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Abstract and summary

Sewage sludge and digester gas are used as fuels in various installations including those participating in the European Emissions Trading System (ETS). Monitoring of the emissions from such fuels shall include all carbon dioxide from fossil sources.

We analysed the distribution of biogenic and fossil carbon and potential dependencies from available data on the wastewater input characterisation based on a number of samples of sewage sludge (20) and digester gas (14) from a wide variety of municipal wastewater treatment plants (WWTPs) in Germany.

The biogenic carbon content of the sewage sludge and digester gas samples were determined by analysing the carbon-14 (^{14}C) content using a liquid scintillation counter (LSC) after combustion to CO_2. CO_2 already present in the digester gas samples was included in the analysis as this CO_2 also originates from the degradation of the contents of sewage.

Based on the results, we suggest the input to municipal WWTPs should be characterised by the share of sewage from industry compared to total water input expressed as inhabitants equivalent. The results of the study show that if the share of sewage from industry is below 45%, sewage sludge contains about 76% biogenic carbon while the respective digester gas contains about 83% biogenic carbon.

The sewage from municipal WWTPs with higher percentages of industrial wastewater (≥45%) can show significantly smaller proportions of biogenic carbon. Biogenic carbon content of about 28% to 71% were determined in sewage sludge from such wastewater plants, while the respective digester gas contained about 11% to 88% biogenic carbon.

The origin of the respective carbon content was not investigated. Sources like cleaning agents and detergents and other persistent synthetic substances among others, were considered as contributors to the fossil carbon in the sewage.

Wastewater from industries processing chemicals etc. and fossil fuels in particular, are responsible for higher proportions of fossil carbon in the sewage sludge and digester gas. Wastewater from food processing, paper, gastronomy and the hotel sector all show the same proportion of biogenic carbon as domestic sewage.

Key words: ^{14}C-analysis, LSC, wastewater treatment plant, biogenic/fossil carbon dioxide, CO_2 emissions, ETS

1 Intention

Annually about 1.8 million tons of sewage sludge (dry matter) are delivered by German municipal wastewater treatment plants (STATISTISCHES BUNDESAMT 2016; UBA 2016). Carbon dioxide (CO_2) and methane (CH_4) are produced as digester gas in the digestion tanks. Most of the sludge and gas is used as fuel either within the wastewater treatment plants (WWTP) or externally. Sludge is dewatered prior to incineration.

About 1 Mt of carbon dioxide are annually emitted into the atmosphere from the share of fuels used by German installations in the European Emissions Trading System (ETS).

Installations within the ETS have to report annual emissions to the respective competent authority. All emissions from fossil sources require the operators to surrender allowances. According to the European Monitoring and Reporting Regulation MRR (COMMISSION REGULATION (EU) No 601/2012), emissions from installations within ETS shall be monitored as accurately as economically feasible. Operators may use standard values if analyses are not economically feasible, however these standard values should not lead to an underestimation of the emissions.

Sludge from sewage treatment plants was formerly classified as pure biomass (i.e. UBA 2006). According to Appendix E of the European Standard EN 15440:2011 sewage sludge and digester gas are both seen as biomass, however, the fossil content within these materials is excluded from this classification.

There have been several studies on the origin of carbon in waste water, sewage sludge and digester gas (LAW et al., 2013; PALSTRA & MEIJER, 2014; MOHN et al., 2008) in various countries. All published data predominately show the origin of biogenic carbon produced over the last few years in these materials.

The German Emissions Trading Authority (DEHSt) at the German Environment Agency sought to gain more information on the fossil carbon content of fuels from a wide variety of wastewater treatment plants. Although we could only include 20 water treatment plants, fuels from a variety of plant sizes, as well as various indirect dischargers and regions, took part in this study.

The range of water treatment plants included very small plants of 180 inhabitants equivalent up to plants of 2.4 million inhabitants equivalent (table 1). About 90 % of Germany's wastewater is treated in plants larger than 10,000 inhabitants equivalent (FRICKE 2009). This study focussed on such plants in particular. They are situated in rural areas as well as in large municipalities. The wastewater originates from food production, breweries, catering and tourism, laundries, motorway stations, pharmaceutical companies, the chemical industry, heavy industry, paper production and refineries.

