coefficient = 0.89; $p < 0.05$), presumably because both reflected the systemic drug levels around the time of ovulation. For those on-drug eggs in which yolk and albumen both contained detectable xylonidine, the average ratio of yolk to albumen concentrations was 4.0 (95% confidence limits: 2.6–5.4). Thus, the xylonidine in yolk was about 4 times as concentrated as that in albumen.

As shown in Table II, the yolk residues after drug withdrawal depended both on the day laid and on whether the egg was the first, second, or third laid posttreatment. Highest yolk residues were seen in the first or second egg from those hens that resumed production the earliest. No residues were detected in any posttreatment albumen samples, and thus albumen and yolk residues were totally uncorrelated for posttreatment eggs. This is probably due to the different time courses of yolk and albumen synthesis. Albumen is synthesized de novo during an approximately 3-h period beginning 18 h before oviposition, while yolk synthesis requires considerably more time, with the rapid growth phase consuming the final 5–11 days that precede ovulation (Sturkie and Mueller, 1976). Thus the yolks from posttreatment eggs probably reflected systemic drug concentrations that were earlier and presumably higher than those reflected by the corresponding albumens.

These results demonstrate the suitability and sensitivity of capillary column GLC–MS for determining xylonidine concentrations in eggs. The data that resulted when these procedures were applied to eggs from hens forced molted by this drug will be used to determine the possible human health implications posed by xylonidine egg residues.

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Storage Stability of Pesticide Residues

Hans Egli

The stability of residues of 19 plant protection agents or plant regulators in different substrates at −20 °C were determined as were the hydrolysis half-life times in neutral solutions at +50 and +70 °C. The following correlations between these two properties were found: (1) residues are stable for at least 1 year if half-life times are above 10 days at 70 °C; (2) residues are unstable if half-life times are below 1 day at 50 °C, especially in crops with a high water content; (3) residue stabilities need examination if half-life times lie in between. On the basis of this, it is proposed that residue stabilities can be derived from hydrolysis data and a residue stability study should be run only in doubtful cases. It is shown that such studies can be performed with fortified samples.

In residue analytical practice samples often cannot be analyzed immediately after sampling. They therefore have to be stored. Although samples usually are deep frozen, the question arises whether residues are sufficiently stable during storage. Several papers dealing with this question have been published up to now: Kawar et al. (1973) gave a comprehensive review on storage stability. Since then papers on the degradation during storage of metribuzin (Webster and Reimer, 1976) and of atrazin (Swain, 1979) in soil appeared. Storage conditions used by the authors differed and so did the stabilities reported. Thus, it is common practice to check the stability of residues of each compound in each substrate under investigation, if samples are to be stored. There is no generally accepted methodology for performing residue stability studies, but several points have to be considered in order to end up with reliable results: What should be done if no field-treated samples with finite residues are available? Do "artificial residue samples", i.e., fortified samples, show the same degradation behavior as do real field samples? How should artificial samples be prepared? What can be done if residues are not stable? To answer these questions is one of the goals of the present paper.

Factors determining the rate of degradation are the rates of hydrolysis, of photolysis, and of oxidation. (Enzymatic degradation by these or other pathways is considered to be of minor importance at low temperatures.) If stored in the dark, residues are not photodegraded; oxidation could sometimes be an important process (e.g., thio compounds), but generally the rate of oxidation of organic compounds is slow. Hydrolysis, however, is suspected to be a main route of degradation. This assumption is supported by observations of several authors (Hamaker, 1972; Kawar et al., 1973; Minett and Belcher, 1970; Swain, 1979) who report data on the dependence of residue stability on the water content of the substrate. Therefore, the second goal of the work presented in this paper is to investigate the suspected correlation of the hydrolytical behavior of a number of chemically different compounds with the storage stabilities of their residues. The existence of such

