon signature, secondary sludge had a much higher potential to produce fossil carbon GHG than primary treatment and secondary effluent.

Our calculation also showed that biogas (average x_f = 0.026, N = 2) and biosolids (x_f = 0.155) had relatively low $\lambda CO_{2,eq}|_{ww}$ of 0.206 and 0 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$, respectively. We then found their respective fossil $\lambda CO_{2,eq}|_{ww}$, 0.005 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$ and 0 $kg_{CO2,eq}\ m_{ww\ treated}^{-3}$. Comparing these with the results from secondary sludge, while secondary sludge had similar x_f as biosolids, secondary sludge would still have the highest potential to release fossil GHG from a WRRF if no further treatment were applied to it. Since stabilizing secondary sludge would reduce the overall GHG emission from WRRFs, it would also decrease the fossil carbon GHG emission simultaneously.[34,35] Therefore, additional secondary sludge treatment such as stabilizing sludge for energy recovery and then land application of the biosolids product could be employed to mitigate the potential GHG emission associated with untreated secondary sludge.

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

For industrial WRRFs, however, there are currently 140 oil refineries in operation in the U.S. with a combined distillation capacity of over 1.7×10^7 barrels per day according to data published by the U.S. Energy Information Administration.[42] The wastewater generated per barrel of petroleum refined varies from 37.9 to 397.5 L;[43,44] thus, 6.4×10^5 to 6.8×10^6 m^3 of refinery wastewater is generated per day in the U.S. alone. The IPCC reports a typical COD range of 400−1600 mg L^{-1} for refinery wastewater, with an average of 1000 mg L^{-1}.[8] Using the average COD of 1000 mg L^{-1}, approximately 1.35 $kg_{CO2,eq}$ $m_{ww\ treated}^{-3}$ would be released, corresponding to an emission of 8.6×10^5 to 9.2×10^6 $kg_{CO2,eq}$ d^{-1}, with 8.4×10^5 to 9.0×10^6 $kg_{CO2,eq}$ d^{-1} being fossil.

Comparison to other WRRFs. A compilation of literature ^{14}C studies in wastewater[12,13,15,45,46] (Table 2) in combination with the current study's results along the wastewater treatment processes is presented in Figure 3. The outliers with excessively elevated ^{14}C input were not included in the analysis, as ^{14}C-contaminated samples were not naturally occurring (and with unpredictable input quantity in the case of Plant 1).[12,13] All of the medians, means, and second and third quartiles of these data were found to be more fossil than modern, suggesting most of the samples taken in municipal wastewater treatment plants contained some fossil carbon. Since these data from the U.S., Canada, Japan, and Australia do not represent influents to wastewater treatment of the whole world, we cannot use these data to speculate on the fossil contribution of municipal wastewater in developing countries. Similarly, we only had one data set available for the secondary treatment trickling filter sludge and effluent (Figure 3, Table 2; thus, we cannot infer generally about the radiocarbon in biofilm treatment processes.

While domestic sewage may contain relatively high fossil content (Figure 3), primary influent appeared to have similar fossil content as the tap water, suggesting possible mixing of domestic sewage with ambient air or possible inputs from other water sources, such as irrigation or precipitation, during transport to the WRRFs. After the primary treatment, primary sludge was separated from primary effluent and appeared to contain higher proportion of modern carbon than the primary effluent (Figure 3). Since the primary sludge exhibited a radiocarbon signature more similar to that of the background atmosphere, this indicates that our hypothesis that food and human waste are mostly particulates also tested true in the WRRFs from literature data.

