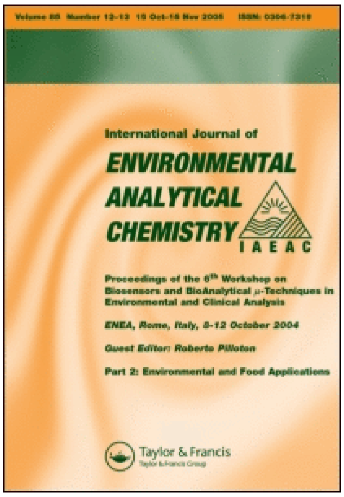

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Holthuis, J. -U. , Baumbach, R. , Friebe, S. and Kraus, G. -J.(1997) 'Multi-Residue Analysis of Frequently Applied Herbicides from Soil Samples Taken in the Area of Halle/S. (FRG)', International Journal of Environmental Analytical Chemistry, 66: 4, 269 — 283

To link to this Article: DOI: 10.1080/03067319708028369

URL: http://dx.doi.org/10.1080/03067319708028369

Intern. J. Environ. Anal. Chem., Vol. 66, pp. 269-283
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MULTI-RESIDUE ANALYSIS OF FREQUENTLY APPLIED HERBICIDES FROM SOIL SAMPLES TAKEN IN THE AREA OF HALLE/S. (FRG)

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(Received 23 July, 1996; In final form 26 December, 1996)

A high-resolution multimethod is presented for simultaneous determination of frequently applied s-triazine and phenoxyalkanoic acid herbicides extracted from soil samples. The method involves precipitation of interfering humic substances, enrichment of analytes by solid-phase extraction (SPE) and identification by reversed-phase high-performance liquid chromatography coupled to diode-array detection (RP-HPLC-DAD).

Frequent contents of s-triazine residues vary between 10 and 30 $\mu g \times kg^{-1}$dry soil. 50 % of investigated pedogenic material shows s-triazine residues in the range of 10 $\mu g \times kg^{-1}$. Heavily impacted areas (orchards, herbicide storage areas) often show contents in the range from more than 100 up to 433 $\mu g \times kg^{-1}$. Phenoxyalkanoic acid herbicides could be shown to diminish completely within three weeks after application.

An example of temporal and spatial variability of soil's adsorptive behaviour is given.

Keywords: Herbicides; HPLC-DAD; soil; bound residues; variability

INTRODUCTION

In the former GDR, the area of Halle with its fertile, chernozem-like soils was characterized by industrialized crop production by agricultural co-operatives. Consequently, most of agricultural acreage has been treated periodically with herbicides.

Once released to the dynamics of soil chemistry, herbicide residues may exercise unintended action in the environment, depending on complex interactions

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between the active ingredient, features of the sampling site and tillage. The knowledge of the importance of these xenobiotics in outdoor soil-ecosystems is still limited[1,2,3].

Partly minute amounts of herbicide residues are strongly retained by the soil matrix, especially by humic substances. This affects extraction efficiency, resulting in low recoveries and the phenomenon of "non-extractable residues"[4,5]. In addition, unambiguous chromatographic identification is disturbed by alteration of the physico-chemical properties of the compound and a background of co-extracted organic matter. Permanent high loadings of organic matter may also shorten the lifetime of chromatographic columns.

As a result, residue analysis from soil samples needs selective extraction and preconcentration techniques, being prerequisites for a rapid and sensitive separation and a reliable identification of analytes.

It is our intention to get a picture of the herbicide burden left by historic land use and to study the behaviour of residues in soils under the specific semiarid climatic conditions of this area (< 500 mm rainfall $\times$ a^{-1}). For this reason, a high-resolution multimethod was developed to enable rapid determination of important, local-specific herbicides (s-triazines, substituted phenoxyalkanoic acids and some of their known degradation products; Table I), taken from humic soil samples. The method is based on removal of disturbing humic substances followed by solid-phase extraction (SPE) of herbicidal residues and their final identification by RP-HPLC-DAD.

EXPERIMENTAL

Standard material

All standards (purity > 98%) are purchased from Dr. Ehrensstorfer (Augsburg, FRG).

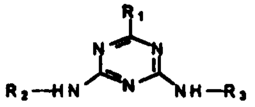
Reagents

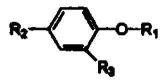
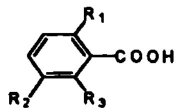
Acetonitrile, (Baker, Groß-Gerau, FRG), methanol (Merck, Darmstadt, FRG) and water (Seral, Ransbach-Baumbach, FRG) are of HPLC-grade quality and have been used as purchased. Sodium chloride (p.a.), RP_{18}-silicagel and silicagel are from Merck (Darmstadt, FRG). Dichloromethane and ethyl acetate are of p.a. quality.