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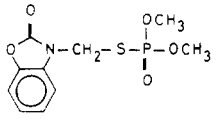
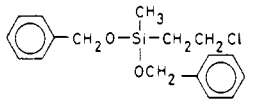
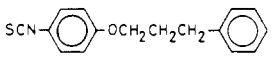
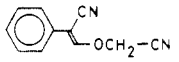
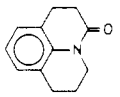
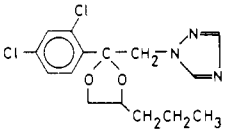
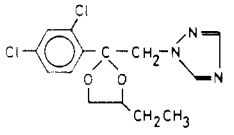
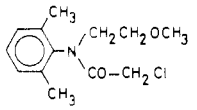
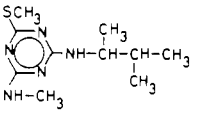
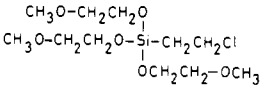
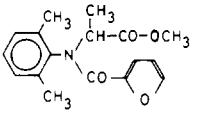
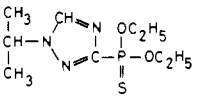
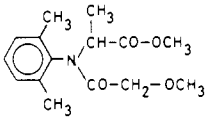
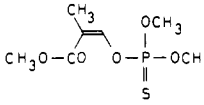
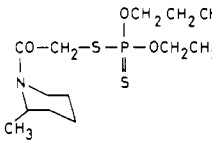
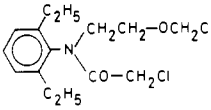
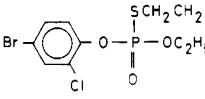
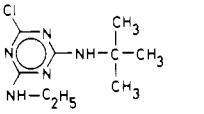
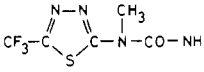
Table I. Chemicals and Substrates Investigated

(1)		azamethiphos	beans milk meat
(2)		CGA 15281	apples
(3)		CGA 28473	cottonseed cotton oil
(4)		CGA 43089 CONCEP®	soil sorghum grain
(5)		CGA 49104	soil
(6)		CGA 64250 TILT®	wheat grain wheat straw
(7)		CGA 64251	apples
(8)		dimethachlor TERIDOX®	soil rape seed
(9)		dimethametryn AVIROSAN®	soil rice grain
(10)		etacelasil ALSOL®	olive oil
(11)		furalaxyl FONGARID®	soil potatoes hops
(12)		isazofos MIRAL®	soil maize grain carrots
(13)		metalaxyl RIDOMIL®	soil lettuce potatoes hops
(14)		methacrifos	wheat grain
(15)		piperophos	soil rice grain
(16)		pretilachlor	soil rice grain
(17)		profenofos CURACRON®	tomatoes grapes cotton oil
(18)		terbuthylazine GARDOPRIM®	soil
(19)		thiazafluron ERBOTAN®	soil

a correlation could lead to proposals for running hydrolysis studies as pretests and—in certain cases—for substituting the quick hydrolysis studies for residue stability studies.

It should be stressed that expressions like "storage stability" or "residue stability" refer to kinetic stability (inertness), not to the thermodynamic stability. Residues never are stable in the thermodynamic sense; responsible for their existence are the slow rates of the thermodynamically, i.e., energetically, favored degradation reactions.

MATERIALS AND METHODS

General. Residue stability studies were run with several chemicals on various crops and in selected extracts. The results were compared with the half-life times of the respective compounds in aqueous solutions at elevated temperatures.

Compounds. Table I shows the chemical structure of all compounds investigated, code numbers or common names, and trade names if existent. All chemicals are either commercial products or are or were under development as plant protection agents or plant regulators.

Residue Samples. Table I also shows the biological material used as the substrate in the studies. If available, field-treated samples with finite residues were used. Additionally, fortified check samples were stored for comparison with the field samples. All samples were prepared for analysis as follows: vegetables and fruits were chopped, as was meat; grains and seeds were milled; fortification experiments in soil were done with "German standard soil No. 2.2" (5% organic matter and 3% water, pH 7.2).

The fortification was done in either of two ways: (1) Bulk samples were fortified with 1% premixes of WP formulations of the chemicals and bolus alba (pure, dry kaolin). Samples were thoroughly mixed in a Turbula shaking mixer (W. A. Bachofen AG, Basel, Switzerland). Homogeneity of distribution was checked by multiple analyses; for storage, bulk samples were divided into 50-g subsamples. (2) Samples of 50 g were spiked with standard solutions in hexane. The whole samples were analyzed; therefore the homogeneous distribution was no problem here. Fortification levels generally were 5 mg/kg.