After primary and secondary sludge were sent to digestion for energy recovery and stabilizing biosolids, biogas was produced (Figure 1). Although the biogas results are a combination of this study and that of O'Sullivan et al. (2010),[45] the data agree well with a narrow range of fossil carbon content of 0.006−0.027 (Figure 3; Table 2). While a mix of both primary (radiocarbon signature near modern) and secondary sludge (radiocarbon signature with higher fossil carbon content) was digested, the biogas appeared to have a radiocarbon signature that is more comparable to primary sludge (near modern), and the biosolids produced exhibited a radiocarbon signature comparable to that of secondary sludge (Figure 3, Table 2). The results confirm that primary sludge organic material was more easily digested and contributed to the more modern radiocarbon signature of biogas and that the biosolids retained more fossil carbon, due to the lower biodegradability of secondary sludge.[36,47] Thus, this reinforces the idea that if sludge is used to produce biogas for energy recovery, little fossil carbon would be directly released as GHG. Likewise, since low $\lambda CO_{2,eq}|_{ww}$ is associated with the land application of biosolids, such stabilized biosolids, which contained more fossil carbons, would not generate much direct GHG emission in a short time span.[34,35] However, there have been efforts underway to achieve more complete digestion of secondary sludge through technologies such as thermal hydrolysis.[53−55] Thus, understanding the radiocarbon composition of the CO_2 in the biogas would be more important for these technologies since the fossil carbon in the sludge could be more easily released in the form of biogas.

Implications of Fossil Carbon in GHG Emission. Our study suggests that the IPCC accounting methodologies thus far overlooked a portion of the GHG release from WRRFs, i.e., the amount attributable to carbon of fossil origin in wastewater. In fact, the current IPCC method for WRRFs and the others aligned with it only account for CH_4 and N_2O emissions. However, a compilation of wastewater radiocarbon data from this study and from literature reveals a relevant prevalence of fossil carbon content in the wastewater (Table 2), and even a strong agreement on the fossil carbon content during some of the treatment processes, such as in primary sludge, ASP off-gas, biogas, and biosolids (Figure 3, Table 2).

To calculate the omitted fossil CO_2 contribution in direct GHG emissions from municipal WRRFs, we used typical Southern California municipal WRRF GHG emission rate of CO_2, CH_4, and N_2O, approximately 0.197, 0.044, and 0.018 $kg_{CO2,eq}$ $m^{-3}_{wastewater\ treated}$, respectively.[57] Using the IPCC method by adding up only CH_4 and N_2O emissions, a typical municipal WRRF would generate about 0.062 $kg_{CO2,eq}$ m^{-3}wastewater treated. However, we calculated that an average WRRF releases direct fossil CO_2 emissions at the rates of 0.006 and 0.008 $kg_{CO2,eq}$ $m^{-3}_{wastewater\ treated}$ from energy recovery biogas combustion and ASP off-gas, respectively, by combining our results of CO_2-equivalent emission from Figure 2 and fossil carbon contribution from Table 2. If fossil CO_2 were accounted for by adding the fossil CO_2 emission to the CH_4 and N_2O emissions, a typical municipal WRRF would generate about 0.077 and 0.070 $kg_{CO2,eq}$ m^{-3}wastewater treated with and without an on-site energy recovery system, respectively. This means with an on-site energy recovery system, including the fossil-origin CO_2, may increase the original IPCC GHG inventory by 22.8%, and by 12.6% if without an on-site energy recovery system. Compared to Law et al.,[13] who estimated 2−12% increase in GHG accounting if fossil CO_2 were included to the IPCC estimation, our estimation for typical Southern California WRRFs without on-site energy recovery was just above the high end of the estimation by Law et al. Therefore, to estimate more accurately the fossil CO_2 release from WRRFs in a specific area or a general region, there is a need to fill the data gap on wastewater radiocarbon fractions, supporting the various current efforts in monitoring and modeling WRRF GHG release.

In addition, our results suggested the practice of digesting secondary sludge and using stabilized biosolids for agricultural biosolids may help mitigate some of the long-term fossil CO_2 emissions,[56] while some of the short-term high-fossil-carbon content in the direct emissions by ASP off-gas (Table 2) opens up the opportunity to develop an on-site carbon sequestration technology to capture the release of gaseous carbon emission. To reduce WRRF GHG emissions from ASP, current technologies known as carbon capture and usage (CCU) exist, which utilize CO_2 to synthesize chemical products such as methanol, formic acid, and hydrocarbons.[48−51] These technologies might capture and convert the ASP CO_2 off-gas to viable products, while abating GHG emission, especially if operated with energy input from renewable sources.