Extracts are filtered through blue-ribbon paper filters (Schleicher & Schüll, Dassel, FRG).

TABLE I Compounds investigated by RP-HPLC-DAD

Basic structure: 1,3,5-s-triazine



Peak No.	*Rt (min)*	**common name**	*R1*	*R2*	*R3*
		2-chloro–1,3,5-s-triazines			
12	25,2	Simazine	Cl	Et	Et
14	30,6	Atrazine	Cl	Et	iPr
18	35,9	Propazine	Cl	iPr	iPr
		2-methylthio-1,3,5-s-triazines			
17	34,4	Ametryne	SCH3	Et	iPr
19	39,2	Prometryne	SCH3	iPr	iPr
		Degradation products			
3	12,8	2-Hydroxy-Simazine	OH	Et	Et
5	14,2	2-Hydroxy-Atrazine	OH	Et	iPr
6	15	Deisopropyl-Atrazine	Cl	Et	H
8	18,3	Deethyl-Atrazine	Cl	H	iPr
2	9,2	Deethyl-Deisopropyl-Atrazine	Cl	H	H
1	5,4	Deisopropyl-2-hydroxy-Atrazine	OH	Et	H
		Basic structure: substituted phenoxyalkanoic acid			
9	20,7	2,4-D	Ac	Cl	Cl
10	22,2	MCPA	Ac	Cl	CH3
11	24,4	Dichlorprop	Prop	Cl	Cl
13	26,2	MCPP	Prop	Cl	CH3
		Degradation products			
7	17,2	4-Chlorophenoxy Acetic Acid	Ac	Cl	H
15	32,2	4-Chloro–2-Methylphenol	H	Cl	CH3
16	32,7	2,4-Dichlorophenol	H	Cl	Cl
		Basic structure: benzoic acid derivative			
14	13,7	Dicamba	Cl	Cl	OCH3

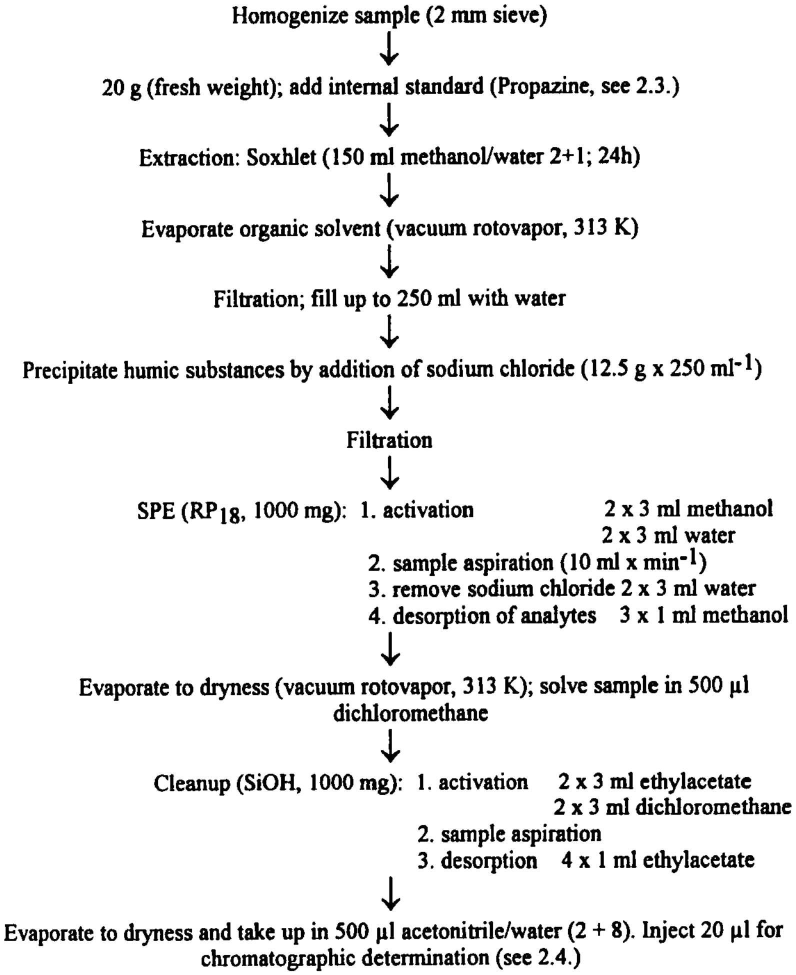
Abbreviations: Ac (acetic acid); Et (ethyl); iPr (isopropyl); Prop (propionic acid)

Sample Preparation

Samples were taken on locations near Halle (Sachsen-Anhalt, FRG) with proved or suspected herbicide past.

