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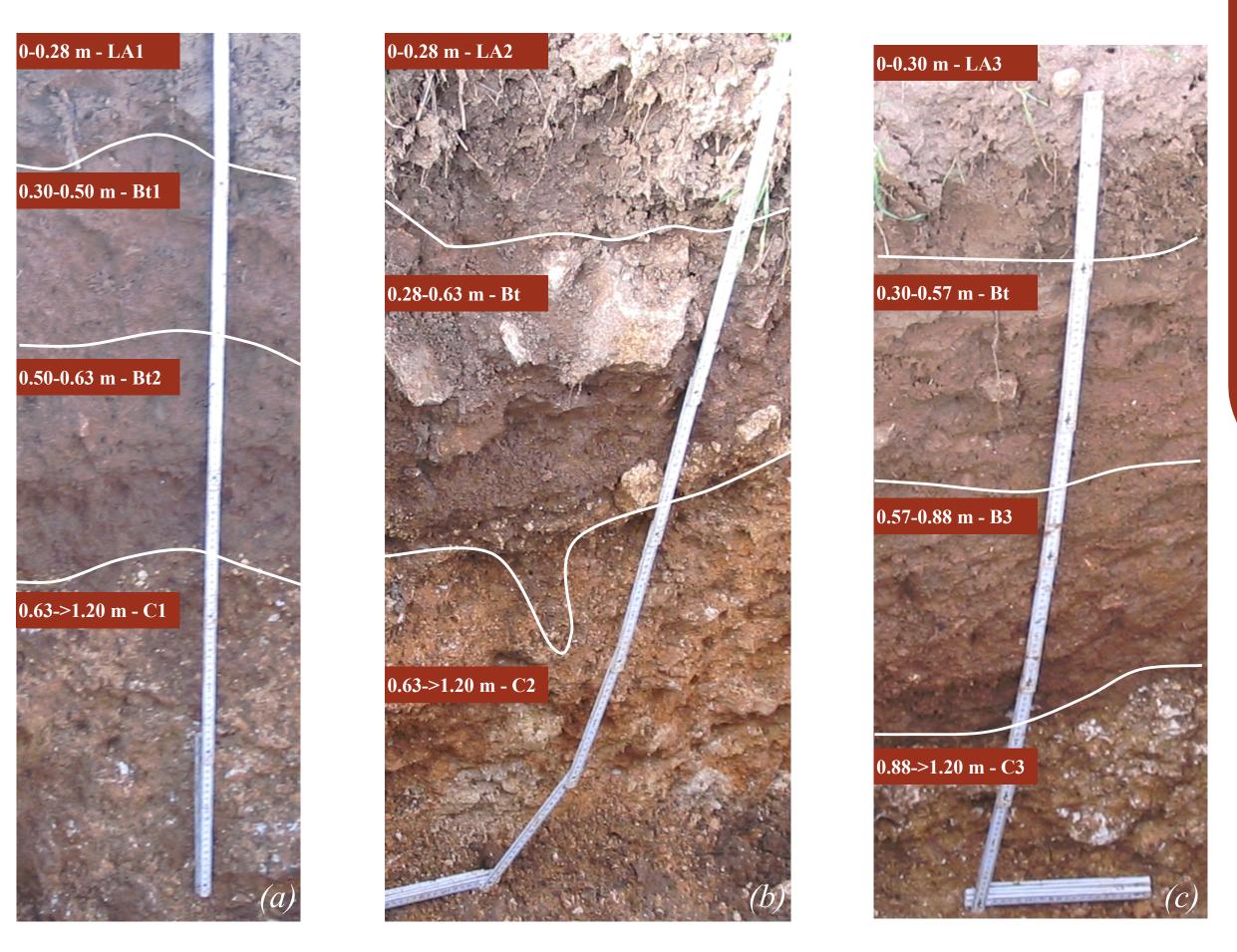
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Summary

