

Ability of the MACRO Model to Predict Long-term Leaching of Metribuzin and Diketometribuzin

Annette E. Rosenbom,[†] Jeanne Kjær,[†] Trine Henriksen,[‡] Marlene Ullum,[¶] and Preben Olsen[§].

[†] Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350 Copenhagen, Denmark.

[§] University of Aarhus, Faculty of Agricultural Sciences, Department of Agroecology and Environment, P.O. Box 50, DK-8830 Tjele, Denmark.

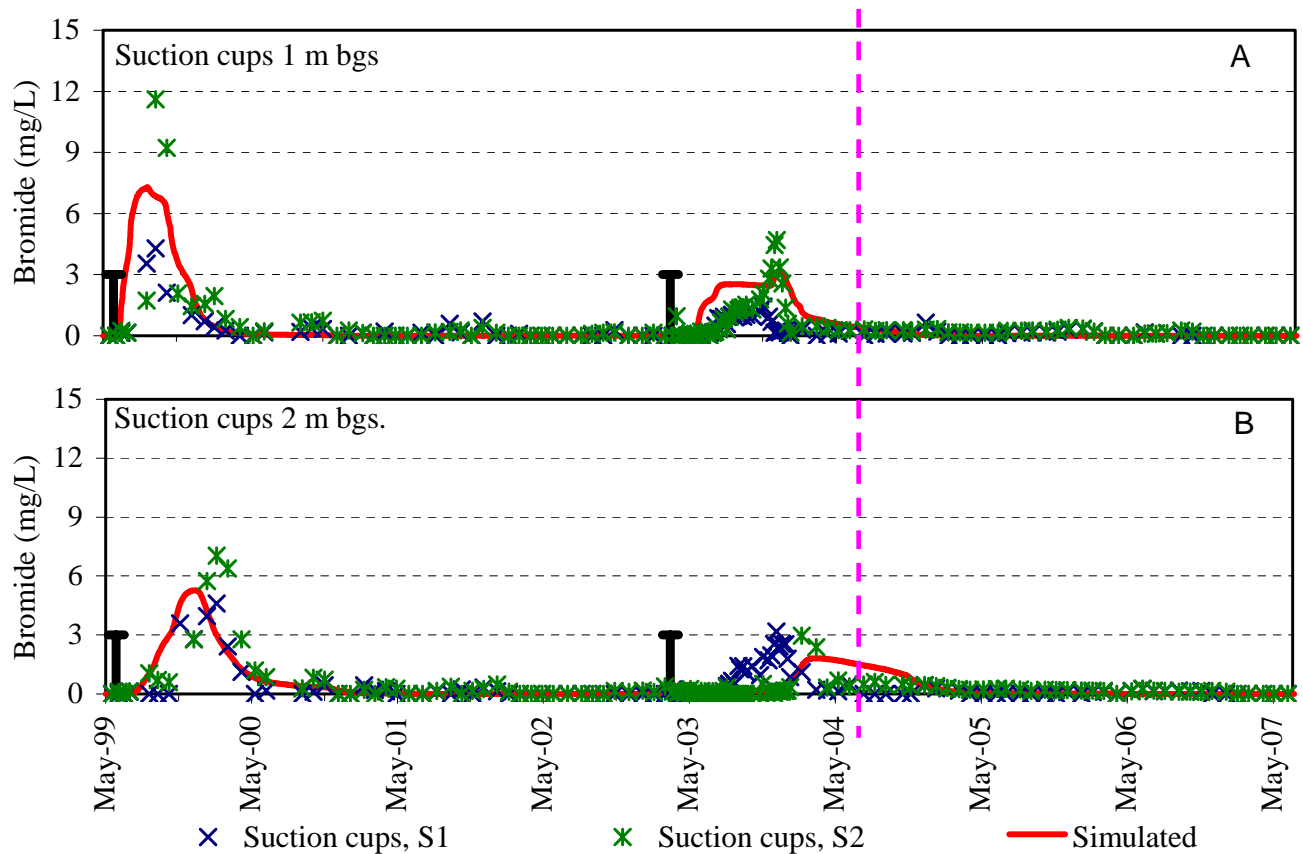
[‡] Department of Clinical Pharmacology, Rigshospitalet, Blegdamsvej 9, DK-2100 Copenhagen Ø, Denmark.