Extracts. Stability tests of residues that proved not to be stable in the substrate were repeated with fortified acetone or toluene extracts of the same substrates. Extractions were done in the following ways: For plant parts, solvent and known amounts of standard solutions were

added. After being macerated and shaken for 2 h, the suspensions were stored. For soil, samples were extracted with the solvent in a hot extractor. Known amounts of standard solutions were added to the solvent before refluxing.

Storage Conditions. The test portions were stored either in glass bottles or in polypropylene bags; the extracts were stored in glass bottles. Storage temperature was −20 °C.

Residue Analyses. Analyses were repeated every few months for 1–2 years, at least in duplicate. Methods for individual compounds are briefly described below; their performance was checked by coanalysis of two samples fortified immediately prior to analysis. Results were corrected for recoveries.

Most final determinations were done by GLC. Chromatographs used were from Varian, Perkin-Elmer, and Hewlett-Packard. Detectors used were a PN-specific thermionic detector (Perkin-Elmer or Hewlett-Packard), an N-specific Hall electrolytic conductivity detector (Tracor) on a Varian chromatograph, and a Cl-specific microcoulometric detector (Dohrmann Instruments) on a Varian chromatograph. Quantitations were done via standard curves.

Azamethiphos (1). For milk, the compound was, after precipitation of proteins with acetone, extracted with dichloromethane and cleaned up by column chromatography (silica gel, activity I; eluent chloroform–acetic acid ethyl ester, 16:5). For plant material and meat, the compound was extracted with methanol by macerating and shaking, diluted with water, reextracted into dichloromethane, and cleaned up by column chromatography (as above). The compound was quantitated by HPLC (LiChrosorb RP 18, 10 μm, 20 × 0.3 cm, mobile phase water–acetonitrile, 2:1, 1.2 cm^3 min^{-1}, UV detection 294 nm, retention time 2.5 min).

CGA 15281 (2). The compound was extracted with toluene by macerating and shaking, cleaned up by gel chromatography (Bio-Beads S-X12; eluent toluene), and quantitated by GLC (microcoulometric detection, Carbowax 20 M, 5% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 210 °C, retention time 6 min).

CGA 28473 (3). For seed, the compound was extracted with acetonitrile–formic acid, 300:2, by macerating and shaking, diluted with water, reextracted into hexane, and cleaned up by column chromatography (alumina acidic, activity III; eluent hexane–dichloromethane, 9:1). For oil, the compound was diluted with hexane, extracted into acetonitrile–acetone, 9:1, and cleaned up by column chromatography (as above). The compound was quantitated by HPLC (LiChrosper SI 100, 10 μm, 30 × 0.3 mm, mobile phase hexane–diisopropyl ether, 99:1, 1.2 cm^3 min^{-1}, UV detection 230 nm, retention time 6 min).

CGA 43089 (4). For soil, the compound was extracted with methanol in a hot extractor, diluted with water, reextracted into dichloromethane, and cleaned up by column chromatography (alumina basic, activity V; eluent hexane–dichloromethane, 5:1). For sorghum, the compound was extracted with acetonitrile by macerating and shaking and partitioned with hexane, the acetonitrile phase was diluted with water, and the compound was reextracted into hexane and cleaned up by column chromatography (as above). The compound was quantitated by GLC (thermionic detection, Carbowax 20 M, 3% Gas-Chrom Q, 0.5 m × 2 mm, 35 cm^3 min^{-1}, 180 °C, retention time 1.1 min).

CGA 49104 (5). The compound was extracted with methanol in a hot extractor, diluted with water, reextracted into dichloromethane, cleaned up by column chromatography (alumina basic, activity V; eluent hexane–dichloromethane, 3:2), and quantitated by HPLC (LiChrospher SI 100, 10 μm, mobile phase hexane–tetrahydrofuran, 8:2, 1.5 cm^3 min^{-1}, UV detection 255 nm, retention time 7.8 min).

CGA 64250 (6) *and CGA 64251* (7). The compound was extracted with methanol by macerating and shaking, diluted with water, reextracted into dichloromethane, cleaned up by column chromatography (alumina basic, activity V; eluent *n*-hexane–dichloromethane, 4:6), and quantitated by GLC (thermionic detection, Carbowax 20 M, 1% Gas-Chrom Q, 1 m × 2 mm, 30 cm^3 min^{-1}, retention time for 6 2.0 min and for 7 1.6 min).