Soil samples (approx. 200 g) represent combinations of subsamples (n=5), separately taken of each visible horizon down to pedogenic material. Samples are stored in PE-bags at 253 K until processing.

A flow chart diagram of the extraction procedure is given in Figure 1.



Homogenize sample (2 mm sieve)

↓

20 g (fresh weight); add internal standard (Propazine, see 2.3.)

↓

Extraction: Soxhlet (150 ml methanol/water 2+1; 24h)

↓

Evaporate organic solvent (vacuum rotovapor, 313 K)

↓

Filtration; fill up to 250 ml with water

↓

Precipitate humic substances by addition of sodium chloride (12.5 g x 250 ml^{-1})

↓

Filtration

↓

SPE (RP_{18}, 1000 mg):
1. activation 2 x 3 ml methanol
   2 x 3 ml water
2. sample aspiration (10 ml x min^{-1})
3. remove sodium chloride 2 x 3 ml water
4. desorption of analytes 3 x 1 ml methanol

↓

Evaporate to dryness (vacuum rotovapor, 313 K); solve sample in 500 µl dichloromethane

↓

Cleanup (SiOH, 1000 mg):
1. activation 2 x 3 ml ethylacetate
   2 x 3 ml dichloromethane
2. sample aspiration
3. desorption 4 x 1 ml ethylacetate

↓

Evaporate to dryness and take up in 500 µl acetonitrile/water (2 + 8). Inject 20 µl for chromatographic determination (see 2.4.)

FIGURE 1 Flow chart diagram of the extraction procedure

To determine the efficiency of the methanolic extraction, an internal standard (ISTD; 5000 ng Propazine contained in 100 μl methanol) is added directly before extraction by dripping a small volume of concentrate on top of the respective sample pile without any mixing or aging. The recovery of the ISTD is not used to correct any data.

The analytes are concentrated by SPE by a factor of approx. 500.

All results are reported on a dry weight (378 K) base.

Chromatographic Equipment

All analysis were performed by a Lichrograph-HPLC-system (Merck, Darmstadt, FRG), coupled to a HP 1050 photo-diode array detector with peripherals (Hewlett-Packard, Waldbronn, FRG).

As analytical column a Merck Superspher 60 RP-select B (250 × 4 mm; 4 μm) (Merck, Darmstadt, FRG) is used, protected by an NH_2 guard column.

HPLC Determination

A gradient mode is used for chromatographic separation of the compounds. The conditions are given in Table II.

TABLE II Chromatographic conditions

Temperature	308 K
Injection volume	20 μl
Mobile phase	A KH_2PO_4 (0.05 m, pH 3.85) B CH_3CN C H_2O (HPLC-grade)

Gradiant Time (min)	*A*	*B*	*C*	*Flow* (ml × min^{-1}
0.0	98	2	0	0.8
5.0	98	2	0	0.8
5.1	80	20	0	1.0
30.0	55	45	0	1.0
40.0	32	68	0	1.0
40.1	0	0	100	1.0
45.0	0	0	100	1.0
45.1	98	2	0	1.0
55.0	98	2	0	1.0

The detecting wavelength is set to 228 nm (bandwidth 4 nm) with a reference of 400 nm (bandwidth 80 nm).

For all investigated compounds five level calibrations in a linear working range of 1–2 ng to 500 ng a.i. × 20 μl^{-1} have been prepared ($r > .998$). All calculations are based on peak areas. The theoretical limit of detection for s-triazines is ~ 1.5 $\mu g \times kg^{-1}$dry soil, for substituted phenoxyalkanoics and all degradation products 3.0 $\mu g \times kg^{-1}$.

In most cases, the identification of peaks is possible by comparing their UV-spectra with a self-made spectral library (matchfactor > 950).

RESULTS AND DISCUSSION

Analytical method

As could be shown by Snyder et al.[6], sonication, SFE and soxhlet are equivalent in efficiency, so soxhlet extraction was chosen.

Table III shows the recoveries obtained by the presented extraction method, compared to the same method but without precipitation of interfering humic substances by NaCl. An analysis of variance (ANOVA) showed no significant differences for any compound between both procedures due to a large spread of data ($p = 0.05$). The major advantage of the precipitation procedure are smoother chromatograms. This facilitates identification of peaks and preserves the chromatographic column, ensuring a long lifetime (> 1000 h).

