Environmental Chemistry

DRY–WET CYCLES INCREASE PESTICIDE RESIDUE RELEASE FROM SOIL

NICOLAI DAVID JABLONOWSKI,*† ‡ ANDREAS LINDEN,† STEPHAN KÖPPCHEN,† BJÖRN THIELE,‡ §
DIANA HOFFMANN,† and PETER BURAUER†

†Institute of Bio- and Geosciences, IBG-3: Agrosphere, Forschungszentrum Jülich, Germany
‡Institute of Bio- and Geosciences, IBG-2: Plant Sciences, Forschungszentrum Jülich, Germany
§BioSpec, Forschungszentrum Jülich, Germany

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Abstract—Soil drying and rewetting may alter the release and availability of aged pesticide residues in soils. A laboratory experiment was conducted to evaluate the influence of soil drying and wetting on the release of pesticide residues. Soil containing environmentally long-term aged (9–17 years) 14C-labeled residues of the herbicides ethidimuron (ETD) and methabenzthiazuron (MBT) and the fungicide anilazine (ANI) showed a significantly higher release of 14C activity in water extracts of previously dried soil compared to constantly moistened soil throughout all samples (ETD: p < 0.1, MBT and ANI: p < 0.01). The extracted 14C activity accounted for 44% (ETD), 15% (MBT), and 20% (ANI) of total residual 14C activity in the samples after 20 successive dry–wet cycles, in contrast to 15% (ETD), 5% (MBT), and 6% (ANI) in extracts of constantly moistened soils. In the dry–wet soils, the dissolved organic carbon (DOC) content correlated with the measured 14C activity in the aqueous liquids and indicated a potential association of DOC with the pesticide molecules. Liquid chromatography MS/MS analyses of the water extracts of dry–wet soils revealed ETD and MBT in detectable amounts, accounting for 1.83 and 0.01%, respectively, of total applied water-extractable parent compound per soil layer. These findings demonstrate a potential remobilization of environmentally aged pesticide residue fractions from soils due to abiotic stresses such as wet–dry cycles. Environ. Toxicol. Chem. 2012;31:1941–1947. © 2012 SETAC

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INTRODUCTION

In agriculture, approximately 80% of all pesticides are used for crop protection, and between 1995 and 2007 pesticide use exceeded 5.0 billion pounds (2.3 million metric tons) annually worldwide [1–5]. Due to the large quantities of pesticides applied annually to fields, the receiving surface soils function as sinks for a number of chemicals and as buffers for deeper soil layers and aquifers. Surface soils exposed to pesticide applications are also subject to various abiotic influences such as repeated and strong drying and wetting cycles and mechanical disruption such as tillage, which influence the fate and disposition of pesticides in soils. Therefore, the impact of changing climatic conditions is also a subject of growing concern with regard to the distribution of chemical pollutants in the environment [6].

Soil organic carbon (SOC) plays an important role in soil fertility and pesticide fate. The effect of soil drying and wetting on the release of SOC has been described elsewhere [7], mainly with regard to soil aggregation, soil aggregate stability [8–10], and decomposition of SOC [7,8,11–14]. A decline in SOC is a matter of growing concern [15], and it is likely to be exacerbated by intensified agricultural production and changing climatic conditions [16], with potentially adverse consequences on soil fertility, soil stability, and food production. Soil organic carbon has a substantial influence on organic pesticide sorption and retention, which influence the fate of these substances in the environment. As a consequence, it can be assumed that a decrease in SOC might also result in increased mobilization of pesticide residues in soils due to missing binding sites. Soil disaggregation, promoted by dry–wet cycles, results in increased release of SOC [9,10] and release of associated pesticide residues, as previously suggested [17]. In turn, released SOC might be subject to increased microbial mineralization [12,18]. In addition, microbially degradable carbon sources in soil may promote the degradation of pesticides cometabolically.