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

By analyzing the fossil carbon contribution in samples from different treatment process and estimating the GHG emissions from WRRFs, our study found varying fossil content in the wastewater during the WRRF processes and in different types of WRRFs and highlights the need for more efforts in combining radiocarbon monitoring with GHG accounting to address the impact of fossil CO_2 on direct GHG emissions. Furthermore, this study draws attention to the current assumption of IPCC's method for carbon accounting in WRRFs that may not be applicable to all types of WRRFs and also presents the implications of digesting sludge for energy recovery and subsequently applying to land or burying biosolids, where the release to atmosphere of the fossil carbon in the digested sludge may be retarded or prevented.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02731.

Figure S-1 (oven-dried sludge vs a lyophilized sludge sample), Figure S-2 (fraction modern (Fm) of the four sample types from the waste stabilization ponds in Australia), and Table S-1 (summary of operating conditions of Plants 1, 2, and 3) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ltseng@colgate.edu. Phone: 315-228-7095.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the Water-Energy Nexus Center (formerly Urban Water Research Center) at the University of California, Irvine (UC Irvine), the U.S. National Science Foundation Partnerships for International Research and Education (OISE-1243543), and the UC Irvine Faculty Mentor Program Diversity Fellowship to L.Y.T. We thank Stuart Harris, Regan Barratt, and Erin Szantyr of Goulburn Valley Water for arranging access to the waste stabilization pond systems in Australia. We are thankful to Drs. Stanley Grant, Barbara Cottrel, and Kartiki Naik for their feedback that led to the improvement of this work. We are also thankful for the valuable suggestions from the anonymous reviewers for further improvement of the manuscript.

■ REFERENCES

(1) Ahn, J. H.; Kim, S.; Park, H.; Rahm, B.; Pagilla, K. P.; Chandran, K. N_2O emissions from activated sludge processes, 2008−2009: Results of a national monitoring survey in the United States. *Environ. Sci. Technol.* **2010**, *44* (12), 4505−4511.

(2) Daelman, M. R. J.; van Voorthuizen, E. M.; van Dongen, U. G. J. M.; Volcke, E. I. P.; van Loosdrecht, M. C. M. Methane emission during municipal wastewater treatment. *Water Res.* **2012**, *46* (11), 3657−3670.

(3) Foley, J.; de Haas, D.; Yuan, Z.; Lant, P. Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Res.* **2010**, *44* (3), 831−844.

(4) Kampschreur, M. J.; Temmink, H.; Kleerebezem, R.; Jetten, M. S. M.; van Loosdrecht, M. C. M. Nitrous oxide emission during wastewater treatment. *Water Res.* **2009**, *43* (17), 4093−4103.

(5) Ni, B.-J.; Ye, L.; Law, Y.; Byers, C.; Yuan, Z. Mathematical modeling of nitrous oxide (N_2O) emissions from full-scale wastewater treatment plants. *Environ. Sci. Technol.* **2013**, *47* (14), 7795−7803.

(6) Czepiel, P. M.; Crill, P. M.; Harriss, R. C. Methane emissions from municipal wastewater treatment processes. *Environ. Sci. Technol.* **1993**, *27*, 2472−2477.

(7) IPCC. *2006 IPCC Guidelines for National Greenhouse Gas Inventories*; Institute for Global Environmental Strategies (IGES): Hayama, Japan, 2006.

(8) IPCC. Wastewater Treatment and Discharge. In *2006 IPCC Guidelines for National Greenhouse Gas Inventories*; Institute for Global Environmental Strategies (IGES): Hayama, Japan, 2006; Vol. *5*, pp 6, 22.

(9) IPCC. Introduction. In *2006 IPCC Guidelines for National Greenhouse Gas Inventories*; Institute for Glabla Environmental Strategies (IGES): Hayama, Japan, 2006; Vol. *5*, p 5.