Dimethachlor (8). For soil, the compound was extracted with methanol in a hot extractor, diluted with water, reextracted into dichloromethane, and cleaned up by column chromatography (alumina basic, activity, V; eluent hexane–diethyl ether, 2:1). For cereals, the compound was extracted with acetonitrile by macerating and shaking, partitioned with hexane, the acetonitrile phase was diluted with water, and the compound was reextracted into hexane and cleaned up by column chromatography (as above). The compound was quantitated by GLC (microcoulometric detector, OV-17, 3% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 220 °C, retention time 2 min).

Dimethametryn (9). For soil, the compound was extracted with methanol in a hot extractor, evaporated, and cleaned up by column chromatography (alumina basic, activity, V; eluent hexane–dichloromethane, 1:1). For grain, the compound was extracted by macerating and shaking with methanol, diluted with water, reextracted into dichloromethane, and cleaned up by column chromatography (as above). The compound was quantitated by GLC (thermionic detection, Carbowax 20 M, 3% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 220 °C, retention time 2.3 min).

Etacelasil (10). Olive oil was diluted with hexane, and the compound was extracted into acetonitrile, evaporated, dissolved in toluene, cleaned up by gel chromatography (Bio-Beads S-X12, mobile phase toluene), and quantitated by GLC (microcoulometric detection, Carbowax 20 M, 3% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 190 °C, retention time 1.1 min).

Furalaxyl (11). For soil, the compound was extracted and cleaned up as for 8. For plant material, the compound was extracted with methanol by macerating and shaking, diluted with water, reextracted with dichloromethane, and cleaned up by column chromatography as described for dimethachlor. The compound was quantitated by GLC (thermionic detection, Carbowax 20 M, 3% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 240 °C, retention time 4 min).

Isazofos (12). For soil, the compound was extracted with acetone in a hot extractor; no cleanup was done. For plant material, the compound was extracted with methanol by macerating and shaking, diluted with water, and reextracted into dichloromethane. The compound was quantitated by GLC (thermionic detection, DC-200, 1.5% Chromosorb G, 0.5 m × 3 mm, 70 cm^3 min^{-1}, 170 °C, retention time 1.2 min).

Metalaxyl (13). The compound was extracted and cleaned up as for 8 and quantitated by GLC (thermionic detection, Carbowax 20 M, 5% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, retention time 2.5 min).

Methacrifos (14). The compound was extracted with acetone by macerating and shaking, diluted with water, reextracted into hexane, and quantitated by GLC (thermionic detection, OV-17, 10% Gas-Chrom Q, 1.35 m × 2 mm, 35 cm^3 min^{-1}, retention time 2.5 min).

Table II. Storage Stability of Residues of Compounds with Hydrolytic Half-Life Times >10 Days at 70 °C

	hydrolysis[b]			recovery of residues[a]		
compd	$t_{1/2}$, days	rank	crop	field, %	fort., %	rank
5	>20	4.5	soil		100	4.5
6	>20	4.5	wheat grain		100	4.5
			wheat straw		100	
7	>20	4.5	apples		95	10
8	19	9	soil		92	11
			rape seed		100	
9	>20	4.5	soil		100	4.5
			rice grain		100	
11	>20	4.5	soil		100	4.5
			potatoes		100	
			hops	100	100	
			lettuce	100	100	
13	>20	4.5	soil		100	4.5
			potatoes		100	
			lettuce	100	100	
			hops	100	100	
16	17	10	soil		96	9
			rice grain		100	
18	>20	4.5	soil	100	100	4.5
19	>20	4.5	soil	100	100	4.5

[a] Percentages recovered after a storage period of 12 months. Field = field treated; fort. = fortified. [b] Hydrolysis at pH 7 and 70 °C.

Piperophos (15). The compound was extracted and cleaned up as for 8 and quantitated by GLC (thermionic detection, Carbowax 20 M, 3% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 240 °C, retention time 4 min).

Pretilachlor (16). The compound was extracted and cleaned up as for 8 and quantitated by GLC (microcoulometric detection, OV-101, 10% Gas-Chrom Q, 0.5 m × 2 mm, 35 cm^3 min^{-1}, 225 °C, retention time 2.2 min).