Experiments on the long-term fate of aged 14C-labeled pesticides in soils are rarely conducted. Outdoor lysimeter studies using 14C-labeled pesticides provide important information in this respect. The influence of dry–wet cycles of soil on the water extractability and release of long term–aged 14C-labeled pesticide residues has not been systematically tested and will provide important information about the remobilization of pesticide residues under changing abiotic conditions. Therefore, the present study investigated the influence of successive dry–wet cycles under laboratory conditions on the release of 14C-labeled residues of the thiadiazolylurea herbicide ethidimuron (ETD; 1-[5-ethylsulfonyl-1,3,4-thiadiazol-2-yl]-1,3-dimethylurea), the dimethyurea herbicide methabenzthiazuron (MBT; 1-[1-benzoathiazol-2-yl]-1,3-dimethyurea), and the triazine fungicide anilazine (ANI; 4,6-dichloro-N-[2-chlorophenyl]-1,3,5-triazin-2-amine) (Fig. 1) in soils aged under environmental conditions for 9 to 17 years. The following aims were addressed: (1) assessment of the influence of successive soil dry–wet cycles compared to permanently moistened soil on the water extractability of the aged 14C-labeled pesticide residues, (2) quantitative and qualitative analyses of the pesticide residues in the soil water extracts, and (3) evaluation of the influence of dry–wet cycles on SOC and total nitrogen (TN) extractability.
MATERIALS AND METHODS

Soil and lysimeter history

All outdoor lysimeters had a surface area of 1 m² and consisted of an undisturbed soil column (soil depth 1.1 m) of an Orthic Luvisol (Cₘₒₜ: 1.2%, sand: 6.4%, silt: 78.2%, clay: 15.4%; pH: 7.2) [19–21]. The time and amount of ¹⁴C-pesticide applications on the lysimeter soils are presented in Table 1. The chemical properties of the parent pesticide compounds are summarized in Table 2.

Soil sampling and ¹⁴C-residue detection

A total of approximately 2 kg of each individual lysimeter soil was sampled randomly in April 2006 from the soil layer at 0 to 30 cm depth of the ETD, MBT, and ANI lysimeter, using a Humax stainless steel soil core sampler, 3 cm in diameter. Because no ploughing simulation was applied on the ETD soil within six years prior to sampling as was performed for MBT and ANI soils, ETD soil was subdivided into 10-cm layers and only the soil from 0 to 10 cm depth was used for this experiment. For further ¹⁴C-residue calculation, estimated bulk soil densities of 1.5 g cm⁻³ for ETD soil and 1.3 g cm⁻³ for MBT and ANI soil were assumed. Soils were air-dried to a residual moisture content of 7 to 12% and then sieved (2 mm), homogenized, and stored in the dark at 3°C. To detect residual ¹⁴C activity in soils, samples of 50 g were dried at 105°C to accelerate the experimental process and ground in a mortar. Volatilization of pesticide residues during the drying process at 105°C can be excluded because results were compared with those obtained from soil samples that were air-dried only and found to be not different. The very low vapor pressure for these compounds (ETD: < 0.001 mPa; MBT: ≈590 nPa; ANI: 910 nPa; all at 20°C [22]) supports this observation. Subsamples were oxidized in five parallels of 1 g (Biological Oxidizer OX500; R.J. Harvey Instrument). Evolving ¹⁴CO₂ was trapped (Oxysolve C-400 scintillation cocktail; Zinser Analytik), and radioactivity was quantified using a liquid scintillation counter with internal quench correction (2500 TR, Tri-Carb; Packard Liquid Scintillation Analyzer).

Soil organic carbon and nitrogen analyses in soil samples

The SOC and TN were determined in triplicates of freeze-dried and homogenized soil samples prior to water-shaking extractions, as described previously [23]. Organic C was determined by radiofrequency heating of a 100-mg sample in flowing oxygen and subsequent infrared absorption by a Leco RC-412 multiphase carbon determinator. A Leco TCH 600 was applied to determine N₂ by thermal conductivity detection using 2-mg samples.

Desorption experiments

For each soil, two parallel experiments (A and B) were established. Triplicates of 10 g for each soil containing the aged ¹⁴C-labeled and nonlabeled ETD, MBT, and ANI residues were either (A) directly mixed with distilled water (1 + 2, w:w) or (B) first oven-dried at 45°C until dryness before adding water (1 + 2, w:w). All samples were simultaneously shaken for 1 h at 150 rpm on a horizontal shaker at room temperature (21 ± 2°C) and subsequently centrifuged to separate the solids from the water phase (60 min, 3,000 rpm, equal to approximately 2,800 g; Allegra 6KR, GH-3.7 Horizontal Rotor; Beckmann Coulter). The resulting supernatants were filtered (0.45 μm, PorafIl MV; Macherey-Nagel) to remove potential particulates from all water-extract samples prior to the detection of dissolved ¹⁴C activity, dissolved organic carbon (DOC), dissolved TN, pH, and electrical conductivity. For setup A, all moistened soil samples were stored after centrifugation and removal of the supernatant in the dark at 3°C, until all samples of setup B were again completely dried at 45°C (approximate drying time 3–4 d), and the cycle could be repeated. Both setups A and B were subject to 20 successive water-shaking extractions.