(10) Tseng, L. Y.; Gonsior, M.; Schmitt-Kopplin, P.; Cooper, W. J.; Pitt, P.; Rosso, D. Molecular characteristics and differences of effluent organic matter from parallel activated sludge and integrated fixed-film activated sludge (IFAS) processes. *Environ. Sci. Technol.* **2013**, *47* (18), 10277−10284.

(11) Oulton, R. L.; Kohn, T.; Cwiertny, D. M. Pharmaceuticals and personal care products in effluent matrices: A survey of transformation and removal during wastewater treatment and implications for wastewater management. *J. Environ. Monit.* **2010**, *12*, 1956−1978.

(12) Griffith, D. R.; Barnes, R. T.; Raymond, P. A. Inputs of fossil carbon from wastewater treatment plants to U.S. rivers and oceans. *Environ. Sci. Technol.* **2009**, *43* (15), 5647−5651.

(13) Law, Y.; Jacobsen, G. E.; Smith, A. M.; Yuan, Z.; Lant, P. Fossil organic carbon in wastewater and its fate in treatment plants. *Water Res.* **2013**, *47* (14), 5270−5281.

(14) Hammond, A. L. Phosphate replacements: problems with the washday miracle. *Science* **1971**, *172* (3981), 361−363.

(15) Nara, F. W.; Imai, A.; Matsushige, K.; Komatsu, K.; Kawasaki, N.; Shibata, Y. Radiocarbon measurements of dissolved organic carbon in sewage-treatment-plant effluent and domestic sewage. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2010**, *268* (7−8), 1142−1145.

(16) Raymond, P. A.; Bauer, J. E. Use of 14C and 13C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: A review and synthesis. *Org. Geochem.* **2001**, *32*, 469−485.

(17) Jeanneau, L.; Faure, P. Quantification of fossil organic matter in contaminated sediments from an industrial watershed: Validation of the quantitative multimolecular approach by radiocarbon analysis. *Sci. Total Environ.* **2010**, *408* (19), 4251−4256.

(18) Rosen, A. A.; Rubin, M. Discriminating between natural and industrial pollution through carbon dating. *J. Water Pollut. Con. F* **1965**, *37* (9), 1302−1307.

(19) Rosen, A. A.; Rubin, M. Natural carbon-14 activity of organic substances in streams. *Science* **1964**, *143* (3611), 1163−1164.

(20) Funabashi, M.; Ohara, K.; Kunioka, M. Accuracy of biobased carbon content of determination of plastic products and related materials by accelerator mass spectrometry. *Polym. Degrad. Stab.* **2014**, *109*, 385−392.

(21) Calder, J. A.; Parker, P. L. Stable carbon isotope ratios as indices of petrochemical pollution of aquatic systems. *Environ. Sci. Technol.* **1968**, *2* (7), 535−539.

(22) Spiker, E. C.; Rubin, M. Petroleum pollutatnts in surface and groundwater as indicated by the carbon-14 activity of dissovled organic carbon. *Science* **1975**, *187* (4171), 61−64.

(23) Bolzonella, D.; Pavan, P.; Battistoni, P.; Cecchi, F. The under sink garbage grinder: A friendly technology for the environment. *Environ. Technol.* **2003**, *24* (3), 349−359.

(24) ASCE. *Standard Guidelines for In-Process Oxygen Transfer Testing*; American Society of Civil Engineers (ASCE): New York, 1997; p 49.

(25) Rosso, D.; Stenstrom, M. K. Comparative economic analysis of the impacts of mean cell retention time and denitrification on aeration systems. *Water Res.* **2005**, *39* (16), 3773−80.

(26) Gasperi, J.; Garnaud, S.; Rocher, V.; Moilleron, R. Priority pollutants in wastewater and combined sewer overflow. *Sci. Total Environ.* **2008**, *407* (1), 263−272.

