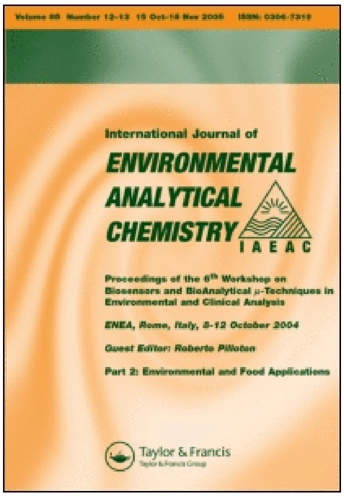

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Organochlorine Pesticide Residues in Styrian Soils and Seeds of the Styrian Oil Pumpkin: An Inventory and a Concept for their Reduction

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ORGANOCHLORINE PESTICIDE RESIDUES IN STYRIAN SOILS AND SEEDS OF THE STYRIAN OIL PUMPKIN: AN INVENTORY AND A CONCEPT FOR THEIR REDUCTION

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The fungicide hexachlorobenzene and other organochlorine pesticides have been detected in agricultural soils of the Austrian federal state Styria and in the seeds of the Styrian oil pumpkin grown on these fields. For monitoring the exact amounts of these contaminants in the single ecological compartments effective extraction and sample pre-treatment techniques have been developed, thus leading to a significant correlation between the concentration of hexachlorobenzene (HCB) in soil and its content in the oil seeds grown there, the factor ranging between 5 and 25. The efficiency of a new concept for the reduction of the pesticide contamination of the pumpkin seeds involving the application of activated charcoal powder could be demonstrated in a field-study. Thus the bioavailability of HCB in soil could be reduced significantly leading to lower HCB-contaminated oil seeds.

Keywords: Hexachlorobenzene; organochlorine pesticides; soil; pumpkin seed oil; gas chromatography

INTRODUCTION

Organochlorine pesticides (OCPs) such as DDTs and HCHs have been released into the environment starting from the early 1950's for agricultural and sanitary purposes. By now, most members of this class of pesticides and fungicides are banned by law [1], but some of these OCPs and/or their metabolites remain in sediments and ground water as potential hazards to human health. Plants can take up and accumulate OCPs from the soil and thus introduce them into the food chain, leading to e.g. OCP deposits in the fatty tissues of animals and humans.

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A specific problem in the southern parts of the Austrian federal state Styria arises from the presence of hexachlorobenzene (HCB) in the terrestric ecological system. This compound was used for fungicidal seed treatment and as a wood preservative, but it occurs as a by-product in the industrial production of other pesticides [2], as quintozen and the herbicide dacthal and has also been identified as a metabolite of lindane (γ-HCH) [3]. Although HCB has been banned in many countries (e.g. in Austria since 1987), persistent residues can be found all over the world, even in remote areas as the Antarctic [4] due to its resistance against thermal or hydrolytic degradation, microbiological effects and its lipophilic character expressed by the log K_{OW} of 6.44 (the octanol-water partition coefficient) [5]. Additionally, it shows a high affinity to soil (K_{OC}= 4000, adsorption constant per gram of the organic carbon in soil) and its high volarity favours ubiquitous distribution. Studies published from 1980 onward showed exceptional high concentrations of HCB in the seeds of the Styrian oil pumpkin [6–8], a plant typically cultivated in southern parts of Austria, Hungary and Slowenia.

The seeds of the Styrian oil pumpkin Cucurbita pepo L. convar. citrullina I. GREB. var. styriaca I.GREB and the cold-pressed non-refined oil thereof are very popular as a salad oil in Austria and are also used as a remedy in the therapy of problems of the prostate gland. Its naked green-coloured seeds contain up to 55% of a fat oil rich in unsaturated fatty acids [9], tocopherols [10] and specific Δ7-phytosterols [11]. However, it proved to be a special "indicator plant" for the presence of HCB and other OCPs in soils. It was claimed that the pumpkin plant takes up HCB via its roots (possibly with ground water or by diffusion) from the surroundings accumulating it in the seeds due to its extreme lipophility. An additional factor is the uptake of gaseous HCB from the soil via the foliage because of its high volarity [12]. The exact transport mechanism however, is not known yet.

