Long-term isoproturon and MCPA mineralization capacity in a recently restored wetland

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Introduction
Diffuse pollution of surface waters by pesticides is difficult to handle. The recent trend of riparian wetland restoration however is considered as a promising technology for mitigation of diffuse pollution of surface waters by pesticides (Viden et al., 2010). Soil microbial communities that have been exposed to xenobiotics like pesticides have been shown to adapt in such a way that they can metabolize these compounds and mineralize them. In this study, we examined the potential of the microbial community of a recently (2009) restored wetland in Sint-Truiden, Belgium to mineralize the mobile pesticides 2-methyl-4-chlorophenoxyacetic acid (MCPA) and isoproturon (IPU) and to determine their long-term dynamics. We hypothesized that seasonal environmental disturbances such as freezing and drying can impact the pesticide degrading community and hence the kinetics of pesticide mineralization.

Material and methods
Surface soil samples (n = 30) were taken from the wetland during several sampling campaigns between August 2011 and June 2013 and were assessed for the mineralization capacity of IPU and MCPA in the laboratory. Production of $^{14}$CO$_2$ from $^{14}$C-labeled pesticides was monitored in a microplate setup, described by Johnsen et al. (2009).

The mineralization curves were modelled with the modified Gompertz equation (modified from Zwietering et al.1990):

$$ y = A \exp\left\{-\exp\left[\frac{\mu}{A} (\frac{\lambda}{c} - (\frac{\mu}{c})t) + 1\right]\right\} + ct \quad \text{eq. 1} $$

with A the % mineralized within the logistic part of the function [%], $\mu$ the maximum rate [% day$^{-1}$], $\lambda$ the lag time [days] and c the endogenous rate [% day$^{-1}$]. Parameters from the modified Gompertz equation were evaluated using the lsqnonlin solver with Matlab 2011b (Mathworks).

Results
Whilst mineralization of MCPA was fast in all samples throughout 2 years of monitoring, the mineralization of IPU was much more heterogeneous within the wetland (Table 1). Generally, samples that originated from spots within the wetland that were constantly inundated by water, performed differently from those samples that were mostly exposed to the air (Figure 1). We observed that the lag times of MCPA were larger in wet samples than in air-exposed samples. This observation was more pronounced for IPU, partly because most samples that did not mineralize IPU originated from inundated sediment and hence had a lag time of 60 days (the length of the experiment). With respect to seasonality, we also found a significant difference between the medians of the maximum rate ($\mu$), the lag time ($\lambda$) and the extent of mineralization (A) of samples taken at different time points for both IPU and MCPA mineralization. As shown in Figure 1, the lag times of mineralization were clearly shorter in
May and August compared to the other months. This may reflect differences in fitness of the pesticide degrading populations or in their density between colder and warmer months.

### Table 1. Maximum mineralization rate (µ) and extent of mineralization (A) of MCPA and IPU

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<thead>
<tr>
<th></th>
<th>µ (%/day)</th>
<th>A (%)</th>
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<tbody>
<tr>
<td></td>
<td>min mean median max</td>
<td>min mean median max</td>
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<tr>
<td>MCPA</td>
<td>0.11 8.40 7.09 30.94</td>
<td>0.71 30.69 30.82 62.33</td>
</tr>
<tr>
<td>IPU</td>
<td>0.00 1.29 0.53 25.58</td>
<td>0.00 8.21 8.21 53.87</td>
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![Figure 1. Boxplots of lag time (λ) of the mineralization curves of MCPA (left) and IPU (right). Each boxplot represents a sampling time point (August, December, January, February, March, May and October) and the data are separated into samples that are exposed to the air (---) and samples that are inundated ( )](image)

Conclusions
- We found that the mineralization capacity of MCPA and IPU was still present in the upper layer of sediment four years after the wetland had been restored
- Whereas the mineralization capacity of MCPA differed only slightly between inundated and aerated samples, a very strong discrepancy was observed for IPU relating to the inundation of the sample
- An effect of seasonality on the kinetics of mineralization was observed for both MCPA and IPU

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References
