# Deutsche Forschungsgemeinschaft

### Pesticide Bound Residues in Soil

Workshop, September 3<sup>rd</sup>-4<sup>th</sup> 1996

Organized by Fritz Führ and Holger Ophoff Forschungszentrum Jülich GmbH

Edited by the Senate Commission for the Assessment of Chemicals Used in Agriculture

Report 2







Preface		
I	Introduction	1
II	Non-extractable Residues of Organic Xenobiotics in Soils –	
	A Review	5
1	Definitions	5
2	Characterization of Bound Residues	7
3	Availability of Xenobiotics from Bound Residues	17
III	Sessions	33
1	Methods of Determining the Nature of the Bond	33
1.1	Using <sup>13</sup> C NMR spectroscopy to characterize the binding	
	of pesticides to humic substances	33
	Andreas Wais	
1.2	Characterization of bound residues from cyprodinil by	
	<sup>13</sup> C-labelling and NMR spectrometry	41
	Konrad Haider, Jerzy Dec, Andreas Schäffer,	
	Jean-Marc Bollag	
1.3	Soil-bound residues of the novel fungicide cyprodinil:	
•	Extraction, size-exclusion and thin-layer chromatography	47
	Andreas Schäffer, Jerzy Dec, Konrad Haider,	
	Jean-Marc Bollag	
1.4	Determination of non-extractable triazine residues by enzyme	
	immunoassay (EIA) – Investigation of model compounds and	
	soil fulvic and humic acids	52
	Andrea Dankwardt, Rupert Simon, Dieter Freitag,	
	Antonius Kettrup, Bertold Hock	

1.5	Detection of bound residues by enzyme immunoassay  Michael G. Weller, Elfriede Simon, Peter Pfortner,  Maria Dosch, Reinhard Niessner	56
2	New Extraction Methods and their Role for Humic Chemistry	
	in General	60
2.1	Using humic substances of different origins to investigate	
	bound residues	60
	Andreas Wais, Peter Burauel, Claudia Roggelin	
2.2	Silylation of humic substance bound residues –	=0
	A new extraction technique	78
0.0	Andreas Wais	
2.3	Conjugation of pesticides in the plant root zone:	
	Some thoughts on the initial steps to the formation of	07
	bound residues	87
3	Rudolf J. Schneider	
3	Assessment of Different Bonds with Respect to Detoxification of Soils (Ionic, Covalent, Complex, H <sup>+</sup> -,	
	Dipole-Dipole-Interactions,)	91
3.1	Time-dependent formation of covalent bonds in	91
5.1	model systems	91
	Andreas Wais, Peter Burauel, Claudia Roggelin	31
3.2	Reversible and irreversible interactions between organic	
0,2	pollutants and dissolved humic substances	95
	Frank-Dieter Kopinke, Jürgen Pörschmann, Ines Lebelt,	33
	Anett Georgi, Ulrich Stottmeister	
3.3	Chloroaniline-lignin conjugates as model systems for	
0.0	non-extractable residues in crop plants –	
	Conformational state effects and hydrolytic behaviour	103
	Bernd Markus Lange, Norbert Hertkorn, Antonius Kettrup,	
	Heinrich Sandermann Jr.	
4	Stimulation of Formation of Bound Residues and their	
	Practical Relevance	109
4.1	Chemical structure of crop protection products and	
	formation of non-extractable radioactivity in soil	109
	Johann A. Guth	
4.2	The effect of organic amendment on metabolization of	
	methabenzthiazuron and formation of bound residues	112
	Harald Printz, Peter Burauel, Fritz Führ	
5	Remobilization of Pesticides and/or Metabolites from	
	Soil and Plants	117

5.1	Influence of soil moisture on the remobilization of	
	previously bound PAH residues in contaminated soils	117
	Sören Thiele, Gerhard W. Brümmer	
5.2	Bioavailability of soil-bound residues of <sup>14</sup> C bentazon	
	for earthworms	122
	Doris Ebert	
5.3	Remobilization of plant-bound 2,4-dichlorophenol by	
	earthworms and succeeding crops	127
	Karlheinz Pawlizki	
6	Uptake of Bound Residues by Plants – Simulation of	
	Rhizosphere Situation	133
6.1	PCDD/PCDF-mobilizing compounds in root exudates	
	of zucchini	133
	Günter Neumann, Anke Hülster, Horst Marschner †	
6.2		
	anilazine and bioavailability of the benzene ring carbon	138
	Werner Mittelstaedt, Fritz Führ	
7	Leaching of Bound Residues in Combinations of	
	Humic Substances	145
7.1	Formation and release of soil-bound residues of <sup>14</sup> C	
	isoproturon during the humification of organic matter	145
	Stephan Reuter, Irene Scheunert	
7.2	Influence of DOC on mobility and ecotoxicity of	
	sparingly soluble substances	148
	Werner Kördel, Ursula Wahle, Werner Klein	
7.3	Active ingredient concentrations in soil solutions of an orthic	
	luvisol after preemergence application of [phenyl-U-14C]	153
	methabenzthiazuron to winter wheat	
	Thomas Pütz, Werner Mittelstaedt, Fritz Führ	
8	Ecotoxicological Relevance of the Soil/Plant System	161
	Fate and ecological significance of pesticide residues	
	in soil and plant	161
	Michael Spiteller	
IV	Results of Discussion and Further Research Requirements	167
	Holger Ophoff, Peter Burauel, Uwe Wanner, Thomas Pütz,	
	Jost Liebich, Stefan Brandt, Konrad Haider, Fritz Führ	
1	Methods for Determining the Type of Bond with	
	Respect to Detoxification in Soil	167
1.1	NMR spectroscopy	167

1.2	Gel-permeation chromatography	168
1.3	Immunoassays	168
1.4	Studies of humic substances by pyrolysis GC-MS	168
2	Consideration of New Extraction Methods and their	400
	Significance for Humic Chemistry in General	169
2.1	Silylation studies	169
2.2	Solid-phase microextraction	169
3	Stimulation of the Formation of Bound Residues and	
	their Practical Relevance	170
4	Quantification of Bound Residues	171
4.1	Chemico-analytical approach	171
4.2	Biological approach	171
5	Translocation of Bound Residues Together with SOM	172
6	Ecotoxicological Assessment of Bound Residues in the	
	Soil/Plant System	173
V	Modification of the Definition of Bound Residues Fritz Führ, Holger Ophoff, Peter Burauel, Uwe Wanner, Konrad Haider	175
VI	Appendix	177
1	Members of the Senate Commission for the Assessment	
	of Chemicals Used in Agriculture	177
2	List of Authors	180