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178

(27) Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999−2000: A national reconnaissance. *Environ. Sci. Technol.* **2002**, *36* (6), 1202−1211.
(28) Grant, S. B.; Saphores, J.-D.; Feldman, D. L.; Hamilton, A. J.; Fletcher, T. D.; Cook, P. L. M.; Stewardson, M.; Sanders, B. F.; Levin, L. A.; Ambrose, R. F.; Deletic, A.; Brown, R.; Jiang, S. C.; Rosso, D.; Cooper, W. J.; Marusic, I. Taking the "waste" out of "wastewater" for human water security and ecosystem sustainability. *Science* **2012**, *337*, 681−686.
(29) Pack, M. A.; Xu, X.; Lupascu, M.; Kessler, J. D.; Czimczik, C. I. A rapid method for preparing low volume CH_4 and CO_2 gas samples for ^{14}C AMS analysis. *Org. Geochem.* **2015**, *78*, 89−98.
(30) Beverly, R. K.; Beaumont, W.; Tauz, D.; Ormsby, K. M.; von Reden, K. F.; Santos, G. M.; Southon, J. R. The Keck Carbon Cycle AMS Laboratory, University of California, Irvine: Status Report. *Radiocarbon* **2010**, *52* (2−3), 301−309.
(31) Stuiver, M.; Polach, H. A. Reporting of ^{14}C data. *Radiocarbon* **1977**, *19* (3), 355−363.
(32) Graven, H. D. Impact of fossil fuel emissions on atmospheric radiocarbon and various applications of radiocarbon over this century. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112* (31), 9542−9545.
(33) Reimer, P. J.; Brown, T. A.; Reimer, R. W. Discussion: reporting and calibration of post-bomb 14C data. *Radiocarbon* **2004**, *46* (3), 1299−1304.
(34) Rosso, D.; Stenstrom, M. K. The carbon-sequestration potential of municipal wastewater treatment. *Chemosphere* **2008**, *70* (8), 1468−1475.
(35) Leifeld, J.; Mayer, J. ^{14}C in cropland soil of a long-term field trial—experimental variability and implications for estimating carbon turnover. *Soil* **2015**, *1* (2), 537−542.
(36) Gori, R.; Jiang, L.-M.; Sobhani, R.; Rosso, D. Effects of soluble and particulate substrate on the carbon and energy footprint of wastewater treatment processes. *Water Res.* **2011**, *45* (18), 5858−5872.
(37) LaFranchi, B. W.; Pétron, G.; Miller, J. B.; Lehman, S. J.; Andrews, A. E.; Dlugokencky, E. J.; Hall, B.; Miller, B. R.; Montzka, S. A.; Neff, W.; Novelli, P. C.; Sweeney, C.; Turnbull, J. C.; Wolfe, D. E.; Tans, P. P.; Gurney, K. R.; Guilderson, T. P. Constraints on emissions of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range using observations of $^{14}CO_2$. *Atmos. Chem. Phys.* **2013**, *13* (21), 11101−11120.
(38) Tans, P. P.; De Jong, A. F. M.; Mook, W. G. Natural atmospheric ^{14}C variation and the Suess effect. *Nature* **1979**, *280*, 826−828.
(39) Hua, Q.; Barbetti, M.; Rakowski, A. Z. Atmospheric radiocarbon for the period of 1950−2010. *Radiocarbon* **2013**, *55* (4), 2059−2072.
(40) Keeling, C. D.; Piper, S. C.; Bacastow, R. B.; Wahlen, M.; Whorf, T. P.; Heimann, M.; Meijer, H. A., Exchanges of atmospheric CO_2 and $^{13}CO_2$ with the terrestrial biosphere and oceans from 1978 to 2000. In *I. Global aspects*; Scripps Institution of Oceanography, San Diego, CA, 2001.
(41) Davisson, M. L.; Esser, B. K.; Herndon, R. L.; Hudson, G. B. In *Tracing and age-daing recycled waste water recharged for potable reuse in a seawater injection barrier, southern California, USA*; International Symposium on Isotope Techniques in Water Resources Development and Management, Vienna, Austria, May 10−14, 1999; Vienna, Austria, 1999.