Only two installations have separate sewer systems, all others have combined sewers.

A majority of installations providing sewage sludge samples for the project use physical, chemical, and biological processes and an activated sludge process with an anaerobic sludge stabilisation. Some use aerobic sludge stabilisation. Additionally, there was sludge collected from pond treatment plants, rotary drums, trickling filters, activated sludge tanks, tank cascades, fluidised bed systems, sequential biological cleaning, dissolved nitrogen flotation and biological phosphor removal.

Although only 20 samples could be included, there is a wide variety of processes involved in order to represent the many engineering options used in Germany.

Various sources provide a large variety of substances in waste water. Human and animal wastes as well as synthetic materials from fossil sources like washing and cleaning agents, health products, medicine and all kinds of substances washed down along with the washing and cleaning agents.

2 Methodological background

The atmospheric ^{14}C-isotope is taken up by all plants and organisms using carbon dioxide for anabolism. The ^{14}C-content of the plants is equal to the atmospheric ^{14}C-content until harvested. The measured ^{14}C-results using the pmC (percent modern carbon) unit are referenced to a 1950 standard (STUIVER & POLACH, 1997).

After carbon dioxide uptake has stopped, the count rate from the β radiation reduces with a half-live of 5730 years. Carbon of some 10 000 years age (i.e. peat, lignite) still has a significant count rate whereas fossil carbon from mineral oil or hard coal does not. The basic assumption is the presence of a binary mixture of modern and fossil carbon in sewage sludge and gas.

Because of additional influxes of ^{14}C into the atmosphere from atmospheric nuclear bomb testing that peaked in the early 1960s (Levin and Kromer, 1997), ^{14}C-activity levels in the last decades were significantly higher than in the standard from 1950. Since then, the ^{14}C-activity has decreased continuously to 101.5 pmC in 2016 (EN 16640:2017).

In parallel to the radio carbon measurements, many parameters, like heating value, elementary analysis, etc. were analysed in order to find an easy-to-analyse proxy for the biogenic/fossil carbon content. One of the more promising parameters is the content of the stable ^{13}C-isotope. Due to isotope fractioning in photosynthesis and metabolism, the $\delta^{13}C$ values might serve as proxy for the overall carbon content.

3 Sampling

Samples were taken by the WWTPs personnel. The sludge samples (20) and gas samples (14) were taken in their delivery condition to incineration plants. If any post-treatment at incineration plants or other plants is done, this was not included.

4 Laboratory processes

Sludge samples were dried at 40 to 60 °C. 20 g of the sample were combusted under pure oxygen in a bomb calorimeter. 15 litres of the gas samples were combusted directly.

All samples were combusted without any further pre-treatment. There was no removal of inorganic carbon (carbonate) from the sludge as well as no separation of CO_2 already in the gas sample at delivery. The main reason being that the samples should represent the material as it is incinerated in the WWTPs or other technical processes.

All gaseous, oxidised carbon (CO_2) was absorbed in a fluid and converted to a measurement sample by addition of a scintillation fluid. The measurement was done in a liquid scintillation counter (LSC, Packard Canberra Tri-Carb 2770 TR/SL). Measuring time was 1600 minutes.

The process was evaluated according to EN 15440:2011 (appendix C.8 und C.7.1, correction factor 105 for modern biomass). In order to show the influence of the correction factor and to allow various evaluations from our findings, the results in table 1 are given in pmC as well as C_{bio} from EN 15440:2011.

The determination of $\delta^{13}C$-values was done by isotope ratio mass spectroscopy (IRMS).

5 Results and Evaluation

The results for sewage sludge in figure 1 show $\delta^{13}C$ values for the TOC between -28.0 to -24.0 $‰_{0VPDB}$. These values are pretty close to typical measurements for C3 plants and animal tissue between -32 to -20 $‰_{0VPDB}$ (CLARK & FRITZ, 1997). Without WWTP 17, mean values are -25.3 ± 0.6 $‰_{0VPDB}$. Therefore WWTP 17 was excluded because most of the sewage originates from a large chemical industry plant.

