

Dissipation of pesticides during composting and anaerobic digestion of source-separated organic waste in full-scale plants

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Introduction

Composting and digestion (i.e., aerobic and anaerobic degradation of organic wastes) are important waste management strategies in Europe. The end products compost and digestate can be used as soil conditioner and fertilizer, thereby recycling nutrients back to agriculture and horticulture. However, compost and digestate contain a wide range of organic pollutants (Brändli et al., 2005; 2007a,b). They enter compost via aerial deposition and splash or spray induced by road traffic on green waste, accidental input (mostly incorrect separation of input materials, e.g. plastic debris) and deliberate input (e.g. pesticides application on fruits, vegetables, ornamental plants and lawn). Brändli et al. (2007b) and Buyuksonmez et al. (2000) showed that pesticides widely occur in compost and digestate. Although concentrations of organic pollutants in compost and digestate were below the contents that are known to impair terrestrial ecosystems and clear negative impacts of compost and digestate on soil organisms were not found (Tørsløv et al., 1997), the occurrence of contaminants raises some concern since recycling products of high quality are expected to be free of hazardous compounds.

Information on the fate of organic pollutants during composting and digestion under full-scale conditions of green waste (originating from private gardens and public green areas) and organic kitchen waste (raw organic leftovers from vegetable production and from private kitchens), i.e. "source-separated" organic waste is, however, still sparse. Thus, the present study aims to characterize the dissipation of pesticides in full-scale plants.

Materials and methods

Composting and digestion plants investigated

This study focuses on open windrow composting and semi-dry thermophilic anaerobic digestion with subsequent aerobic treatment. These systems are widely used in the recycling of source-separated organic waste. Additionally, open windrow composting allows for feasible sampling. Dissipation of pesticides during composting was characterized by the investigation of three different windrows in two commercial composting plants. One windrow consisted of mostly green waste (windrow "CG"), the second one of a mixture of green and organic kitchen waste (windrow "CK"), respectively, and the third one comprised output material from a thermophilic anaerobic digestion plant (windrow "CDK"). In order to prepare the windrows to be investigated, waste materials were shredded, thoroughly mixed and heaped up to windrows with a front loader. All three windrows were covered with air-permeable fabric, irrigated with fresh water if necessary and turned regularly during composting.

The study of pesticides dissipation during thermophilic anaerobic digestion took place in a plant that employed the Kompogas process (for details on this process: see Brändli et al., 2007c). The output of the fermenter undergoes solid-liquid separation resulting in digestate

(solid phase with a dry matter [d.m.] content of about 35%) and presswater (liquid phase with a d.m. content of about 12%). The digestate was submitted to subsequent aerobic treatment (open windrow composting: CDK; see above).

Details on the composting process parameters such as temperature development, moisture content, turning and irrigation frequencies are provided in Brändli et al. (2007c).

Sampling and processing of the samples

Sampling periods at the composting plants reflected three phases of the process: thermophilic, cooling and maturation stage (Semple et al 2001). Accordingly, sampling took place on day 0 (input material) and on day 14, 56 and 112 of composting. Before each sampling, the windrows were turned at least twice. The most suitable sampling techniques for obtaining composite samples were used according to the structure of the material: digging a transect or collection of drilling cores on both sides of the windrow over the entire transect about every three meters of the windrow. The volume of aliquots was large (>1 litre) and the number thereof plentiful (>100). The composite sample was thoroughly mixed and reduced to 600 litres for input material and to 60 litres of material collected on day 14, 56 and 112 for transport to the laboratory.

At the digestion plant input material was sampled on day 0 from every shovel of the front loader filling the feeding tank (54 m³, which continuously loads the fermenter over 24 hours). Mixing and volume reduction of the gathered composite sample were performed as for compost samples (see above). Material for inoculation of the fermenter (i.e. the output of the fermenter before solid-liquid separation) could not be sampled directly because the fermenters output pipe was not accessible. Instead, the digestate was sampled continuously over half a day and the corresponding input presswater (50 litres) was simultaneously collected from its storage tank. After 12 days the output material was sampled. Presswater was again taken from the storage tank. Digestate was sampled directly from the windrow at the composting plant where the material underwent aerobic treatment (windrow CDK).