[¶] COWI A/S, Parallelvej 2, DK-2800 Kongens Lyngby, Denmark.

Supporting Information Available (SI):

7 pages, **1** figure (FIGURE S1), **1** SI-paragraph with supporting information to paragraph “FIELD RESEARCH SITE STUDIES” and **1** table with references (TABLE S1).

FIGURE S1. Simulated and measured bromide concentration in the unsaturated zone at Tylstrup: Simulated and measured bromide concentration at 1 m bgs (A) and 2 m bgs (B). The measured data in A and B derive from suction cups installed 1 m bgs and 2 m bgs at location S1 and S2 (see Lindhardt, B.; Abildtrup, C.; Vosgerau, H.; Olsen, P.; Torp, S.; Iversen, B. V.; Jørgensen, O. J.; Plauborg, F.; Rasmussen, P.; Gravesen, P. *The Danish Pesticide Leaching Assessment Programme: Site characterization and monitoring design*; Geological Survey of Denmark and Greenland: Copenhagen, 2001). The black vertical lines indicate the dates of bromide application, whereas the broken pink vertical line indicates the beginning of the validation period (July 2004 – June 2006).



SUPPORTING INFORMATION TO PARAGRAPH “FIELD RESEARCH SITE STUDIES”

Site Description The field research site is located at Tylstrup in northern Jutland. The field covers an area of 1.1 ha (70 m x 166 m) and is surrounded by a 2–4.5-m wide buffer zone with windbreaks along the eastern and western borders. The topography is flat, and the groundwater table is located at a depth of 3–4.5 m (1, 2).

The field is located on an approximately 20-m layer of fine-grained Late-Glacial marine sand deposited in the shallow Arctic Sea – the Yoldia Sea. The soil is classified as a Humic Psammentic Dystrudept (3). The geological setting was described by means of three 1.6-m deep excavations and 11 boreholes established in the buffer zone (2). The upper 5 m of the variably saturated marine sand consisted of three geological/pedological layers: Horizon A (0–0.32 m) composed of very dark, greyish-brown, organic matter-rich (TOC: 1.6% C), noncalcareous, sandy topsoil (USDA texture: loamy sand; 6% clay; 13% silt) with a pH of 4.5; Horizon B (0.33 to 0.75 m) composed of dark brown, oxidised, organic matter-rich (TOC: 1.1% C), noncalcareous, weathered, fine-grained silty sand (USDA texture: sandy loam; 5.5% clay; 19% silt) with a pH of 4.6; and Horizon C (0.76–5 m) composed of yellowish brown, organic matter-poor (TOC: 0.1% C), noncalcareous sand (USDA texture: loamy sand; 3% clay; 13% silt) with a pH of 4.8. In order to comply with the FOCUS guidelines (6) it was necessary to divide horizon C into two sub-horizons – C1 (0.76–1.00 m bgs) and C2 (1.01–5.00 m bgs).

Agricultural Management. The research field at Tylstrup was cultivated in accordance with conventional agricultural practice in the area. Pesticides were always applied strictly in accordance with the regulations (1,2). Data on pesticide use in the field is available for the period 1989–2007. Metribuzin (Sencor WG) has been applied to potato crops growing in the field on several occasions: 10 May 1990 (0.7 kg/ha), May 1992 (0.5 kg/ha), 16 May 1994 (0.3 kg/ha), 25 May 1999 (0.2 kg/ha) and 7 June 1999 (0.15 kg/ha). Since the exact date of metribuzin application in 1992 is unknown, 10 May 1992 was assumed in the model setup. Bromide tracer (30 kg/ha KBr) was applied to the field in May 1999 and April 2003 to confirm that the water samples collected at the site actually originated from the

field (4). During the potato growing seasons in which metribuzin was applied to the field, irrigation was performed only once – 33 mm was applied on 12 September 1999, some three months after the last application of metribuzin (4).