Starting in 1988 and involving the cultivators and traders of pumpkin seeds as well as the University of Graz a long-term study was undertaken to investigate the uptake of various OCPs from soil and their deposition in the pumpkin seed. The environmental fate and possible sources of HCB contamination were elucidated and efforts have been made in reducing the bioavailability of this compound from the soil. In the course of this study specific techniques for the extraction, purification and enrichment of OCPs in different biological matrices and the subsequent high resolution capillary gas chromatography analysis have been developed [13–16] and a statistical study was carried out on the results obtained to draw conclusions regarding the applicability and costs.

MATERIALS and METHODS

Sample collection

Dried pumpkin seed samples have been collected from commercial products of Biosonn company (Graz-Raaba, Austria) originating from the southern parts of Styria. Soil samples were collected randomly from each agricultural field, dried and sieved according to a standard protocol applied to soil analysis.

Sample Preparation

Methods for both the determination of the OCPs in oil seeds and soils were developed in our laboratories and have been reported earlier [13–16]. All solvents used for residue analysis (petroleum benzene, etc.) as well as anhydrous sodium sulphate p.a. were purchased from Merck (Darmstadt, Germany) or Baker (via Müller-Scheer, Linz). Pesticide standards and internal standards pentachlorobenzene and Mirex (10 ng/μl in cyclohexane) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Silica gel (No. 7734 from Merck, particle size 0.063–0.200 mm) was heat treated at 450°C for 3 h and adjusted to a water content of 10% (w/w). For details see literature cited.

Oil-seed samples

Pumpkin seed samples have been analysed using a solid-phase extraction method with standardised silica gel (polarity adjusted by a water content of 10%, w/w) developed by Filek and Lindner [13].

To 5 g of the oil seed granulate stock solutions of the internal standards and 50 ml of petroleum benzene were added. After one minute of ultrasonification, the suspension was extracted by gently shaking for 12 h. Sample clean-up was performed with self-made columns (2 g of anhydrous sodium sulphate p.a. was overlaid with 8 g polarity adjusted silica gel as adsorbent in glass columns of 20 cm length and 1.5 cm i.d. with a glasswool type frit at the bottom), onto which an aliquot of 3 ml oil extract was transferred after sedimentation of the seed suspension. With a solvent mixture of petroleum benzene- tert. butylmethyl ether (70 ml, 98:2, v/v) the pesticides HCB, α-HCH, β-HCH, γ-HCH (Lindane), Heptachlor, cis-Heptachlorepoxid, o,p′-DDE, p,p′-DDE, Dieldrin, Endrin, o,p′-DDT and p,p′-DDT could be quantitatively eluted, while interfering substances of plant origin as e.g. triglycerides, chlorophyll and carotinoids were retained on the column. The extract was concentrated to 1 ml by means of a Kuderna-Danish type concentrator and was directly injected into the GC system. This convenient sample pre-treatment technique is not confined to pumpkin seed samples, but can be applied to many oil seeds and vegetable oils, as has been evaluated in our laboratories (data not shown).

Soil samples

OCPs were extracted from the soil samples by application of a simultaneous water steam distillation-organic solvent extraction (SDE) method published by Seidel and Lindner [14]. The SDE apparatus was a newly designed modification of an apparatus created by Likens, Nickerson [17] and Godefroot and co-workers [18, 19], respectively. Petroleum benzene was used as lipophilic solvent for the extraction of OCPs from soil samples (sample amount: 50 g). With this method the OCPs are extracted with high recoveries and selectively from interfering matrix compounds in a single step operation, followed by sample concentration to 1 ml with a Kuderna-Danish type concentrator. The application of this method for the enrichment and determination of OCPs in milk and milk powder was described by Filek et al. [20].

Adsorption material

Charcoal powder SA 20 from Norit (Amerefoort, the Netherlands) was chosen with a particle size distribution of 10 μm (30%) –150 μm (>150 μm: 4%) and a specific internal surface area of 800 m^2/g. This charcoal powder is suitable for decolorisation and purification of various food products, potable and waste water treatment and meets the requirements of the US Food Chemicals Codex (3rd edition, 1981). The adsorption material was added to the soil prior to the planting and growth season of the pumpkin plants.