TABLE III Recovery (%) of spiked humic soil samples (Plaggenesch Ap)

Precipitation (NaCl)	*Yes* *mean (= 3)/SD*	*No* *mean (= 4)/SD*
2-Hydroxy-Atrazine	–	–
Deisopropyl-Atrazine	48.9 +/– 29.8	74.0 +/– 29.7
Deethyl-Atrazine	62.7 +/– 30.4	91.3 +/– 34.5
MCPA	–	–
Simazine	79.5 +/– 49.8	83.2 +/– 44.4
MCPP	70.0 +/– 42.3	101.8 +/– 68.2
Atrazine	61.7 +/– 33.2	82,1 +/– 28.4
Metazachlor	65.3 +/– 31.4	97.3 +/– 26.2
4-Chloro-2-methylphenol	50.5 +/– 22.3	73.1 +/– 33.11
Propazine (internal standard)	46.9 +/– 23.8	56.3 +/– 17.6
Prometryne	30.3 +/– 6.9	28.0 +/– 9.6

It has to be emphasized that this procedure is valid only for the specific reactive humic material used for investigation ("Plaggenesch" Ap 0–5 cm; C_{org} 9.3%; pH_{H2O} 6.80; silty sand). Any other matrix will show different behaviour due to the heterogenous nature of soil constituents (see 3.2) and needs adaption to the specific problems involved, cf.[7].

Separation and analysis of relevant weakly basic s-triazines besides acidic phenoxyalkanoic herbicides is enabled by the gradient mode. The adjustment of the buffer to pH = 3.85 allows baseline separation of all compounds (Figure 2); any change in pH may cause coelution (e.g. Dichlorprop/Simazine, Simazine/MCPP), due to changes in the retention of ionizable substances. The order of elution of s-triazines is dominated by increasing polarity of the substituents in position 2 of the ringsystem (i.e. -OH > -Cl > $-SCH_3$), modified by alkylchains [8]. The eluting behaviour of substituted phenoxyalkanoics is influenced by the size of their alkyl moiety (i.e. acetic acid > propionic acid). Generally, degradation products of 5-triazines show an increased polarity, whereas degraded phenoxyalkanoics result in more unpolar substances (exception: 4-Chlorophenoxy acetic acid). This gradient can be extended to include more herbicides besides the mentioned (e.g. Metazachlor, R_t 33.6 min.; not shown in Figure 2). For protection ofthe analytical device it is essential to remove any buffer-residues at the end of the gradient by washing with water (minutes 40.1 - 45.0). Otherwise there might be precipitation of buffer salt inside capillaries if another chromatographic run initiates with higher organic solvent contents.

Qualitative analysis is performed by comparison of the UV-spectra of compounds with those of a spectral library. From experience, the reported matchfactor should exceed 950 for positive identification. Because of identical

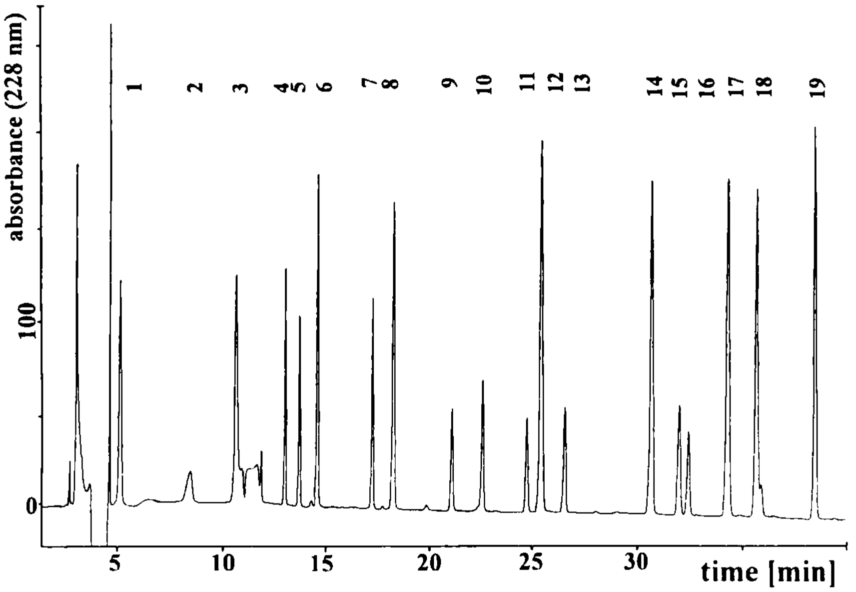


FIGURE 2 Standard chromatogram. For peak identification cf. table 1. Amount of injected herbicides ~ 320 ng each

chromophore structures, both s-triazine and phenoxyalkanoic acids possess similar spectra. Hence, the identification is to be supported by retention data.