Monitoring Data. Intensive monitoring was performed at the field research site from May 1999–June 2007 to determine the water balance and study leaching of pesticides and bromide (1,5).

To avoid pesticide leaching artefacts, all installations and all soil sampling deeper than 20 cm were restricted to the buffer zone surrounding the field. Thus, suction cups were installed from excavation pits in the buffer zone via drilled holes placing them in the soil profiles of the treated area with a horizontal distance of at least 2 m to the edge of the field. Data on the structural and hydraulic setting and on the climatic conditions during the period 1989–2007 are presented in Barlebo et al. (4) and Kjær et al. (1), respectively.

Water Samples. Water was sampled monthly for six years from the unsaturated zone of the Tylstrup field site using 16 Teflon suction cups clustered 4 by 4 at depths of 1 and 2 m bgs and from the groundwater using 34 screens located 3–9 m bgs. The metribuzin concentration in the soil water samples from 1 m bgs was below the limit of detection (LOD) of 0.01 µg/L (Figure 1). Metribuzin was only detected in three soil water samples from 2 m bgs. Here the concentration ranged from 0.01 to 0.02 µg/L. In contrast to metribuzin, diketometribuzin leached from the root zone (1 m bgs) in average concentrations considerably above the EU limit value for drinking water (0.1 µg/L) for as long as 3½ years following application of metribuzin (Figure 2).

The same pattern was found with groundwater. Thus metribuzin was not detected in any of the groundwater samples, whereas diketometribuzin was detected in 99% of the samples. During the first four years of the monitoring period the annual average concentration of diketometribuzin exceeded the EU limit value of 0.1 µg/L in 90% of the groundwater samples analysed (5). As the EU pesticide authorisation procedure (i.e. the FOCUS guidelines) uses leaching 1 m bgs as the reference when determining whether a pesticide can be approved for use (6), the present evaluation of the MACRO model focuses on the leaching of metribuzin and diketometribuzin in the upper 1 m of the soil.

Soil Samples. The soil concentration of metribuzin and its primary metabolites were measured in samples of topsoil (0.05–0.20 m bgs) collected from the Tylstrup research field on 22 October 2002, 28 January 2003 and 23 April 2003. A total of 25 soil samples were collected diagonally across the field, homogenised, mixed, and sieved through a 2-mm mesh *in situ*. A 0.5 kg portion of the sieved soil was frozen at -20°C until analysis. The LOD for metribuzin was approximately 2 µg/kg, while that of diketometribuzin was 20 µg/kg. Three and a half years after application of metribuzin the pesticide was still present in the soil in levels corresponding to 8% of the applied dose (5). No metabolites were detected, however (Figure 1).

Degradation and Sorption of Metribuzin and Diketometribuzin. Degradation and sorption of metribuzin and its primary metabolites were studied by means of batch experiments in soil samples from two depths: 0.05–0.2 m bgs (topsoil) and 3–4 m bgs (subsoil, just above groundwater level) (4). Metribuzin was found to degrade in the topsoil, resulting in the formation of diketometribuzin and other metabolites. The degradation kinetics of metribuzin in the topsoil was best described using a two-compartment model, whereas that of diketometribuzin did not fit any of the tested kinetic models. In the subsoil (3–4 m bgs) the degradation kinetics of metribuzin was best described by a first-order model, whereas that of diketometribuzin fitted a two-compartment model. The study thus indicates that the degradation kinetics of both metribuzin and diketometribuzin *in situ* could deviate from the first-order kinetics used in the pesticide authorisation procedure. Sorption and desorption in the topsoil was found to be larger for metribuzin than for DK with a more pronounced difference in desorption. The subsoil showed much lower sorption capacity, why desorption studies were neglected. As the study was based on a mixed soil sample from each depth at a single location, the degree to which degradation and sorption (DT_{50} and K_d) vary throughout the Tylstrup field research site is unknown. We thus used estimates of metribuzin DT_{50} and K_d obtained from three field research sites (Ulsted, Hørby, and Ajstrup) with a similar geological and climatic setting to Tylstrup (7, 8) to determine realistic values for the variation in metribuzin DT_{50} and K_d at the Tylstrup field site (Table 1). The actual estimates are provided in Table S1.