Gaseous fuels have typically lighter values due to further metabolic fractionation. Our results were $\delta^{13}C$-TC from -40.3 to -25.5 $‰_{0VPDB}$. Without WWTP 17, mean values are -29.8 ± 2.1 $‰_{0VPDB}$.

WWTP 17 contained -40.3 $‰_{0VPDB}$ in the gas: a significant difference. There had been more WWTPs with light $\delta^{13}C$-TC in the gas (WWTP 15 and 18) where no significant chemical industry sewage was treated. From $\delta^{13}C$ we could not deduce the fossil carbon content in the fuels, however there are significant differences which could be further investigated.

In sludge, we found 29.0 ± 2.5 to 93.6 ± 2.4 pmC and in digester gas 11.3 ± 1.3 to 100.8 ± 2.4 pmC (table 1). From these values using the reference value for modern biomass of 105 from EN 15440:2011, we calculated biogenic carbon contents between 28% and 89% in the sludge and 11% to 96% in digester gas. The counts of the digester gas were significantly higher than those of the sludges, except for WWTP 17, where gas and sludge have different origins (gas mainly from chemical industry sewage sludge).

Fresh biomass biologically degrades better than complex carbon molecules in the digestion process of sludge to digester gas (LAW et al., 2013). This explains the higher biogenic carbon content of the digester gas. None of the other parameters proved to be sufficient in finding a proxy for the carbon content found by the count rates. The only distinction we could make was a mean fossil carbon content in most WWTPs when they treat sewage from predominantly municipal sources.

We calculated the share of the actual number of people in the catchment area and the total treated inhabitant equivalences (from the mean capacity utilisation). If this population share was 55% or above (share of industrial sewage less than 45%), the carbon counts remained pretty constant (figure 2). In all plants with predominantly industrial sewage treatment, no prediction of the carbon content from the share of industrial input seems to be of value. The weighted mean value of the 16 WWTPs with less than 45% share of industrial input was 78.5% ± 2.5% biogenic carbon content in the sludge and 86% ± 2.6% for digester gas. These values were weighted by the number of total treated inhabitant equivalences and calculated using the 105 pmC reference from EN 15440:2011. A conservative estimation (in terms of fossil carbon) has to consider at least 24% fossil carbon content in sludges and 17% fossil carbon content in digester gas. These values should be used as standard values if no more detailed information is available than the sewage originating from mainly municipal sources.

From the information we took back, together with the samples, a more in-depth analyses of the industries attached to the various WWTPs could be done. All WWTPs with 45% or less industrial share had no significant differences in the fossil carbon content of the sludge and gas. Only plants with a higher share of industrial sewage had more fossil carbon. We could not find influences from food (baby food) and fodder production, breweries, catering and hotels, laundries, paper production and textile industry. Relevant shares of fossil carbon came only from chemical industries, minor shares are attributable to chemical and mineralogical production, mechanical engineering, (heavy and metal), fossil fuel, and mineral industries.

The project only looked at the share of fossil carbon in the sludge and gas; its origin was not explored. Obviously cleaning agents and detergents (private and industrial sources) contribute to the fossil carbon content as well as other sources. The task is open for further investigations.

6 Interpretation and discussion

The concentration of ^{14}C-isotope in the sludge and gas samples from various wastewater treatment plants in Germany was significantly lower than from pure biomass. Although the reference count for 100 % biomass is reducing every year, we used the pmC reference for modern biomass of 105 from DIN EN 15440:2011 (appendix C.7.1). The reduction in the reference can be explained by the dilution of the significant over-count arising from atmospheric atomic bomb tests in the 1950s, and by the subsequent emission of fossil carbon into the atmosphere. Rates are dropping by 0.4 to 0.5 counts per year. The samples were taken in 2016 while the reference value of DIN EN 15440:2011 reflects the situation in 2008. There is therefore some justification to lower the pmC_{ref} for 2016 to 101 or 102. Reference values from the German Spirit Monopoly Commission for crops from 2014 are already as low as 98.5 pmC.