Subsequent to the entire experiment, total ¹⁴C recovery was calculated for all individual soils as a sum of total ¹⁴C activity.

Table 1. Application time and total quantities of applied ¹⁴C-labeled and nonlabeled ethidimuron (ETD), methabenzthiazuron (MBT), and anilazine (ANI) on lysimeter soils

| Soil  | Date of application (dd/mm/yyyy) | Applied a.i. a (mg m⁻²) | Total applied a.i. (kg ha⁻¹) | Applied ¹⁴C activity (MBq m⁻²) | Specific ¹⁴C activity (kBq mg⁻¹) |
|-------|---------------------------------|-------------------------|----------------------------|-------------------------------|--------------------------------|
| ETD   | 13.11.1997                      | 123.3                   | 1.23                       | 107.3                         | 870.0                          |
| MBT   | 29.11.1994 (last application)   | 879.0b                  | 8.79b                      | 261.6b                        | 297.7                          |
| ANI   | 13.06.1989 (last application)   | 1978c                   | 19.78c                     | 372.5c                        | 188.4                          |

a a.i. = active ingredient.
b In total after three applications, 1988, 1992, and 1994.
c In total, after five consecutive annual applications, 1985-1989. Sampling of all lysimeter soils was performed in April 2006.
extracted from each soil sample and the residual $^{14}$C activity remaining in the water-extracted soil samples, as well as $^{14}$C activity adsorbed to the fillers.

**Determination of water-extracted $^{14}$C activity**

The amount of dissolved $^{14}$C activity was determined in triplicates for each soil extract by mixing 1 ml of the liquid samples with 10 ml of scintillation cocktail (Instant Scint-Gel Plus, PerkinElmer), and radioactivity was detected by liquid scintillation counting. An external standard was used for quenching correction using 1 ml of distilled water with 10 ml of scintillation cocktail.

**Carbon and nitrogen analysis of water extracts**

All aqueous samples were analyzed for total DOC and dissolved TN content, using a Shimadzu Total Organic Carbon/Nitrogen Analyzer (TOC-5050A, ASI-5000A Auto Sampler).

**Liquid chromatography MS/MS analysis of water extracts**

**Reagents and materials.** Bayer Crop Science AG provided ETD, MBT, ANI, dihydroxyanilazine (di-OH-anilazine), and dimethoxyanilazine (di-OMe-anilazine), and isoproturon (IPU) and d$_5$-2-hydroxyatrazine (purchased from Dr. Ehrenstorfer GmbH) were used as internal standards for quantification of ETD, MBT, and ANI and of di-OH-anilazine and di-OMe-anilazine, respectively. Ammonium acetate (Fractopur), formic acid (100%, Suprapur), and acetonitrile (LiChrosolv) were obtained from Merck. Water obtained from a Milli-Q-Plus Ultra-Pure water purification system (Millipore) was used to prepare all samples and mobile phases.

**Liquid chromatography–atmospheric pressure chemical ionization–tandem mass spectrometry analysis.** Liquid chromatography–atmospheric pressure chemical ionization–tandem mass spectrometry analysis (LC-APCI-MS/MS) was applied in accordance with our method described elsewhere [24]. Briefly, an Agilent 1100 series HPLC coupled with a Thermo Electron TSQ Quantum triple quadrupole mass spectrometer was used. Liquid chromatographic separations were carried out with a Phenomenex Synergy 4u, Polar RP18 column, 150 × 3.0 mm I.D. A 1 mM ammonium acetate + 0.1% formic acid (A)/acetonitrile + 0.1% formic acid (B) gradient was applied for ETD and MBT, while ANI and ANI metabolites were separated with 5 mM ammonium acetate (A) and acetonitrile (B). The mass spectrometer was operated in the positive atmospheric pressure chemical ionization (APCI(+)) mode for the detection of ETD and MBT and in the negative atmospheric pressure chemical ionization (APCI(−)) mode in case of ANI and ANI metabolites. Multiple reaction monitoring was used to quantify all analytes and standards.

**Calibration and quantification.** Quantification was carried out using the internal standard method as stated previously [24]. Analysis of MBT/ETD was performed with IPU as an internal standard and that of ANI and ANI metabolites with d$_5$-2-hydroxyatrazine.