Profenofos (17). For soil, the compound was extracted with acetone in a hot extractor, diluted with water, and reextracted into dichloromethane. For plant parts, the compound was extracted with methanol by macerating and shaking, diluted with water, and reextracted into dichloromethane. The compound was quantitated by GLC (thermionic detector, Carbowax 20 M, 10% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 220 °C, retention time 1.5 min).

Terbuthylazine (18). The compound was extracted with methanol in a hot extractor, evaporated, cleaned up by column chromatography (alumina, activity V; eluent hexane–diethyl ether, 2:1), and quantitated by GLC (Hall detection, Carbowax 20 M, 5% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 240 °C, retention time 3 min).

Thiazafluron (19). The compound was extracted with methanol in a hot extractor, evaporated, cleaned up by column chromatography (alumina, activity V; eluent dichloromethane–acetone–water, 25:75:4), and quantitated by GLC (thermionic detector, Carbowax 20 M, 3% Gas-Chrom Q, 1 m × 2 mm, 35 cm^3 min^{-1}, 210 °C, retention time 1.5 min).

Hydrolysis. The hydrolytic half-life times were determined in diluted (10 μg cm^{-3} or below, according to solubility) aqueous buffer solutions (phosphate buffer, pH 7.0; ionic strength 0.15) at 50 and 70 °C. These two temperatures allowed determination of half-life times of both fast and slow hydrolyses (reactions running around room temperatures are accelerated by a factor of 2–3 on increasing the temperature by 10 °C, as is well-known from chemical kinetics). Solutions were stored in the dark at 50 and 70 °C. Analyses were done similarly to residue analyses (cleanup omitted).

RESULTS AND DISCUSSION

General. Ramdom errors of analytical results increase with decreasing concentration. At the milligrams per kilogram level the relative standard deviation is at least 0.1 (Püschel, 1968; Horwitz et al., 1980). In residue analysis—in addition to random errors—the dispersion of the results is further increased by the possible inhomogeneity of the samples, which leads to unknown and variable "true" contents of the subsamples and apparently high random errors. For example, the following residues of 13 in field-treated lettuce (7 days after treatment) were found by replicate analyses: 0.77, 1.05, 0.92, and 1.12 mg/kg. A similarly high dispersion also occurred when analyzing the bulk fortified mixtures (fortification method 1).

Dispersion of results is lower if the homogeneity of samples has no influence, i.e., if subsamples were fortified (method 2) and analyzed as a whole or if homogeneity is obvious (oil, milk).

Nevertheless, the poor reproducibility of residue analytical results still makes it difficult to give exact rates of degradation or even to derive kinetic equations. The residue stabilities were expressed as percentages of the initial concentrations found after 12 months; these values were calculated by linear regression analysis of the experimental data ($y = ax + b$; y = milligrams per kilogram and x = months). The relative standard deviation is about 0.1.

The results of hydrolytic studies are more exact since variation due to cleanup and coextractives is far less. Therefore, the kinetics of the hydrolyses could be calculated; all reactions follow first-order equations. Results are given as half-life times.

Stability of Residues. All percentages of residues still present after 1 year of storage in artificial mixtures, in field-treated samples, and in extracts are grouped according to hydrolytic stabilities in Tables II–IV, Table II representing results of hydrolytically "stable" compounds, Table III of "fairly stable", and Table IV of "unstable" ones.

Field-Treated vs. Fortified Samples. Where field-treated samples with residues could be compared with artificial mixtures, they showed similar degradation (Table II, compounds 11, 13, 18, and 19; Table IV, compound 17). It can therefore be concluded that stability tests with artificial mixtures are valuable substitutes if field-treated samples with finite residues are not available.

Residue Stability in Extracts. Tables III (compounds 12 and 15) and IV (compounds 1, 2, 10, 14, and 17) show

Table III. Storage Stability of Residues of Compounds with Hydrolytic Half-Life Times Below 10 Days at 70 °C but Above 1 Day at 50 °C

	hydrolysis[b]			recovery of residues[a]		
compd	$t_{1/2}$	rank	crop	fort., %	extr., %	rank
3	5 days	11	cotton seed	82		13.5
	31 h		cotton oil	98		
4	13 days	12	soil	100		4.5
	1 days		sorghum	100		
12	2 days	13	soil	83	100	12
	9 h		maize	97		
			carrots	94		
15	1 days	14	soil	82	100	13.5
	4 h		rice grain	100		

[a] Percentages recovered after a storage period of 12 months. Field = field treated; fort. = fortified; extr. = extracted. [b] Hydrolysis at pH 7 and 50 °C (top) or 70 °C (bottom).