The active ingredients or their degradation products interact in different physico-chemical ways with the soil matrix, resulting in an increasing retention of the compounds with time ("aging"). Caution is recommended with these "aged" residues which might exhibit changed spectra (Figure 3). There may be spectral shifts as results from charge transfer complexes between matrix constituents and the residues, inducing additional absorption bands not being present in the single compounds[9]. Even with experience it is difficult to confirm presence of these altered "aged" residues in soil samples. To avoid erroneous positives, at least in doubtful cases, additional independent confirmation (GC-MS, LC-MS) was carried out.

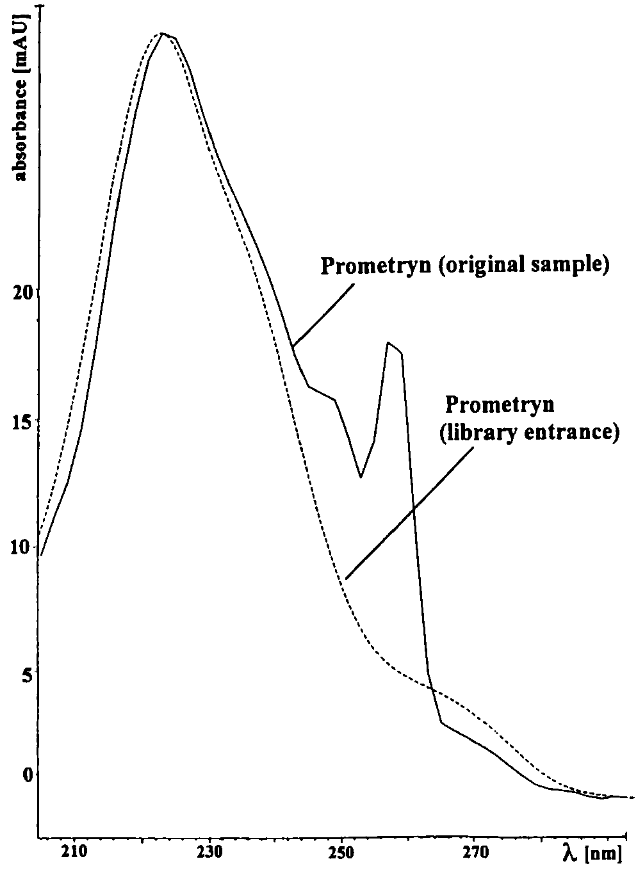


FIGURE 3 Spectrum of an "aged" Prometryne residue, compared with the library entrance. The reported matchfactor is 812. Prometryne could be verified by LC-MS

Herbicide burden and dynamics in the area of Halle

Temporal and spatial changes in the adsorptive behaviour of soils

According to our intention, we studied the dynamics of herbicide residues under outdoor conditions. For this reason, we installed a long-term observation area on a conventionally treated field northwest of Halle.

The fate of herbicide residues in soils is governed by simultaneous acting factors of adsorption to soil particles, transport and material transformation. Adsorption influences the extent of the latter processes, because only desorbable portions are available to biota, mobile in the soil column and accessible to different kinds of extraction. Conventionally, adsorption is directly determined in equilibrated aqueous suspensions. These experiments show a partitioning of a chemical between the solid and the liquid phase, which may be expressed by the K_D-value[9].

The primary objective of the following investigation was to demonstrate a suspected remobilization of "non-extractable" residues by conventional agricultural practice. Additionally, our experimental design allowed us to get indirect information about a changing adsorptive behaviour of soil matrices by changed recoveries of the internal standard (ISTD), though it is criticized, that the addition of an ISTD does not reflect the behaviour of native residues in soils[10]. The ISTD may neither serve as a quantitative measure of adsorption like e.g. KD nor act as an estimate of the true behaviour of analytes, but any differences in the recovery within given matrices show tendencies, indicating variations of soil features in time and space.

First, results from the intimately investigated long-term observation area are presented. Its square dimension is 50m × 50m. It is situated on a porphyry height (inclination 5 %), showing a transition from a ranker (NE) to a cambic cambisol (SW). Within this area is a pH-gradient from approx. 8.0 (ranker) to approx 6.0 (cambisol).

The topsoil (0 – 5 cm) had been sampled systematically at 5m intervals on a square grid. In addition, the underlaying ploughlayer (5 – 20 cm) had been sampled, using a larger grid (10m × 10m). This deeper grid was necessary to prove the absence of any residues which might be ploughed up. Samples were taken on two occasions, once before (t_0) and once after ploughing (t_1). From these samples, several properties like recovery of ISTD, contents of residues, C_{org} and pH_{H2O} were measured.

The results of the investigations aiming at potential remobilizations and dynamics of adsorption are summarized in Figure 4. It reveals several interesting features concerning temporal and spatial variability of soils induced by tillage.