At the laboratory, samples collected on day 0 and 14 were cut by a shredder (Althaus, Ersigen, Switzerland, Model 300 K1) and mixed thoroughly in a concrete mixer before sub-samples (1000g) for analysis were taken. They were dried at 40 °C until the weight remained constant (up to seven days) and stored at room temperature in the dark. Before analysis, the samples were milled in a ball mill at a particle size of <2 mm. Further details on the sampling and processing of the samples are given in Brändli et al. (2007c).

Compounds analyzed

Within the analytical program, 271 common pesticides were analyzed including the following compound classes (representatives are given in brackets): amides (alachlor, metolachlor), anilinyrimidines (cyprodinil), benzimidazoles (thiabendazole), carbamates (aldicarb), dicarboximides (captan, folpet), imidazoles (imazalil), organochlorines (endosulfane, DDT), organophosphorous (chlorpyrifos), sulfonyleureas (foramsulfuron), triazines (atrazine), triazoles (difenoconazole) and ureas (isoproturon). The exhaustive list of analyzed compounds is given in Brändli et al. (2007b). For the detection of 160 fungicides or insecticides and 80 herbicides, double analysis by liquid-chromatography coupled to tandem mass spectrometry (LC-MS/MS) was performed. For organochlorine pesticides analysis by gas chromatography with electron capture detection (GC-ECD) and for organophosphorous pesticides analysis by gas chromatography with nitrogen phosphorous detection (GC-NPD) was applied. A confirmation of pesticides identity was carried out by gas chromatography with ion trap mass spectrometry detection (GC-MS). A detailed description of the analytical method is given by Ortelli et al. (2004, 2007).

Calculation of dissipation rates

To follow dissipation of organic pollutants during organic matter degradation, normalization of the measured concentrations to a conservative tracer is necessary. Crude ash turned out to be the most reliable reference parameter as compared to other potentially suitable candidates such as heavy metals (Brändli et al., 2007c). The concentrations measured were converted to μg per kg crude ash as follows:

$$C_{i,norm} = \frac{C_{i,norm}}{C_{ash}} \times 1000$$

where $C_{i,norm}$ denotes the normalized concentration of the compound i ($\mu\text{g kg crude ash}^{-1}$), $C_{i,meas}$ is the quantified concentration of the compound i ($\mu\text{g kg d.m.}^{-1}$) and C_{ash} is the crude ash content (g kg d.m.^{-1}) in the same sample. A dissipation rate (in %) was used to quantify the concentration change of a compound in the substrate. It was calculated as follows:

$$\text{Dissipation rate} = \frac{(C_{i,norm,day 0} - C_{i,norm,day 112})}{C_{i,norm,day 0}} \times 100$$

where $C_{i,norm,day 112}$ denotes the normalized concentration of the compound i ($\mu\text{g kg crude ash}^{-1}$) on day 112 and $C_{i,norm,day 0}$ is the normalized concentration of the compound i ($\mu\text{g kg crude ash}^{-1}$) on day 0 (i.e. in the input material).

Since anaerobic digestion is a continuous process where output substrates are reintroduced to the input material for inoculating and conditioning the substrate, determination of dissipation rates as carried out for composting is not feasible. Instead, a mass balance of the fermenter was calculated and dissipation rates were derived from this (a description of the method is given in Brändli et al., 2007c).

Dissipation rates of $\leq 100\%$ indicate almost complete or exhausting disappearance, whereas a rate of 0% points to the persistence of a compound. Taking into account uncertainties of sampling, processing and analysis, calculated dissipation rates of $>50\%$ include pesticides that can be removed during composting or digestion to a relevant extent. Compounds with dissipation rates of $\leq 50\%$ are considered to be persisting or slightly removable.