(42) United States Energy Information Administration (U.S. EIA). Petroleum & Other Liquids. http://www.eia.gov/dnav/pet/pet_pnp_cap1_dcu_nus_a.htm (accessed Oct 20, 2015).
(43) United State Environmental Protection Agency (US EPA). Water & Energy Efficiency by Sectors. http://www3.epa.gov/region9/waterinfrastructure/oilrefineries.html (accessed Oct 20, 2015).
(44) IPIECA. *Petroleum refining water/wastewater use and management*; IPIECA, 2010; p 27.
(45) O'Sullivan, G.; Min, B.-J.; Bilyk, J. M.; Ciezki, R.; Calosing, R.; Sandau, C. D. Forensic geo-gas investigation of methane: Characterization of sources within an urban setting. *Environ. Forensics* **2010**, *11* (1−2), 108−116.
(46) Schneider, A. G.; Townsend-Small, A.; Rosso, D. Impact of direct greenhouse gas emissions on the carbon footprint of water reclamation processes employing nitrification−denitrification. *Sci. Total Environ.* **2015**, *505*, 1166−1173.
(47) Gori, R.; Giaccherini, F.; Jiang, L.-M.; Sobhani, R.; Rosso, D. Role of primary sedimentation on plant-wide energy recovery and carbon footprint. *Water Sci. Technol.* **2013**, *68* (4), 870−878.
(48) Olah, G. A.; Goeppert, A.; Prakash, G. K. S. Chemical recycling of carbon dioxide to methanol and dimethyl esther: Greenhouse gas to renewable environmentally carbon neutral fuels synthetic hydrocarbons. *J. Org. Chem.* **2009**, *74*, 487−498.
(49) Centi, G.; Perathoner, S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal. Today* **2009**, *148* (3−4), 191−205.
(50) Yu, K. M. K.; Curcic, I.; Gabriel, J.; Tsang, S. C. E. Recent advances in CO_2 capture and utilization. *ChemSusChem* **2008**, *1* (11), 893−899.
(51) Müller, T. E.; Leitner, W.; Markewitz, P.; Kuckshinrichs, W. Opportunities for Utilizing and Recycling CO_2. In *Carbon Capture, Storage, and Use*; Kuckshinrichs, W., Hake, J.-F., Eds.; Springer International Publishing: Switzerland, 2014; pp 67−100.
(52) Levin, I.; Kromer, B.; Hammer, S. Atmospheric $\Delta^{14}CO_2$ trend in Western European background air from 2000 to 2012. *Tellus, Ser. B* **2013**, *65*, 20092.
(53) Abelleira, J.; Pérez-Elvira, S. I.; Portela, J. R.; Sánchez-Oneto, J.; Nebot, E. Advanced thermal hydrolysis: Optimization of a novel thermochemical process to aid sewage sludge treatment. *Environ. Sci. Technol.* **2012**, *46* (11), 6158−6166.
(54) Abelleira, J.; Pérez-Elvira, S. I.; Sánchez-Oneto, J.; Portela, J. R.; Nebot, E. Advanced thermal hydrolysis of secondary sewage sludge: A novel process combining thermal hydrolysis and hydrogen peroxide addition. *Resour. Conserv. Recy.* **2012**, *59*, 52−57.
(55) Bougrier, C.; Delgenès, J. P.; Carrère, H. Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties, and anaerobic digestion. *Chem. Eng. J.* **2008**, *139*, 236−244.
(56) Tian, G.; Granato, T. C.; Cox, A. E.; Pietz, R. I.; Carlson, C. R., Jr.; Abedin, Z. Soil carbon sequestration resulting from long-term application of biosolids for land reclamation. *J. Environ. Qual.* **2009**, *38*, 61−74.
(57) Sobhani, R.; Larson, L.; Rosso, D. Peak amplication of energy demand, energy cost, and carbon emission in water reclamation and purification processes during diurnal cycles. *Proceedings of the Water Environment Federation. Energy* **2013**, 143−152.
(58) Southon, J. R.; Santos, G. M. Life with MC-SNICS. Part II: Further ion source development at the Keck carbon cycle AMS facility. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *259*, 88−93.

DOI: 10.1021/acs.est.6b02731
Environ. Sci. Technol. 2016, 50, 12166−12178