Nevertheless, we decided to use 105 as our reference value for two main reasons. The first reason being the direct use of the study results in the European Emission Trading System. The participants have to use international standards for the analysis of relevant parameters of their fuels. DIN EN 15440:2011 as the only basis of ^{14}C-measurements, does not provide lower reference values than 105. Secondly we aimed at a somewhat conservative approach so as not to underestimate the fossil carbon content. However, we discussed the use of a higher reference value than 105 since wood fibres in toilet paper and biogenic carbon grown in the years during atmospheric atomic bomb tests and shortly thereafter, is contained in the samples. Our final solution without more information on the share of various carbon sources was to use the lowest available reference value from DIN EN 15440:2011. For later investigations we explicitly included our measurement results in counts together with the calculated carbon content in table 1.

The ongoing dilution of the originally high content of ^{14}C from atmospheric atomic bomb tests in the atmosphere by emitted fossil carbon, will lead to further reduced references in the future years. The radioactive decay of ^{14}C is much too slow to significantly add to this effect.

In the full report we also tried to find other parameters of the samples which could be used as a proxy for the fossil carbon content, such as heating value, content of other substances in the samples, type of treatment process, etc. Only the calculated share of industrial sewage in the catchment area of the WWTPs could to some extend describe the carbon content. There is a breakpoint between 40% and 50% of that share. Industrial sewage is to some extent identical to sewage from private households. Only if the companies' effluents are highly affected by the industrial process do differences become significant. Our suggestion is to separate the fuels from WWTPs at a break point of 45% of industrial share. Below that, the sewage has a mean fossil carbon content of 24% which sufficiently characterises the samples taken. If higher shares are treated in a plant, the samples have to be analysed individually. For national reporting, or at undue cost in the Emissions Trading System, the fossil carbon content of sludge and gas from mainly industrial sewage might also be set to 100%.

While the goal of this study was met by providing reliable standard data on fuels from WWTPs, further scientific investigations might explore the influence of the various substances in the sewage. At compound level, the processes in the WWTPs from ad- and absorption to biological digestion, might have effects. Those might explain the differences in the biogenic carbon content between the samples. A possible explanation could be that synthetic substances-containing fossil carbon are predominately ad- and absorbed in the sludge without significant biological decomposition.

7 Conclusion

There is a significant share of fossil carbon in the products of wastewater treatment plants for which a conservative standard value of 24% carbon for sewage sludge and 17% for digester gas should be used, if the sewage originates from municipal sources. Since fossil carbon is accounting for global warming, the incineration of sludge and gas from WWTPs adds to the global warming potential in a significant manner. Sources of fossil carbon – among others – might be cleaning agents, detergents and other persistent synthetic products. The results were taken from German WWTPs. The municipal sewage sludge and gas annually incinerated in German installations participating in the ETS release about 1 Mt of CO_2 to atmosphere, 240kt of that CO_2 would have to be counted as fossil carbon.

8 Acknowledgement

We would like to thank the WWTPs for their contribution of samples as well as information on processes and sewage sources. We would particularly like to thank the municipal WWTPs of Pfaffenhofen/Ilm, Schweitenkirchen, Geroldshausen, Niederthann, Ampertshausen, Gmund/Tegernseer Tal, Tirschenreuth and Bonn/Salierweg.

The study was initiated and commissioned by the German Emissions Trading Authority (DEHSt) at the German Environment Agency. The complete study is available as report from the library of the German Environment Agency in Dessau, Germany.

9 Disclaimer

This paper does not necessarily reflect the opinion or the policies of the German Environment Agency or those of the German Emission Trading Authority (DEHSt) at the German Environment Agency.

