Availability and biodegradation of metribuzin in sandy soils as affected by temperature and soil characteristics

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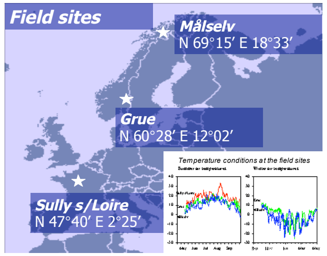
Introduction

In cold climatic territories, like northern Europe and Scandinavia, agricultural areas are small and pesticides risk assessment needs to be followed with more attention, particularly with respect to the climatic effects upon degradation and transport. Soil temperature plays a major role in determining rates of microbial degradation and pesticide degradation will generally be faster in a warmer than in colder regions, if all other factors (i.e. water, oxygen, different nutrients and C-substrates) are the same.

Metribuzin [4-amino-6-tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)-one] is commonly used in Norway for weed control in potato crop. It has potential for leaching[1] according to its fairly high solubility in water (1200 mg/l at 20°C). Metribuzin dissipation is mainly due to microbial breakdown[2]. In subartic soils from Alaska, Conn et al. (1996)[3] have shown in a lysimeter study under field conditions, that a relatively rapid degradation of metribuzin combined with sorption processes explained a low ability to leaching for metribuzin and its residues.

The **objective** was to characterize the microbial degradation of metribuzin under different climatic conditions and the consequences on the availability of metribuzin residues for leaching in alluvial soils with low binding capacities (low clay and organic carbon contents) and high groundwater levels. A first goal was to quantify the effect of temperature on metribuzin biodegradation and more precisely on the residual concentration of herbicide or metabolites able to leach. A second question investigated here was whether or not any observed differences in metribuzin biodegradation could be described by microbial characteristics of the soils when testing sandy loam soils from three climatically different sites



Materials and methods

Field sites, Målselv northern Norway, Grue southern Norway, and Sully s/Loire France were selected to represent temperate, nordic and subartic conditions along a south-north **climatic gradient**[4].

The three sites corresponded to **alluvial soils** with low binding capacities (low clay and organic carbon contents) and high groundwater levels. Therefore they constituted vulnerable areas to pesticide contamination.

Initial microbial characterization of fresh soil samples from the 3 sites (September-October 2004) showed similar microbial biomass and a lower dehydrogenase activity in Målselv soil.

Temperature has a postive effect on total **soil organic carbon mineralization** and on **the specific respiration** at all sites.

Physical and chemical characteristics

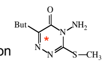
		Field sites: Sully Ap (0-28 cm)	Grue Ap (0-30 cm)	Malselv Ap (0-27 cm)
Water content WHC	(mass %)	29,1	35,7	36,2
Gravel (> 2 mm)	(%)	1,6	0,4	0,3
Sand (2-0,06 mm)	(%)	79,6	46,8	63,9
Silt (0,06-0,002 mm)	(%)	9,2	49,0	33,9
Clay (< 0,002 mm)	(%)	11,3	4,3	2,8
pH		6,8	5,9	6,6
Soil organic carbon	(%)	0,55	0,9	1,09
Kjeldahl N	(%)	0,06	0,07	0,07
C/N		9	13	11
CEC	(meq/100 g)	5,5	3,6	6,3

Microbial characteristics

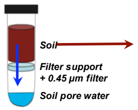
		Sully	Grue	Malselv
Microbial biomass C	(%SOC)	44,9	57,1	37,4
Deshydrogenase activity	(10^{-3} mg TPF g^{-1} dry soil $24\ h^{-1}$)	11,9	13,9	4,0
Specific respiration	(C mineralized/ biomass C)			
At 5°C		0,66	0,57	0,69
At 15 °C		1,64	1,89	2,20
At 28 °C		10,6	8,71	12,2

