Pesticide environmental fate parameters and their quantitative relationship with soil and climatic conditions

W. Chen*[1], W. Koskinen[2], A. Farenhorst[3], V. Laabs[4], A. Ritter[5], R. Kookana[6], A. Sabljic[7], R. Sur[8], R. Ahmad[9], E. Carazo[10], J. A. Guerrero D.[11], K. S.B. Miglioranza[12], V. Cesio[13], J. Zhou[14]
*Corresponding: wenlin.chen@syngenta.com. Author affiliations are listed at the end of poster

INTRODUCTION/ABSTRACT

Background: Pesticide sorption and degradation in soil are two critical, interlinked and extensively studied processes for assessing a pesticide's potential environmental mobility and persistence. There is a wealth of data on this in published literature. This presentation summarizes the results of a recent IUPAC research project (2010-018-2-600) focusing on quantitative relationships of the environmental fate processes of pesticide with broader soil properties, climatic variables, and potential molecular structure-activity. Results are expected to benefit data deficient regions with limited pesticide fate studies (e.g. tropical soils, and scientifically emerging regions in Africa, Asia and South America).

METHODS

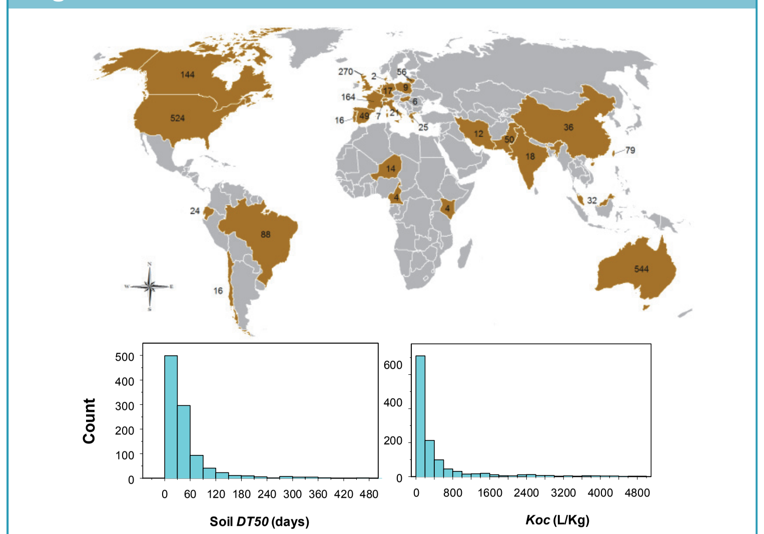
Literature data collection process

- Parameters to be collected, including Kd/Koc, DT50 (or half-life), soil properties, and related experimental conditions.
- Spreadsheets with required format for data entry.
- Scope of literature coverage: focus on quality papers with insight into "relationships" (no attempt to encompass all papers ever published).

Database development

- Portable database (Degradation And Sorption of Pesticide, or DASP) for data collation and query.
- New information on chemical class, SMILES codes, and mode of action from Pesticide Properties DataBase (PPDB, http://sitem.herts.ac.uk/aeru/iupac/).

Figure 1. Distribution of data collected



Data analysis/modeling

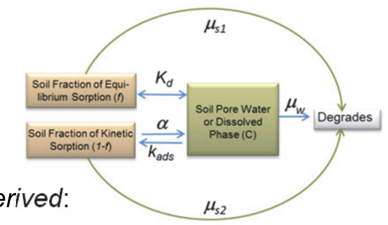
1. Kinetics

For kinetics data sets, the two-site sorption model with differential degradation is used (*Chen et al., 2014*):

$$dC/dt = -B_f \mu_w C \quad (1)$$

where B_f is bioavailability:

$$B_f = 1\Big/\left[1+\frac{\rho}{\theta}\left(fK_d+\frac{dS_2}{dC}\right)\right] \quad (2)$$



Two expressions for B_f *are derived*:

$$\text{Short-term}: B_{fS} = 1\Big/\left(1+fK_d\theta_g^{-1}\right) \quad (3)$$

$$\text{Long-term}: B_{fL} = 1\Big/\left[1+K_d\theta_g^{-1}\left(f+(1-f)\alpha/(\alpha+\lambda_1)\right)\right] \quad (4)$$

where λ_1 is a macro rate constant; θ_g is gravimetric water content. DT50 (or half-life for constant B_f) is an inverse function of B_f:

$$DT50 = Constant/(B_f\mu_w) \quad (5)$$

2. Mixed-effect model

For data without kinetics measurements, linear mixed-effect regressions are used to explore relationships of degradation with sorption (Koc, L/Kg), soil organic carbon ($OC\%$), and temperature (T, °C) in the form of Eq. 5 but on a log scale. Specifically,

$$LN(DT50_{ij}) = (a_0 + a_{0i}) + a_1 LN(Koc_{ij}) + a_2 LN(OC_{ij}) + a_3 LN(T_{ij}) + \varepsilon_{ij} \quad (6)$$

where a_0, a_1, a_2, and a_3 are regression constants; ε is regression error; and subscripts i and j represent chemical i in study j.