References

- (1) Kjær, J.; Rosenbom, A. E.; Olsen, P.; Juhler, R. K.; Plauborg, F.; Grant, R.; Nygaard, P.; Gudmundsson, L.; Brüsch, W. The Danish Pesticide Leaching Assessment Programme: Monitoring Results, May 1999–June 2007; Geological Survey of Denmark and Greenland: Copenhagen, Denmark, 2008.
- (2) Lindhardt, B.; Abildtrup, C.; Vosgerau, H.; Olsen, P.; Torp, S.; Iversen, B. V.; Jørgensen, O. J.; Plauborg, F.; Rasmussen, P.; Gravesen, P. *The Danish Pesticide Leaching Assessment Programme: Site characterization and monitoring design*; Geological Survey of Denmark and Greenland: Copenhagen, 2001.
- (3) Soil Survey Staff. *Soil Taxonomy. A basic system for soil classification for making and interpreting soil surveys*, 2nd ed.; U.S. Department of Agriculture: New York, 1999.
- (4) Barlebo, H. C.; Rosenbom, A. E.; Kjær, J. *Evaluation of pesticide scenarios for the registration procedure*; Environmental Project No. 1178; Danish Environmental Protection Agency, 2007.
- (5) Kjaer, J.; Olsen, P.; Henriksen, T.; Ullum, M. Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer. *Environ. Sci. Technol.* **2005**, 39 (21), 8374–8381.
- (6) FOCUS. *Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration*; EC Document Reference Sanco/10058/2005 version 2.0, 2008. Available at: <http://viso.jrc.it/focus/dk/doc/finalreportFOCDegKin04June06linked.pdf>.
- (7) Vinther, F. P.; Brinch, U. C.; Elsgaard, L.; Fredslund, L.; Iversen, B. V.; Torp, S.; Jacobsen, C. S. Field-scale variation of microbial activity and soil properties in relation to sorption and degradation of pesticides in a sandy soil. *J. Environ. Qual.* **2008**, *In press*.
- (8) Barlebo, H. C.; Brinch, U. C.; Elsgaard, L.; Ernstsén, V.; Iversen, B. V.; Jacobsen, C. S.; Jacobsen, O. H.; Juhler, R. K.; Møller, I.; Olesen, S. E.; Rasmussen, J.; Torp, S. B.; Vinther, F. P.; Vosgerau, H. *Investigations of post-glacial marine sand in the Yoldia Plains*; 3; Geological Survey of Denmark and Greenland and Danish Institute of Agricultural Sciences: Copenhagen, 2004.

TABLE S1. Equilibrium and non-equilibrium dissipation and sorption parameters for metribuzin and diketometribuzin estimated on disturbed soil samples from horizons A, B, C1 and C2 at the Tylstrup field research site (numbers in bold) and similar geological settings close by (see references).