The phenylurea herbicide isoproturon, 3-(4-isopropylphenyl)1-1-dimethylurea (IPU), is occasionally found in ground, drainage and surface waters. Degradation in soils is a key process for assessing the risk of water resources contamination by IPU. The degradation properties of various samples from surface and subsurface soil of a heterogeneous field in the Beauce agricultural region of France were studied using ¹⁴C-IPU. Laboratory incubations were carried out at 22 and 10°C and at water contents representing 90 and 50% of the soil water holding capacity (WHC). Degradation was found to be more sensitive to water content variations than to temperature variations in the ranges that we used. For surface layers, at 10 and 22°C, the degradation half-life increased by a factor 10 and 15, respectively, when water content decreased from 90 to 50% WHC. Under optimal degradation conditions, monodemethyl-isoproturon was the main metabolite in surface samples. In subsurface samples, IPU half-lives were larger than 100 d, IPU was the main identified compound after 92 d of incubation and the main metabolite was an unidentified polar metabolite. These results suggest an alternative metabolic pathway probably involving hydroxylations in subsurface materials. Clay content seemed to play a major role in IPU degradation in both surface and subsurface horizons by decreasing IPU availability in soil solution and/or by limiting water availability for microorganisms.



Fig 1. Description of the three soil profiles situated within the agricultural field of the Beauce region. LA horizons correspond to ploughed organo-mineral layers, Bt horizons to clay-enriched illuvial horizon, B to a heavy red clay horizon and C to weathered limestone horizons



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Temperature and water content effects on the degradation of isoproturon in surface and subsurface soils

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Context

⇒ The tertiary aquifer of the Beauce region (one of the largest groundwater resources in France) is polluted by several pesticides

⇒ The phenylurea herbicide isoproturon, 3-(4-isopropylphenyl)1-1-dimethylurea (IPU), used to control pre- and post-emergence of grass weeds and broad-leaved weeds in cereal crops is among the major pollutants.

 \Rightarrow The fate and behaviour of this herbicide is determined by the sorption and degradation capacities of the soil materials.

Objectives

Determine the IPU degradation properties of various materials sampled from surface (plough layer) and subsurface soil materials down to 1 m depth in a heterogeneous agricultural field of the Beauce region

Evaluate the effects of water content and temperature on the kinetics of IPU degradation and on the proportions of the various molecular forms produced through IPU degradation

Materials and Methods

- Field site of 25 ha in the Beauce Region (France)

- Main soil types: Orthic Luvisol, Eutric Cambisol and Calcic Cambisol

- Soil samples from surface layers (LA1, LA2 and LA3) and subsurface layers (Bt1, B3, C1, C2 and C3)

- Laboratory incubations with ¹⁴C-IPU during 92 days

- Temperatures: 22 and 10 °C

- Water contents: 90 and 50 % of the estimated water holding capacity (eWHC) corresponding to actual water potentials between -56 kPa and -660 kPa

- Herbicide analysis: HPLC + PhotoDiode Array + Radioactive flow detector

Table 1. Characteristics of the surface (LA1, LA2, LA3) and subsurface soil depths (Bt1, B3, C1, C2, C3) of the three profiles (a, b and c) situated within the field site in the Beauce region

Plot	Layer	Depth (m)	pН	Clay	Silt	Sand	OC	CaCO ₃	eWHC ^a	pF _{eWHC} ^b
				(0-2 µm)	(2-50	(50-2000 µm)	(g kg ⁻¹)	$(g kg^{-1})$	(g g ⁻¹)	
					μm)					
				$(g kg^{-1})$	$(g kg^{-1})$	$(g kg^{-1})$				
a	LA1	0-0.28	6.26	247	711	41	13.7	<1	0.217	2.78
	Bt1	0.30-0.50	7.02	340	630	29	6.31	<1	0.217	3.11
	C1	0.68->1.20	8.55	193	240	48	5.32	512	0.217	2.52
b	LA2	0-0.28	6.49	278	621	99	14.1	1.7	0.217	3.03
	C2	0.63->1.20	8.56	201	82	36	3.12	670	0.217	3.00
С	LA3	0-0.30	5.93	223	701	75	11.1	1.3	0.217	2.48
	B3	0.57-0.88	7.70	565	306	124	5.25	4.7	0.263	6.07
	C3	0.88->1.20	8.44	339	57	16	3.58	564	0.217	3.82

vater holding capacity estimated from Bruand et al. (2003 ^b Soil water matric potential, Ψ_m , at eWHC, expressed in pF=log₁₀ $|\Psi_m|$, where Ψ_m is in hPa