Results and discussion

Pesticide prevalence and concentrations

Out of the 271 pesticides analysed, 28 were detected. The three windrows CG, CK, and CDK contained 13, 15, and 21 different compounds, respectively, on day 0 and 8, 5 and 10 pesticides, respectively, on day 112. These numbers of occurrences in finished products were at the lower end of those reported by Brändli et al. (2007b) who found between 7 and 28 compounds in 18 samples of compost and digestate. Fungicides dominated in terms of numbers of detected compounds. Triazoles were the most important fungicides. Compounds such as atrazine or organochlorines that formerly occurred in composts (Buyuksonmez et al., 2000) were not found in the present study at contents higher than $10 \mu\text{g kg d.m.}^{-1}$.

Total pesticide concentrations were between 36 and $101 \mu\text{g kg d.m.}^{-1}$ in input materials of the windrows CG, CK, and CDK and in the range of 8 and $20 \mu\text{g kg d.m.}^{-1}$ in composts on day 112. Such numbers are lower by a factor of 3 to 7 than the average concentration reported by Brändli et al. (2007b).

Fungicides clearly dominated over other pesticides with respect to concentrations. The content of the sum of fungicides ranged from 29 to 94 $\mu\text{g kg d.m.}^{-1}$ for input materials and from 7 to 19 $\mu\text{g kg d.m.}^{-1}$ for composts on day 112. In addition to the dominating triazoles accounting for up to 100% of the total amount of pesticides determined (windrows CG, CK on day 112), the post-harvest fungicides imazalil and thiabendazole were other important compounds. Together, they constituted up to 37% of total pesticides concentrations in input material and up to 11% in compost on day 112 for windrow CDK.

The sum of pesticides concentration in the input material of the digestion plant was 92 $\mu\text{g kg d.m.}^{-1}$. Concentrations of digestate used for inoculation and submitted to subsequent aerobic treatment (windrow CDK on day 0) were 36 and 101 $\mu\text{g kg d.m.}^{-1}$, respectively. This coincides with numbers of Brändli et al. (2007b) who found concentrations for digestate ranging from 30 to 257 $\mu\text{g kg d.m.}^{-1}$. There were higher concentrations for presswater ranging up to 182 $\mu\text{g kg d.m.}^{-1}$. Fungicides represented the most significant fraction of pesticides in digestate and presswater (between 76% and 95% of the total, respectively). In contrast, herbicides accounted for 56% of the sum of pesticides in digestate used for inoculation with mecoprop as the dominant compound. This herbicide is commonly used on lawns and therefore, it can be assumed that this digestate contained a high portion of lawn trimmings or other materials treated with mecoprop.

Dissipation rates during composting

Twenty five compounds of the windrows CG, CK and CDK were detected in the input material and, therefore, enabled the calculation of dissipation rates (Table 1). Sixteen compounds exhibited dissipation rates of 96 - $\leq 100\%$ in one to three windrows. Fifteen of them were not detectable after 56 days of composting and in some cases even after 14 days. This applied to carbendazim, pyrifenoxy, spiroxamine and pririmicarb for all three windrows. On the other hand, difenoconazole, propiconazole and tebuconazole persisted in one or two windrows. In some cases, negative dissipation rates (i.e. higher normalized concentrations in the compost on day 112 compared to the input material) were observed, probably due to sampling uncertainties.

Out of the seven compounds indicating persistence (i.e. dissipation rates of $\leq 50\%$) triazoles dominated with five representatives. This is not surprising since several triazoles are known to exhibit half lives in soil of up to 200 days and more (Bromilow et al., 1999). Slightly dissipating or persisting compounds during composting such as triazoles tended to exhibit considerably higher half lives in soils than those of readily dissipating compounds (Tomlin, 1997). However, correlations between dissipation rates and available soil half lives were not found.

Dissipation rates during anaerobic digestion

The mass balance resulted in negative dissipation rates for 20 out of 24 compounds detected in the input material, and 15 of them were out of the range of usual uncertainties due to sampling, processing and analysis of about 30%. This indicates methodological difficulties leading to biased results. Additionally, it has to be noted that anaerobic digestion of organic waste is a continuous process with internal flows. Characterization of the fate of organic compounds in similar systems such as wastewater treatment requires for repeated sampling campaigns. Future studies should take this into consideration.