Table IV. Storage Stability of Residues of Compounds with Hydrolytic Half-Life Times Below 1 Day (50 °C)

	hydrolysis[b]			recovery of residues[a]			
compd	$t_{1/2}$, h	rank	crop	field, %	fort., %	extr., %	rank
1	6.4	16	beans		65		15
			meat		0	65	
			milk		70		
2	3	17.5	apples		0	0	18.5
10	<1	19	olive oil		0	0	18.5
14	23	15	wheat		64	100	16
17	3	17.5	tomatoes	10	65	100	17
			grapes	82	88	100	
			cotton oil		100		

[a] Percentages recovered after a storage period of 12 months. Field = field treated; fort. = fortified; extr. = extracted. [b] Hydrolysis at pH 7 and 50 °C.

extracted residues to be stable in most cases of poor stability on the crops. This fact demonstrates that storage of extracts often is a possibility to circumvent stability problems. If chemicals degrade within hours or days even in extracts (Table IV, compounds **2** and **10**), there is no other possibility but immediate analysis—if there is any need for analysis at all: As a certain stability of the compound is a prerequisite for the existence of residues, unstable compounds cannot remain as residues; thus, there is no reason for parent residue analysis and the stability on storage needs no proof.

Correlation of Residue Storage Stability with Hydrolytic Stability. *Facts and Hypothesis.* Table II shows results of hydrolytically "stable" chemicals (half-life times of hydrolysis above 10 days at 70 °C); obviously all residues are stable as well. Table III summarizes residue stabilities of hydrolytically "fairly stable" compounds (half-life times below 10 days at 70 °C but above 1 day at 50 °C); most residues of this group are less stable. Instability of residues of hydrolytically "unstable" compounds (half-life times below 1 day at 50 °C) is demonstrated by Table IV. The surprising stability of compound **1** in milk (Table IV) can be explained by the fact that milk contains about 4% fat, which extracts the lipophilic compound, thus decreasing the apparent rate of hydrolysis. The difference in stability of compound **17** on tomatoes between field-treated and fortified samples (Table IV) cannot be explained. These results give rise to the hypothesis of residue stability being dependent on rate of hydrolysis.

Testing of Hypothesis. The hypothesis postulated can be statistically supported by testing the rank correlation. To this end ranks are assigned to compounds in the order of decreasing hydrolytic half-life times (Tables II–IV, third columns) and of decreasing residue stability (last columns), respectively. Ranks of identical results are averaged; as an example, hydrolysis ranks 1–8 are occupied by eight compounds with identical half-life times (>20 days, Table II); all compounds therefore have the rank 4.5 ($^1/_8\sum_{k=1}^{8}k$, k denoting the ranks). From all pairs of ranks the correlation coefficient c (cf. textbooks on statistics) is calculated to be 0.90. Since $c = 0$ if no correlation exists and $|c| = 1$ if perfect correlation exists, $c = 0.90$ is a highly significant proof of correlation between hydrolytic half-life times and residue stability.

Conclusions. The strong correlation allows derivatization of the approximate storage stability of residues of a compound once its hydrolytic behavior is known. On the basis of half-life times each compound can be associated with one of the three groups (Tables II, III, and IV): If the half-life time of a compound is above 10 days at 70 °C, its residues (if any) are stable for at least 1 year at −20 °C. Residues of compounds with half-life times below 10 days (70 °C) but above 1 day (50 °C) are of uncertain stability, whereas compounds with half-life times below 1 day (50 °C) yield unstable residues.

Proposals. For checking residue stability the following procedure is suggested. (1) Determine the hydrolytic half-life times in aqueous buffer solution (pH 7) at 70 °C and at 50 °C. (2) If the half-life time is above 10 days at 70 °C, consider residues to be stable for at least 1 year if stored at −20 °C. (3) If the half-life time is below 1 day at 50 °C, either analyze samples within a few weeks or store extracts (and check their stabilities). (4) If the half-life time lies in between, run stability tests to decide whether the chemical is stable or not on the crop under investigation. Stability tests can be run with artificial mixtures. Prepare these mixtures by fortifying subsamples following method 2 in order to avoid homogenization problems.