Res	sults and Dis	cussio	n	Degradation half-life		
				- In surface samples, $T_{1/2}$ ranged from the second se		
	. Degradation half-lives (<i>T</i> at incubation conditions testion	1/2/		- In subsurface samples, T _{1/2} were l		
Layer	Incubations conditions	T _{1/2} (days)	R ²	- Degradation was more sensitive t		
	90% eWHC – 22 °C	11	0.86			
LA1	90% eWHC – 10 °C	23	0.76	Surface samples LA1: T _{1/2}		
	50% eWHC – 22 °C	157	0.90			
	50% eWHC – 10 °C	223	0.98	- Clay content seemed to limit IPU		
LA2	90% eWHC – 22 °C	12	0.88	Subsurface samples Bt1 an		
LA3	90% eWHC – 22 °C	10	0.84	with clay content ⇒ lower		
D41	90% eWHC – 10 °C	111	0.94			
Bt1	50% eWHC – 10 °C	866 165	0.87			
B3	90% eWHC – 10 °C		0.99	Fig. 2. Distribution kinetics of applied ¹⁴ C bet		
C1	90% eWHC – 10 °C	106	0.96	bound residues, methanol extract, water extract and in surface samples (LA1) and subsurface samples (
	50% eWHC – 10 °C	462 0.81		C1) and distribution kinetics of isoproturon and		
C2	90% eWHC – 10 °C	203	0.97	metabolites in the pooled water and methanol ext		
C3	90% eWHC – 10 °C	990	0.90			

- Mineralization decreased with depth and organic carbon content

- ⇒ Maximum of 16.5 % of applied ¹⁴C after 92 d at 22 °C and 90 % eWHC in surface samples (Fig. 2a)
- \Rightarrow Minimum of 0.02 % of applied ¹⁴C after 92 d at 10 °C and 50 % eWHC in subsurface samples

- Mineralization was strongly affected by water availability in subsurface samples

Non-extractable residues

- Sensitivity of bound residues formation to soil water content

- Correlations of non-extractable residues proportions with organic carbon content and mineralization
 - \Rightarrow Microbial activity is probably involved in the formation of nonextractable residues

Extractable fraction

- Strong effect of the water content on the extractability of ¹⁴C (Fig. 2a,b)

- In surface samples, MDIPU was the main metabolite under optimal incubation conditions (i.e. 22 °C, 90 % eWHC)

- In subsurface samples, IPU was the major molecular form after 92 d and the main metabolite was an unidentified polar metabolite probably a hydroxylated metabolite (Sørensen et al., 2003)

 \Rightarrow In subsurface layers, degradation of IPU was low and did not lead to the "usual" metabolites (MDIPU, DDIPU or 4IA)

IPU: isoproturon MDIPU: monodemethyl-isoproturon DDIPU: didemethyl-isoproturor 4IA: 4-isopropyl-aniline

Conclusion

1- Degradation of IPU was the most important in surface layers but was still active in subsurface layers

2- Soil water content variations had stronger effects on mineralization, bound residues formation, degradation, and extractability than temperature variations in the ranges that were considered

3- In subsurface samples, degradation of IPU was very slow and the formation of polar metabolites following an alternative degradation pathways for IPU was significant

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11 to 223 days depending on incubation conditions (Table 2)

er than 100 days (Walker et al., 1999)

ater content variations than to temperature variations

eased by a factor 15 at 22°C and 10 at 10°C

ailability and/or water availability to microorganisms

1 (similar water potential, near pF 5.1, at 50% eWHC): T_{1/2} increased availability due to sorption on clay particles