Conclusions

Within the present study, dissipation of currently used pesticides during composting in full-scale plants was observed. More than two third of all pesticides detected in the input materials showed dissipation rates higher than 50% during composting. Many of them

were not detectable any more after 112 days. In contrast, levels of triazoles remained largely unchanged. This gives strong evidence of persistence during composting of these widely-used fungicides as previously observed in soil.

Dissipation of pesticides during composting due to mineralization mitigates potential toxic effects of compounds occurring in the input material. However, dissipation rates as determined here bears the risk that the part of compounds occurring in composts as bound residues are erroneously considered as degraded. Still, even if this would apply it can still be assumed that toxic effects are reduced since formation of bound residues decreases the bioavailability of pollutants (Hatzinger and Alexander, 1995). It can therefore be concluded that the quality of produced composts is improved compared to the corresponding input materials with respect to the occurrence and the bioavailability of pesticides.

The investigation on semi-dry thermophilic anaerobic digestion suggests that pesticides preferentially end up in presswater after solid-liquid separation. However, further research is needed to assess thoroughly this topic. The experimental design of the present study was not sufficient for characterizing pesticides dissipation during anaerobic digestion. Similar to other continuously operated systems such as wastewater treatment repeated sampling campaigns are required.

Table 1: Dissipation rates of pesticides during composting of green waste (CG), a mixture of green and organic kitchen waste (CK) and output material from a thermophilic anaerobic digestion plant (CDK) after 112 days of composting

| Chemical class | | Compound | CG | CK | CDK |
|------------------|---------------|---------------------|---------------|---------------|---------------|
| Fungicides | Triazole | Cyproconazole | 1–50% | 51–95% | 1–50% |
| | | Difenoconazol | 0% | 0% | 51–95% |
| | | Fenbuconazole | Not available | 96–≤100% | 96–≤100% |
| | | Flusilazole | Not available | Not available | 51–95% |
| | | Myclobutanil | 1–50% | Not available | 1–50% |
| | | Propiconazole | 0% | 0% | 51–95% |
| | | Tebuconazole | 1–50% | 0% | 51–95% |
| | | Triadimefon | Not available | Not available | 96–≤100% |
| | | Triadimenol | Not available | Not available | 51–95% |
| | Morpholine | Dodemorh | 96–≤100% | 96–≤100% | 51–95% |
| | | Fenpropidin | Not available | Not available | 96–≤100% |
| | | Fenpropimorph | Not available | Not available | 96–≤100% |
| | Benzimidazole | Carbendazim | 96–≤100% | 96–≤100% | 96–≤100% |
| | | Thiabendazole | Not available | 96–≤100% | 96–≤100% |
| | Imidazole | Imazalil | Not available | 96–≤100% | 51–95% |
| Pyridine | | Pyrifenox | 96–≤100% | 96–≤100% | 96–≤100% |
| Spiroketalamine | Spiroxamine | 96–≤100% | 96–≤100% | 96–≤100% | |
| | Strobilurine | Azoxystrobin | Not available | 96–≤100% | Not available |
| Herbicides | Triazine | Terbuthylazine-2-h. | Not available | Not available | 1–50% |
| | | Terbutryn | 96–≤100% | Not available | Not available |
| | Oxadiazole | Oxadiazon | Not available | 1–50% | Not available |
| | Urea | Diuron | 96–≤100% | Not available | 96–≤100% |
| Insecticides | Carbamate | Carbofuran | Not available | 96–≤100% | Not available |
| | | Primicarb | 96–≤100% | 96–≤100% | 96–≤100% |
| Growth regulator | Triazole | Paclobutrazol | 51–95% | Not available | 96–≤100% |

Acknowledgments

The Federal Office for the Environment and the Swiss Federal Office of Energy are acknowledged for financial support, and the personnel from the plants Oensingen, Fehraltorf and Oetwil am See is thanked for good collaboration.

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