Metribuzin biodegradation and availability

Laboratory controlled soil incubation at 5, 15 & 28 °C
Soil moisture at 80% water holding capacity
^{14}C ring labeled metribuzin application (1,6 µg/g dry soil - ca 220 g/ha)
Measurement of the mineralization of ^{14}C metribuzin and total soil organic carbon



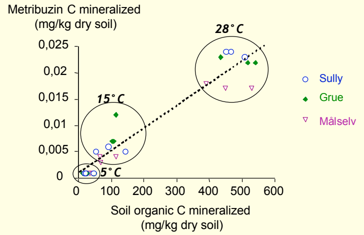
At time 0, 14 and 49 days,



1. Solution recovered by centrifugation at 1000 g → ^{14}C metribuzin - LSC analysis
2. $CaCl_2$ extraction
3. Methanol extraction → ^{14}C metabolites - HPLC Analysis
4. Non extractable residues → Soil combustion - Oxidizer

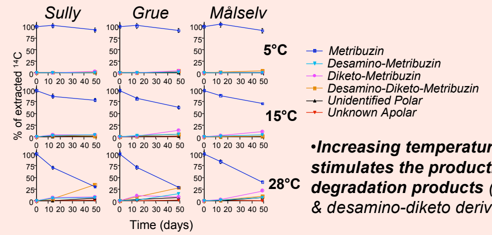
Results

➢Metribuzin biodegradation



*•**Low mineralization capacity of soil microflora** (maximum of 3% of initial amount after 49 d)*

*•**Relation between overall microbial activity** (respiration) **and metribuzin mineralization***

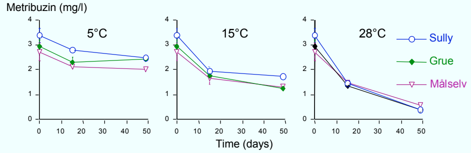


DT50 /days	Sully	Grue	Målselv
(5°C)	385	385	310
(15°C)	161	76	105
(28°C)	27	26	36
Activation energy Ea /kJ mol^{-1}	81	80	64

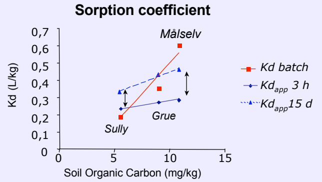
*•**Increasing temperature stimulates the production of degradation products** (desamino & desamino-diketo derivatives)*

*• **Estimation of activation energies from first order degradation rate constants shows a lower activation energy for the northern site** (Målselv)*

➢Metribuzin in soil pore water

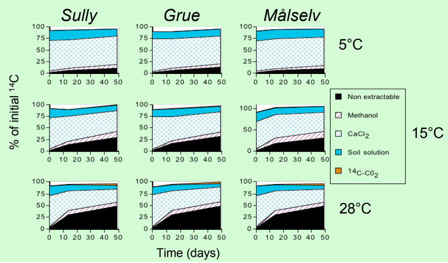


•Temperature strongly affects the availability of metribuzin
- ***✓This is due to biodegradation***
- ***✓Similar decrease of soil pore water concentration in the 3 soils***



•Apparent sorption coefficient $K_{d\ app}$ from measurement of metribuzin in soil pore water shows an increase of metribuzin sorption with time
- ***✓A greater increase in sorption observed in the more organic soil** (Målselv)*

➢Non extractable residues



•Soil pore water and $CaCl_2$ fractions decrease while non extractable residues increases with time
•Related to the temperature effect on biodegradation, a much slower evolution is observed at 5°C
•Similar time evolution is observed in the 3 soils

Conclusion : *Climate **is very important for metribuzin degradation and leaching potential***

- *Temperature increase from 5°C to 15°C reduce the soil pore water concentration by 25%, but the mobility remains high one month after spraying*
- *In all sites, metribuzin mineralization was low and metribuzin residues will be slowly degraded during cold periods*
- *There is an increased risk of groundwater pollution (autumn rain, snow melt) for metribuzin residues under cold climates in soils with low sorption and degradation capacities. These findings were also supported by field monitoring studies at the 2 Norwegian sites*

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References

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