**Electrical conductivity and pH analyses of water extracts**

To determine the potential loss of soil minerals as a result of the successive dry–wet cycles, the electrical conductivity of previously filtered water extracts was measured using a WTW device (Cond 340i/SET, WTW). The pH of all filtered water extracts was monitored using a Metler Toledo pH meter (PTB01 ATEX 2166X, Type 1120X).

**Statistical analysis**

For statistical analysis, the independent two-sample $t$ test was applied to determine the significance of differences between mean values.

**RESULTS AND DISCUSSION**

**Soil analyses**

Even after long-term environmental aging (9–17 years) (Table 1), a major fraction of residual $^{14}$C activity was still present in the upper soil layer of 0 to 10 cm depth for ETD soil and 0 to 30 cm depth for MBT and ANI soil, accounting for 18.7% (ETD soil), 34.8% (MBT soil), and 43.2% (ANI soil) of total initially applied $^{14}$C activity (Table 3). Considering additionally the detected residual $^{14}$C activity in the ETD soil layers at 10 to 20 and 20 to 30 cm depths, the residual detected $^{14}$C activity accounted for 16.4 and 12.2% (data not shown), respectively. In this case, the total residual $^{14}$C activity accounted for 47.3% of initially applied $^{14}$C activity in the entire ETD soil layer at a depth of 0 to 30 cm. As presented in another environmental long-term study using $^{14}$C-labeled atrazine [23,25,26], most of the residual $^{14}$C activity was located in the upper 10-cm soil layer and is most likely associated with the higher organic carbon content in this soil layer [26–28].

The SOC and TN contents in the soils at the date of sampling accounted for 1.14 ± 0.06% and 0.15 ± 0.00%, respectively. Because all soil monoliths were taken at the same field plot, minor differences in SOC content can be attributed to potential differences in the soil management of the lysimeters [24].

An association of ETD, MBT, and ANI with SOC has previously been demonstrated [21,29]. Even after long-term environmental aging, SOC plays a major role in pesticide residue retention in the upper soil layers, where the SOC content is generally higher than in deeper layers.

A decrease in SOC content could be related to intensified agricultural production and climatic changes leading to a potential increase of SOC microbial turnover; however, current scientific data on SOC decline in soils are rather inconsistent with regard to this issue [30–34]. A decrease in SOC could be facilitated by soil drying and rewetting due to a subsequent increase in microbial SOC turnover [35]. Reemtsma et al. [17] suggested that the contaminant release from soils

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### Table 2. Chemical properties of ethidimuron (ETD), methabenzthiazuron (MBT), and anilazine (ANI)*

| Pesticide | Molecular formula | Chemical family | Molecular weight (g Mol$^{-1}$) | Solubility in water (g L$^{-1}$ at 20°C) |
|-----------|-------------------|-----------------|-------------------------------|---------------------------------------|
| ETD       | C$_7$H$_{12}$N$_3$O$_3$S$_2$ | Urea; thiadiazole | 264.33 | 3.0 |
| MBT       | C$_{10}$H$_{11}$N$_3$OS | Urea; benzothiazole | 221.29 | 0.059 |
| ANI       | C$_5$H$_{15}$N$_4$ | Triazine; organochlorine | 275.54 | 0.008 |

*Information taken from The Agrochemicals Handbook [22].
might be influenced by microbial activity over time, altering the long-term function of soils as a sink or source of organic contaminants.

Considering a potential decline in SOC in agricultural soils, it can be assumed that the buffering function of the soils for pesticides and their metabolites could be reduced. This might result in greater remobilization of pesticides in soils due to altered SOC content.

Analyses of water extracts

Liquid chromatography MS/MS analyses. Even after long-term environmental aging, liquid chromatography MS/MS analyses revealed the parent compounds ETD (nine years after application, Table 1) and MBT (12 years after application, Table 1) in water extracts of dry–wet soils, as presented in Figures 2 and 3, right y axis. The parent compound ETD was found in the first five water extracts of dry–wet soils and in the first two water extracts of constantly moistened soils, albeit in much smaller quantities (Fig. 2, right y axis), totaling 15.1 and 2.8 μg kg⁻¹ of the water-extractable parent compound ETD, respectively (Table 3). As shown in Table 3, these values correspond to 1.83 and 0.34%, respectively, of the initially applied parent compound.

In the case of MBT, the parent compound was detected in the first four water extracts of dry–wet soil samples, totaling 0.23 μg kg⁻¹ water-extractable parent compound MBT (Table 3). No MBT was detected in water extracts of constantly moistened soils (Fig. 3, right y axis). The detected amount of water-extractable MBT equals 0.01% of the initially applied parent compound.