Input Parameter	Horizon	Metribuzin	Diketometribuzin
EQUILIBRIUM PARAMETERS			
DT₅₀ [days]	A 0-0.32 m bgs	32 ^a , Tylstrup, 0.05–0.20 m bgs 92 ^b , Ulsted, 0.05–0.25 m bgs 66 ^b , Hørby, 0.05–0.25 m bgs 187 ^b , Ajstrup, 0.05–0.25 m bgs	29 ^{e+a} , Tylstrup, 0.05–0.20 m bgs
	B 0.33–0.75 m bgs	79 ^e , Tylstrup 227 ^b , Hørby, 0.4–0.6m bgs >500 ^b , Ajstrup, 0.4–0.6m bgs	72 ^e
	C1 0.76–1.00 m bgs	107 ^e , Tylstrup >500 ^b , Ulsted, 0.4–0.6m bgs	97 ^e
	C2 1.01–5.00 m bgs	> 500 ^a , Tylstrup, 3–4m bgs >500 ^b , Ulsted, 0.95–1.15m bgs 227 ^b , Hørby, 1.1–1.3m bgs	> 500 ^a , Tylstrup, 3–4m bgs
K_d [L/kg]	A 0–0.32 m bgs	0.94 ^a , Tylstrup, 0.05–0.20m bgs 0.3–2.2 ^c , Ulsted, 0.05–0.25m bgs 0.7±0.03 ^b , Ulsted, 0.05–0.25m bgs 0.6±0.01 ^b , Hørby, 0.05–0.25m bgs 2.3±0.1 ^b , Ajstrup, 0.05–0.25m bgs	0.72 ^a , Tylstrup, 0.05–0.20m bgs
	B/C1 0.33–1.00 m bgs	0.94 ^e , Tylstrup 0.01–1.5 ^c , Ulsted, 0.4–0.6m bgs 0.1±0.002 ^b , Ulsted, 0.4–0.6m bgs 0.1±0.006 ^b , Hørby, 0.4–0.6m bgs 0.04±0.01 ^b , Ajstrup, 0.55m bgs 0.2±0.01 ^b , Ajstrup, 0.5–0.7m bgs	0.72 ^{e+a} , Tylstrup
	C2 1.01–5.00 m bgs	0.001 ^a , Tylstrup, 3–4m bgs 0.1±0.005 ^b , Ulsted, 0.95–1.15m bgs 0.03±0.009 ^b , Hørby, 1.1–1.3m bgs 0.2±0.004 ^b , Hørby, 1.0–1.5m bgs 0.1±0.001 ^b , Ajstrup, 1.2–1.7m bgs	0.001 ^a , Tylstrup, 3–4m bgs
Freundlich coefficient [-]	A B C1/C2	0.56 (0.73±0.17) ^a , Tylstrup 0.56 ^e 0.56 ^e	0.58 (0.53±0.05) ^a , Tylstrup 0.58 ^e 0.58 ^e
NON-EQUILIBRIUM PARAMETERS			
Kinetic sorption rate coefficient α_k [1/day]	All	1.04 ^d	1.01 ^e
Fraction of sorption sites available for kinetic sorption , f_{ne} [-]	All	0.95 ^e	0.95 ^e

^aHenriksen, T.; Svensmark, B.; Juhler, R. K. *J. Environ. Qual.* **2004**, 33 (2), 619–627; ^bBarlebo, H. C.; Brinch, U. C.; Elsgaard, L.; Ernstsen, V.; Iversen, B. V.; Jacobsen, C. S.; Jacobsen, O. H.; Juhler, R. K.; Møller, I.; Olesen, S. E.; Rasmussen, J.; Torp, S. B.; Vinther, F. P.; Vosgerau, H. *Investigations of Post-Glacial Marine Sand in the Yoldia Plains*; 3; Geological Survey of Denmark and Greenland and Danish Institute of Agricultural Sciences: 2004; ^cVinther, F. P.; Brinch, U. C.; Elsgaard, L.; Fredslund, L.; Iversen, B. V.; Torp, S.; Jacobsen, C. S. *J. Environ. Qual.* **2008**, *In press*; ^dLadlie, J. S.; Meggitt, W. F.; Penner, D. *Weed Sci.* **1976**, 24 (5), 477–481; ^eAssumed based on the DT₅₀ depth distribution recommended by “FOCUS. *Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration*; EC Document Reference Sanco/10058/2005 version 2.0; 2008”. Values in bold and **black** are site-specific while values in **grey** are either minimum or maximum values.