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Quantitation and Characterization of Arsenic Compounds in Vegetables Grown in Arsenic Acid Treated Soil

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Several vegetable crops were field grown in Matapeake silt loam soil treated with 100 ppm of arsenic as arsenic acid. Total arsenic (As) contents of the edible plant parts were generally low, ranging from 3.00 ppm for potato peel to trace quantities in cabbage and corn. The highest As concentrations in broccoli, cabbage, corn, green beans, lettuce, and potato peel were found in the methanol/water phase. Arsenic in the nonextractable or chloroform phases was predominant in beets, potato flesh, swiss chard, and tomato. Methylarsonic acid and/or arsenate were identified in the methanol/water phases of broccoli, lettuce, potato flesh, potato peel, and swiss chard. The quantity of arsenate and methylarsonic acid recovered by arsine generation was lower than the total As present in the methanol/water phases. However, digestion of the methanol/water phases in hot 2.0 N NaOH yielded total recovery as arsenate. Hence, most of the arsenic contained in the methanol/water phases appears to be a complex organic arsenic compound.

Arsenic is a ubiquitous element, and although trace quantities of arsenic occur throughout the lithosphere, concentrations may be significantly higher in certain locations as a result of weathering processes and anthropogenic activities such as metal refining and pesticide use (Schroeder and Balassa, 1966). Arsenic is rarely found as the free element in soil but is frequently present as a component of sulfidic minerals ("Arsenic: Medical and Biological Effects of Environmental Pollutants", 1977). Arsenates are naturally occurring in oxygenated environments, while arsenite is probably the dominant form under moderately reducing conditions, for instance, in flooded soils ("Arsenic: Medical and Biological Effects of Environmental Pollutants", 1977; Walsh and Keeney, 1975). Inorganic arsenic compounds found in the environment may be converted into organic arsenic compounds by microorganisms. For example, Challenger et al. (1933) found that arsenic trioxide is methylated to trimethylarsine by *Scopulariopsis brevicaule*.

Traditionally, concentrations of arsenic compounds found in environmental samples have been reported as total arsenic following digestion (Chapman, 1926). However, the toxicological properties of arsenic compounds are dependent on the chemical nature of the arsenic compound, as well as the quantity present. Therefore, it is essential to discern the various arsenic compounds present in environmental samples before rational decisions can be made regarding potential health problems. Although other methods have been reported recently (Braman et al., 1977; Lakso et al., 1979; Lunde, 1973) the advent of an interface to couple a liquid chromatograph to a graphite-furnace atomic absorption spectrophotometer allows one to separate and detect low concentrations of many arsenic compounds in both model and natural systems (Brinkman et al., 1977; Stockman and Irgolic, 1979).

Arsenobetaine and *O*-phosphatidyltrimethylarsoniumlactic acid (sic) have been found naturally occurring in lobster and algae, respectively, but information regarding the chemical nature of As compounds formed upon incorporation of arsenic into terrestrial plants is rare (Edmond et al., 1977; Cooney et al., 1978). This is possibly due to the low concentrations of arsenic sorbed by plants (typically less than 1 ppm) as compared with marine organisms. However, in this study, residues were characterized by solubility in methanol, water, and chloroform. The selectivity and sensitivity of liquid chromatography coupled with graphite-furnace atomic absorption spectroscopy were employed to determine the presence or absence of arsenate, arsenite, methylarsonic acid (MA), and dimethylarsinic acid (CA) in the methanol/water extracts of several vegetables. Residues were also characterized for solubility in chloroform and nonextractability.

EXPERIMENTAL SECTION

Reagents. All chemicals were reagent grade unless otherwise specified. Vineland Chemical Co. and The Ansul Chemical Co. supplied methylarsonic acid (97%), and dimethylarsinic acid (92%), respectively. Antifoam agent was purchased from Hodag Chemical Co., Chicago, IL, and a lecture bottle of trimethylarsine was obtained from Ventron-Alfa Products. Trimethylarsine oxide was prepared by combining stoichiometric quantities of trimethylarsine and 30% hydrogen peroxide and rotary evaporating the resulting solution to dryness at 80 °C.

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