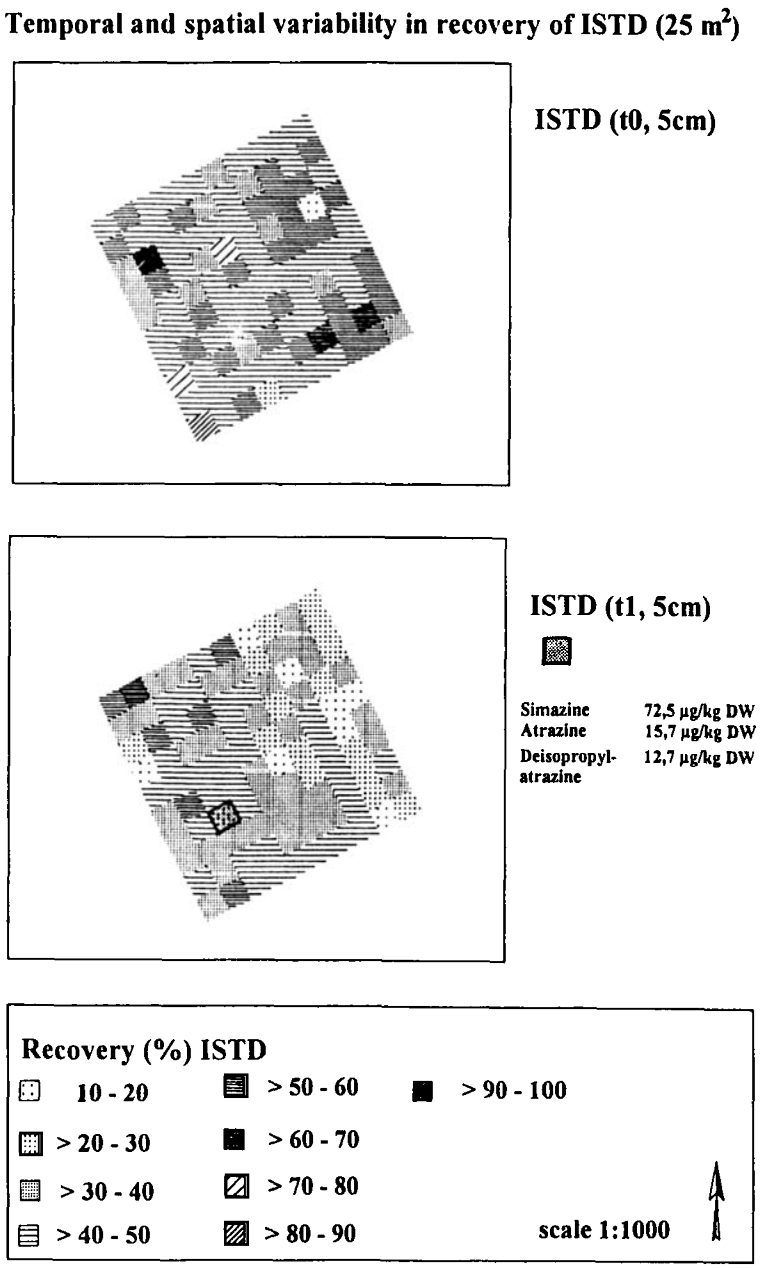


FIGURE 4 Effect of tillage and/or climatic changes on recovery of the ISTD and on remobilization of "non-extractable residues". t_0 = before tillage, t_1 = 1 month later (after tillage). The framed square at t_1 indicates the location of a remobilization event. The residues are at least 5 years old. Amounts of residues (µg × kg^{-1}): Simazine 72.5; Atrazine 15.7; Deisopropylatrazine 12.7

Within the presented area, the recovery of the freshly added ISTD varied by a factor of 10 × (approx. 9 % up to 99 %). In addition, samples taken on the same location, but four weeks later in time (t_1) showed a remarkably lower recovery (mean recovery t_0 48.5 ± 10.5%; mean recovery t_1 36.8 ± 10.5%; n=100). Parallel the pH-values of the plots increased batween t_0 and t_1 in the range of 0.5 to 1 unit as a consequence of tillage (not shown). It is well-known that changes in the pH of a soil can have marked effects on the adsorptive behaviour of the matrix, particulary for weak bases like s-triazines (pK_a chloro-s-triazines ~ 1.7, methylthio-s-triazines ~ 4.4). In low pH, s-triazines are protonated to their corresponding cationic forms. These are stronger adsorbed to the matrix than the free base due to the CEC of soils[9]. Any increase in pH, therefore, should lower the affinity of the ISTD (s-triazine) for the matrix. This is in contradiction to our results, where a slight increase in pH (0.5 – 1 pH-unit) led to a distinct increase in adsorption (the mean recovery on t_1 is reduced to 75% of t_0).