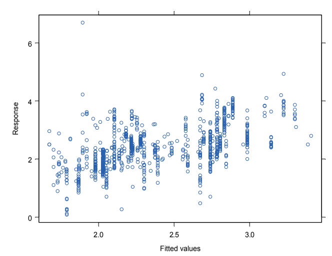
The mixed-effect model similar to Eq. 6 is also used to explore potential sorption poly-parameter linear free energy relationship (pp-LFER).

Mixed-effect model analysis

Figure 5. Koc Linear solvation energy relationship

```
Random effects:
 Formula:  ~ 1 | Soil.in.Country
         (Intercept)  Residual
StdDev:      0.4380    0.6665

Fixed effects: Log.Koc ~ A + B + S + E + V
               Value Std.Error  D.F.  t-value  p-value
(Intercept)    2.486    0.181    994   13.725   <.0001
          A   -0.587    0.113    994   -5.188   <.0001
          B   -0.136    0.044    994   -3.090   0.0021
          S    0.013    0.067    994    0.190   0.8493
          E   -0.169    0.080    994   -2.124   0.0339
          V    0.274    0.105    994    2.616   0.0090
```



- A: H-bond acidity (H-donor or electron acceptor).
- B: H-bond basicity (H-acceptor or electron donor)
- E: Excess molar refraction (dispersion force interactions via polarisability of pi-/n-electrons)
- S: Polarity/polarisability (electrostatic interactions or dipole-dipole interactions).
- V: McGowan characteristic molar volume.

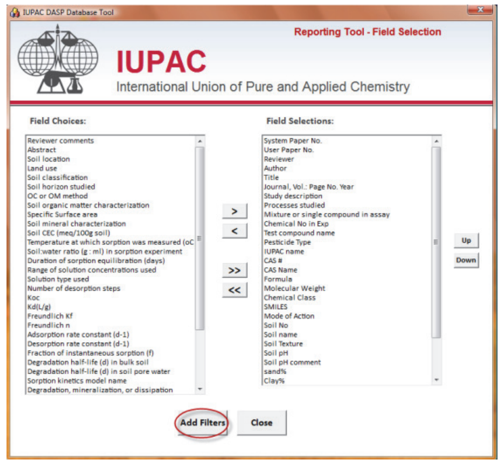
- Koc statistically relates to solvation energy descriptors except S.
- Significant intercept & larger variability → country/region- & soil-dependence

RESULTS

DASP database

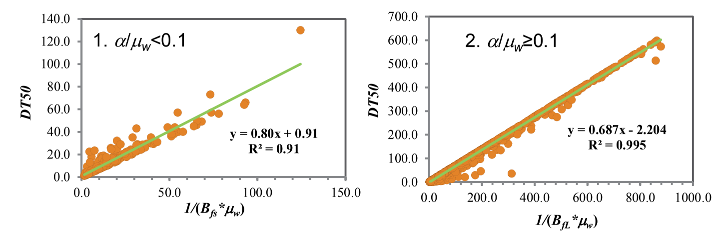
- >2500 data records of 129 compounds in 29 countries & regions; >50 specific parameters targeted for collection, including Kd/Koc, DT50 (half-life), & related auxiliary data.

Figure 2. Compound specific parameters for collection



Kinetics analysis

Figure 3. Relationship between DT50 & bioavailability B_f



DT50 correlates well with the short-term B_{fS} when desorption is much slower than degradation (left). Likewise, DT50 is related to the long-term B_{fL} when desorption is much faster than degradation (right). Results are from 5000 Monte Carlo simulations (Chen et al., 2014).