This observation must be attributed to a combination of a generally higher water solubility of ETD (Table 2; 3.0 g ETD vs 0.059 g MBT L⁻¹ at 20°C), a low adsorption affinity to soils, as well as a much higher environmental persistence in soils compared to MBT [22,24,36,37]. Although ETD is much more water-soluble, its biodegradability is much lower than that of MBT, resulting in proposed environmental half-lives of 162 to 2,059 d compared to approximately 24 to 230 d for MBT [21,37,38]. Furthermore, MBT was found to be biodegradable [38–40], giving an additional explanation for the overall smaller MBT residue fractions in the water extracts. In contrast, the microbial ETD degradation in soil was found to be very limited [21].

In the case of ANI, neither the parent compound nor dihydroxy-ANI as its main metabolite was detected in the water extracts. This fact must be attributed to the very low water solubility of ANI (Table 2; 0.008 g L⁻¹ at 20°C), its high adsorption affinity to the soil matrix, and the extended environmental aging time of 17 years (Table 1) as a driving factor for the formation of soil-bound residues [22,29,41,42].

As shown in a previous study, drying and wetting soils containing phenanthrene and di(2-ethylhexyl)-phthalate reduced the biodegradability, extractability, and uptake by earthworms [43]. In our case, however, the parent pesticide compounds ETD and MBT were detected in the water phase after long-term aging and thus could be more accessible for biodegradation or uptake. Generally, the increased release of aged pesticide residues from dried and rewetted soils could be due to disruption of soil aggregates, facilitating the release of entrapped pesticide molecules, which are normally excluded from remobilization under moistened conditions. These observations might also be valid for a number of other pesticide residues in soils, which could be remobilized by environmentally relevant dry–wet cycles. These data help to assess the chemical nature of long-term aged pesticide residues in soils and their remobilization potential. Biological and toxicological effects such as endocrine disrupting activity, as discussed for small concentrations of atrazine [44], are so far not published for the pesticide compounds described herein. Therefore, further research is needed to evaluate the biological or toxicological relevance of our findings.

Water-extracted residual ¹⁴C activity and DOC/TN determination. The results showed a significant increase in desorbed ¹⁴C activity in water extracts of all soils after drying, accounting for 44% (ETD), 15% (MBT), and 20% (ANI) of residual ¹⁴C activity in soil samples after 20 dry–wet cycles compared to water extracts of constantly moistened soils (Figs. 2–4, left y axis).

As shown in Table 3, total water-extractable ¹⁴C activity in soil samples after 20 dry–wet cycles compared to MBT 

**Table 3.** Total residual ¹⁴C activity per soil layer and total water-extracted ¹⁴C activity after 20 consecutive water extraction steps

| Soil (layer in cm) | Residual ¹⁴C activity of total applied in soil layer (%)a | Total water-extractable ¹⁴C activity in sample (%) | Total water-extractable parent compound (μg kg⁻¹) | Parent compound of initially applied calculated for m² and soil layer (%)a |
|-------------------|--------------------------------------------------------|--------------------------------------------------|-------------------------------------------------|---------------------------------------------------------------------|
| ETD (0–10)       | 18.71                                                  | Dry–wet: 43.8±5.5                                 | 15.1±3.7                                        | 1.83                                                                |
|                   |                                                        | Wet: 15.5±1.7                                     | 2.8±1.2                                         | 0.34                                                                |
| MBT (0–30)       | 34.84                                                  | Dry–wet: 153.0±9                                   | 0.23±0.06                                       | 0.01                                                                |
|                   |                                                        | Wet: 4.6±0.9                                      | −                                               | −                                                                    |
| ANI (0–30)       | 43.24                                                  | Dry–wet: 19.5±1.6                                  | −                                               | −                                                                    |
|                   |                                                        | Wet: 6.1±0.4                                      | −                                               | −                                                                    |

a Estimated soil density for calculation: Ethidimuron (ETD) soil 1.5 g cm⁻³; methabenzthiazuron (MBT) / anilazine (ANI) soil 1.3 g cm⁻³; ± standard deviation of n = 3 to 9.
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The overall results demonstrate long-term binding and sequestration mechanisms of organic pesticides in soils. The data suggest that environmentally relevant dry–wet cycles may...
change interfacial soil properties intensively. This may result in increased remobilization and release of aged pesticides or pesticide metabolites in surface soils. However, the experimental setup was designed to describe a maximum possible remobilization potential of the aged residual pesticide fractions present in our experimental soils.

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