For the same site, Figure 4 shows besides the changed adsorptive behaviour the proof of a remobilization event of six year old "non-extractable" s-triazine residues on t_1, induced by tillage (ploughing) and/or drastic climatic changes (rains after a long dry spell, leading to enhanced mineralization of soil organic matter).

This indicates changes in the adsorptive behaviour of this particular matrix caused by agricultural practice. It might be simply the result of ploughing up underlying, more adsorbing material. But this is not the case, because the ploughlayer is a homogeneous horizon and the pH is comparable to that of the surface. Additionally, deeper soil horizons adsorb to lesser extents than surface horizons due to reduced organic matter contents. We assume that the inconsistent behaviour which we met is to be explained by the influence of hydrogen ions on humic substances. Probably, the flexible, spongelike structural network of humic substances partly disintegrates by a decline of hydrogen bonding with the observed alkalinization of the medium[11] or by microbial activity. In this way, the adsorptive surface is enlarged, resulting in the observed enhanced adsorption. On the other hand, physically incorporated residues may become accessible for extraction from this opened structure. This explains the reoccurence of "non-extractable" residues. Further investigations on this topic as expressed by the coefficient of adsorption (K_D-value) are in progress.

These observations clearly demonstrate the exceptional importance of the choice of time and place of sampling for residue analysis in soils. The use of an ISTD may not replace the necessity of determing parameters of adsorption, but it provides a simple and powerful tool to recognize the dynamic behaviour of soil-ecosystems. On the other hand, the great variability in the recovery rate even within a small area shows the restrictions of the ISTD in developing quantitative extraction methods or in modeling its environmental behaviour.

The mentioned features of dynamics of soil(bio)chemistry should be borne in mind when regarding the general burden of soils with herbicide residues.

Herbicide burden of soils in the area of Halle/S. (FRG)

The presented procedure enabled the retrospective determination of residues of persistent s-triazines and their monodealkylated or hydroxylated degradation products (Prometryne, Simazine, 2-Hydroxy-S., Atrazine, Deisopropyl-A., Deethyl-A, 2-Hydroxy-A) left by former intensive cultivation. Many samples contained both active ingredient and degradatives. Different triazine-residues in one sample were not uncommon. In the following, we shall not distinguish between these compounds, because all but the hydroxylated compounds possess at least little phytotoxic potential. The term "residue" is used to indicate their presence. The reported values are not summations of single compounds.

40 representative agricultural soil profiles in the area of Halle were selected, including 123 distinguishable horizons. Nowadays, many of the sampling sites are either fallow land or treated with non-persistent herbicides. Irrespective of soil types, it was useful to arrange the sampling sites in four classes, according to their former use (Table IV).

TABLE IV Classification of sampling sites according to their historic use

Class	*profiles (n)*	*horizons (n) total*	*horizons (n) negative findings*	*horizons (n) positive findings*	*% positive findings of total*
I. conventional agriculture	25	75	39	36	48.0
II. long-term cultures (hop, fruit)	6	17	9	8	47.1
III. herbicide stores, nurseries etc.	6	22	5	17	77.3
IV. orchards	3	9	2	7	77.8
Σ	40	123	55	68	

From Table IV it is obvious that there exist marked differences between areas with "conventional" (cl. I and II) or "intensive" herbicide past (cl. III and IV). The first two classes are characterized by normal agricultural herbicide input (cl. I) or by major application of other biocides like fungi- or insecticides (cl. II). Within these classes, residues could be detected in about 50 % of all investigated horizons. Classes III and IV show residues in more than 75% of the horizons, due to enhanced historic herbicide-input.

Table V gives an impression of the amounts and the distribution of triazine-residues in soil profiles in the area of Halle. Again, there is separation between conventional and intensive herbicide application.

Classes I and II show in about 60% of investigated surface horizons triazines residues. The bulk of residues (approx. 50%) varied between 10 to 30 μg × kg^{-1}. In about 40% of the investigated pedogenic horizons, residues could be detected, the bulk of them again between 10 and 30 μg × kg^{-1} (cf. Figure 5).

Nurseries, former herbicide storage locations and orchards (cl. III and IV) are generally contaminated to a larger extent and to deeper soil layers than conventional acreage (cf. Figure 6).