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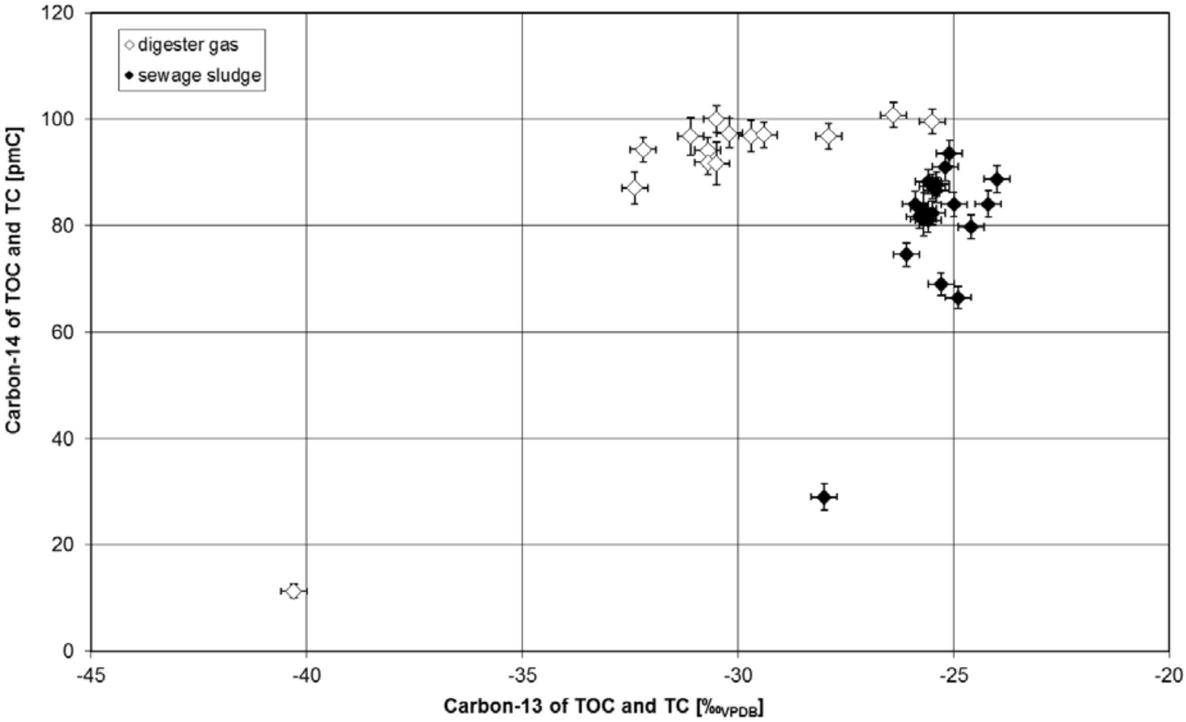
Table 1: Overview of the WWTPs with industrial share and ^{14}C-value as well as C_{bio} content of sewage sludge and digester gas samples

No. of WWTP	mean capacity utilisation (rounded)	population equivalents	share of industrial waste water (calculated)	sewage sludge		digester gas	
				^{14}C-TOC	C_{bio}	^{14}C-TC	C_{bio}
	(PE)	(P)	(%)	(pmC)	(%)	(pmC)	(%)
WWTP 1	66	172	0	84.1 ± 2.3	80	-	
WWTP 2	2100	300	86	74.6 ± 2.2	71	-	
WWTP 3	2800	1780	36	93.6 ± 2.4	89	-	
WWTP 4	2800	2035	27	81.7 ± 2.2	78	-	
WWTP 5	16100	9021	44	81.2 ± 3.0	77	99.6 ± 2.4	95
WWTP 6	28800	17684	39	88.8 ± 2.6	85	-	
WWTP 7	35000	n/a	0	86.7 ± 2.3	83	96.9 ± 3.0	92
WWTP 8	37200	30869	17	87.4 ± 2.3	83	97.1 ± 2.5	93
WWTP 9	39100	40860	0	81.0 ± 2.2	77	94.2 ± 2.4	90
WWTP 10	40300	33000	18	84.0 ± 2.3	80	97.4 ± 2.7	93
WWTP 11	56600	44600	21	83.2 ± 3.0	79	96.8 ± 3.5	92
WWTP 12	66700	66828	0	82.4 ± 2.2	79	96.8 ± 2.4	92
WWTP 13	82600	49500	40	91.1 ± 2.6	87	100.8 ± 2.4	96
WWTP 14	90000	60000	33	88.3 ± 2.3	84	100.1 ± 2.5	95
WWTP 15	110000	95000	14	84.1 ± 2.5	80	94.3 ± 2.4	90
WWTP 16	284000	175385	36	87.8 ± 2.3	84	-	
WWTP 17	510000	65892	87	29.0 ± 2.5	28	(11.3 ± 1.3)	(11)
WWTP 18	1300000	1150000	12	79.8 ± 2.3	76	87.1 ± 3.0	83
WWTP 19	1500000	709546	52	66.5 ± 2.1	63	(91.9 ± 2.3)	(88)
WWTP 20	1750000	887869	49	69.0 ± 2.1	66	(91.7 ± 4.0)	(87)