Measured results of eight compounds in seven published kinetics studies (Chen et al., 2014)

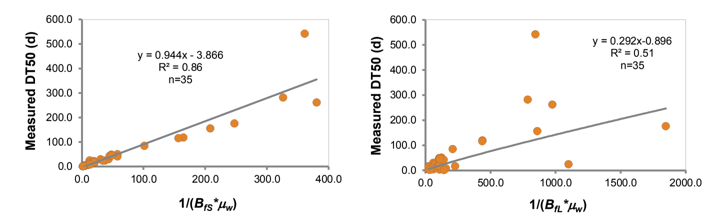
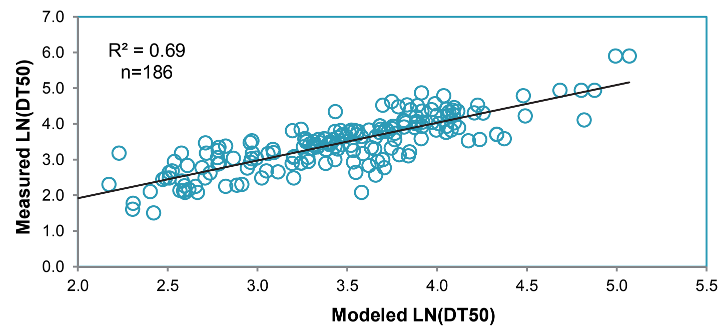


Figure 4. Mixed-effect model of DT50 as a function of Koc, OC, T, and chemistry




```
Random effects:
 Formula:  ~ 1 | Compound.name
         (Intercept)  Residual
StdDev:      0.645     0.458

Fixed effects: log(DT50) ~ log(OC)+log(T)+log(Koc)
               Value  Std.Error  DF  t-value  p-value
(Intercept)    5.10    0.468    160   10.88   <.0001
    log(OC)   -0.29    0.0622   160   -4.65   <.0001
  log(Temp)   -0.81    0.127    160   -6.36   <.0001
   log(Koc)    0.15    0.0391   160    3.715   0.0003
```

- Significant DT50 correlation with Koc, OC, and T.
- Koc, OC and T ~ bioavailability & biodegradability.
- Significant intercept with StdDev 0.65 (i.e., a_0+a_{0i} in Eq. 6) → correlation is chemical-specific (or conditional on chemistry).

DISCUSSION AND CONCLUSION

- DASP database is developed and populated with >2500 data records of 129 compounds in soils of 29 countries/regions.
- Coupled sorption and degradation kinetics show that DT50 is inversely related to bioavailability and biodegradability (i.e. degradation rate in soil pore water). Factors influencing both are expected to determine soil degradation under specific conditions.
- Significant DT50 correlation with Koc, soil OC, and temperature is found in 186 studies having both degradation and sorption data. This correlation is chemical-dependent.
- Preliminary regression shows a statistical linear solvation energy relationship with sorption (Koc). However, large variability indicates strong influence of soil properties and local conditions.
- More studies investigating both degradation and sorption on the same soil are needed for developing more robust predictive models.

REFERENCE

Chen, W., Laabs, V., Kookana, R., Koskinen, W. *In* Non-First Order Degradation and Time-Dependent Sorption of Organic Chemicals in Soil. Chen, W., Sabljic, A., Cryer, S. Kookana, R. (*Eds.*). American Chemical Society. 2014.

ACKNOWLEDGMENTS

This project is funded by IUPAC Division VI Chemistry and the Environment. Financial sponsorship was received from Syngenta. Contributions to data collection were also received from N. Song (China); M. Gonzalez (Argentina); D. Gallaway (Syngenta Intern); Database DASP was developed by J. Whitcomb (Resourceful Consulting, Inc.). The original IUPAC project team members include:

W. Chen (Chair), Syngenta, USA
R. Kookana, CSIRO Land and Water, Australia
A. Farenhorst, Univ. of Manitoba, CANADA
W.C. Koskinen, USDA-ARS, USA
V. Laabs, BASF, Germany
R. Ahmad, Pir Mehr Ali Shah Arid Ag. Univ., PAKISTAN
A. Sabljic, Institute Rudjer Boskovic, Croatia
Y. Nakagawa, Kyoto Univ., JAPAN
J. Zhou, Nanjing NIES, P.R. China
V. Cesio, Univ. de la República, Uruguay
El. Carazo, Univ. de Costa Rica, COSTA RICA
R. Parker, OPP/EPA, USA
K.D. Racke, Dow AgroSciences LLC, USA
D. Shaner, USDA-ARS, USA
J. Linders, RIVM, The Netherlands
A. Katayama, Nagoya Univ., JAPAN

AUTHOR AFFILIATION

1 Syngenta Crop Protection, LLC, USA
2 University of Minnesota, USA
3 University of Manitoba, Canada
4 Volker Laabs, BASF, Germany
5 Waterborne Environmental, Inc., USA
6 CSIRO Land and Water, Australia
7 Institute Rudjer Boskovic, Croatia
8 Bayer CropScience LP, USA
9 Punjab Agricultural Research Board, Pakistan
10 Universidad de Costa Rica, Costa Rica
11 Universidad Nacional de Colombia, Colombia
12 Universidad Nacional de Mar del Plata, Argentina
13 Universidad de la República, Uruguay
14 Nanjing Institute of Environmental Science, China