Table V shows that nearly 90% of these surface horizons are contaminated with residues, slightly decreasing to deeper soil layers (approx. 80%). The distribution of amounts is different from classes I and II. The high level of historic input (frequent application of the same herbicide, leakage), together with reduced tillage caused 78% of these surface samples to be contaminated with triazine residues in the range > 30 μg × kg^{-1}. In the uppermost soil layers, class III often showed residues in the range >100 μg × kg^{-1} (nursery: 433 μg × kg^{-1}Simazine). Class III contributed 80% (four from five horizons) to the amounts > 100 μg. Class IV generally ranged from 30 – 100 μg × kg^{-1}. These difference adjust in deeper horizons, so three quarters of pedogenic horizons showed residues ranging from 10 – 30 μg × kg^{-1}.

Substituted phenoxyalkanoic acids could be shown to be only short-lived in soils. MCPP could not be detected longer than three weeks after application due to fast microbial breakdown and high mobility[12]. As a metabolite of MCPP, 4-Chloro-2-methylphenol could be detected in the field five days after application.

TABLE V Distribution and amounts of s-triazine residues in soil profiles

Herbicide application	"conventional"; Cl. + II (33 profiles)			"intensive"; Cl. III + IV (9 profiles)			
Residues ($\mu g \times kg^{-1}$)	< 10	10 – 30	>30	<10	10 – 30	30 – 100	> 100
Surface horizons n (%)	3 (9.1%)	15 (45.5%)	5 (15.2%)*	n.d.	1 (11.1%)	2 (22.2%)	5 (55.6%)*
Pedogenic material n (%)	2 (6,1%)	8 (24.2%)	3 (9.1%)*	n.d.	7 (77.8%)	n.d.	n.d.

* : % missing to 100% represent horizons without residues

CONCLUSION

These results frequently indicate a build-up of an anthropogenic background of persistent s-triazines caused by intensive cultivation in the area of Halle. The ecological consequences and behaviour of these residues need further elucidation because soils may redistribute chemicals to other parts ofthe environment rather than act as a final sink.

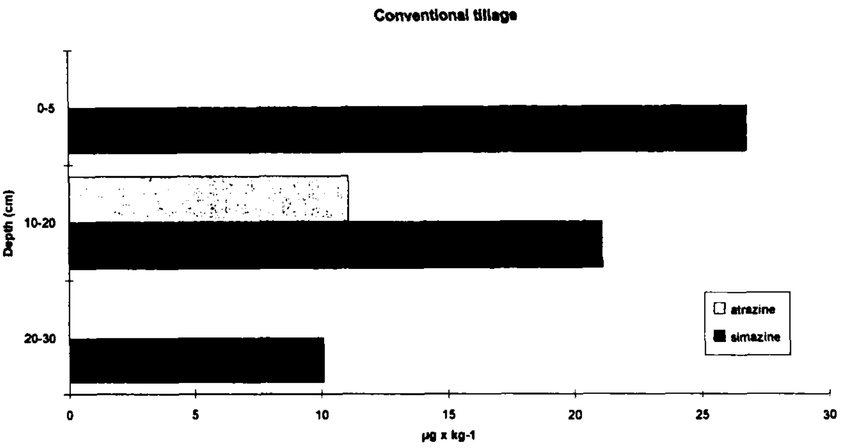


FIGURE 5 Example of triazine residues found under conventional agricultural practice. The residues are at least 5 years old

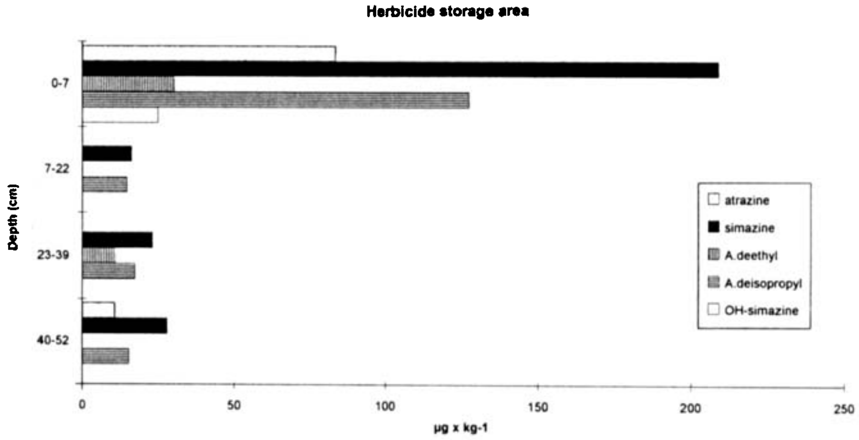


FIGURE 6 Triazine residues found in a soil under a former herbicide storage area

Acknowledgements

This work was funded by financial support and a grant for J.-U. Holthuis from the Centre for Environmental Research Leipzig-Halle Ltd. The authors wish to thank M. Prehn for her fundamental cooperation.

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