Portion of industrial waste water: calculated as mean capacity utilisation of population equivalents minus affiliated citizen number

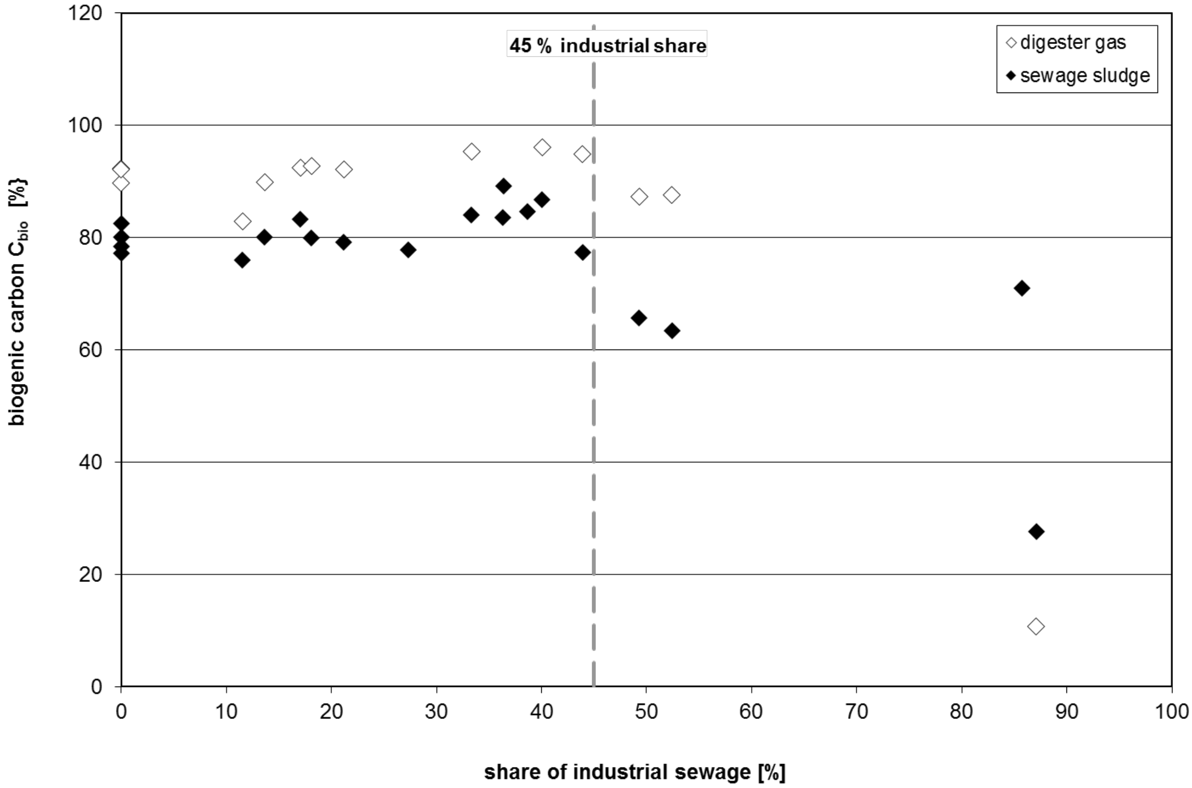
PE: number of population equivalents
P: number of inhabitants/population
TOC: total organic carbon
TC: total carbon
C_{bio}: calculated using correction factor for 105 pmC according to DIN EN 15440:2011 (appendix C.7.1)
(…): sample of digester gas not directly related to sample of sludge.

Figure 1: Presentation of δ^{13}C-values of TOC (sewage sludge) and TC (digester gas) depending on the ^{14}C-values.



Source: own representation, Hydroisotop GmbH

Figure 2: Carbon content given in C_{bio} depending on the share of industrial sewage



Source: own representation, Hydroisotop GmbH