GC-Analysis

For the analysis of both the soil and oil seed samples a Hewlett Packard 5890A gas chromatograph with a ^{63}Ni ECD equipped with an HP autosampler 7673 A and a fused silica capillary column (RTX 35, 30m × 0.25 mm i.d., 0.25μm film thickness from Restec) was used. Carrier gas and make-up gas was nitrogen (quality 6.0) at 125 kpa (18 psi) column head pressure. Via the autosampler a sample volume of 1 μl was injected with a 10 μl Hamilton syringe into a capillary inlet with a liner (gas volume: 990 μl, HP-part No. 19251–60540) in the splitless mode (time of closed split valve: 60 s). The injector temperature was 290°C, the detector temperature 325°C. The temperature programme started with an initial temperature of 100°C for 1 min, then rate 12°C/min to 220°C, rate A 1.5°C/min to 240°C and finally rate B 6°C/min to final temperature 290°C for 5 min. GC control and data processing were performed by a HP Chem Station equipped with Windows 95 software.

Quantitation

The quantitation of OCPs in soil and oil seed samples was performed via internal standard calibration with pentachlorobenzene and Mirex in spiked soil and seed samples. Recoveries of the OCPs were between 75 and 90%, both methods showed excellent reproducibility as well as ruggedness and have been crossvalidated throughout the years by interlaboratory control.

Recovery values were found to be between 72% for γ-HCH, 80% for Heptachlor, cis-Heptachlorepoxid and DDEs and up to 88–90% for HCB, Dieldrin and DDTs; limits of determination ranged between 1 ng/g for HCB, 2 ng/g for α-HCH, Dieldrin and Heptachlor, 3 ng/g for cis-Heptachlorepoxid and 5 ng/ g for γ-HCH, DDTs and DDEs [13] in pumpkin seeds. HCB recovery from soil using the SDE method was 100%, detection limit for HCB in soil was 0.05 ng/g, for detailed processing parameters see [14].

RESULTS AND DISCUSSION

OCP content of pumpkin seed samples

Starting in 1988 up to 200 commercial pumpkin seed samples per year from various fields all over Styria have been analysed for their content of OCPs. Almost every sample contained HCB, selected results are presented in Table I. The majority of the samples (about 98 %) were under the Austrian intervention level of 250 ng/g and as Germany raised its maximum residue limit from 10 ng/g to 50 ng/g in 1995 (a setpoint for other countries of the European Union), about 75% of the samples did not exceed this value. Extremely low levels found in 1997 were due to the infection of this years crop with the Zucchini-yellow-mosaic virus and also resulted in a low oil content of the seeds (average 45% in comparison to up to 55% in normal years). Other OCPs as e.g. Dieldrin were less often detected, a survey of the years 1995 to 1997 is shown in Table II (OCPs selected according to EPA methods 608 and 612, for determination limits see Materials and Methods).

TABLE I HCB contamination of Styrian pumpkin seeds

Year	*Number of samples (from different fields)*	*<10 ng/g (%)*	*< 50 ng/g (%)*	*< 250 ng/g (%)*
1988	149	28.8	-	98.0
1989	166	13.9	-	97.3
1990	176	19.9	-	96.6
1995	197	27.4	75.1	98.0
1996	215	11.6	66.5	97.2
1997	72	48.6	83.3	100.0

TABLE II OCP contamination of Styrian pumpkin seeds, positives defined as values exceeding the detection limit (see Materials and Methods)

OCP	*Positives 1995 (%) of investigated samples (n= 197)*	*Positives 1996 (%) of investigated samples (n= 215)*	*Positives 1997 (%) of investigated samples (n= 72)*
Dieldrin	40	27	54
α-HCH	0.5	0	0
β-HCH	0	0	0
γ-HCH	0	0	0
Heptachlor	28.0	21.5	1.5
cis-Heptachlorepoxid	5.5	13.6	23.1
o,p'-DDE	0	0.9	0
p,p'-DDE	0	0.9	0
Endrin	2.5	1.4	1.5
o,p'-DDT	6.0	1.9	29.1
p,p'-DDT	4.0	4.0	0

Sources of the HCB uptake

Principle sources of residues in crops are carry-over from insecticide application to soil and/or to growing crops, leaching of pesticides into ground water, translocation of soil applied pesticides into growing crops and effluents of pesticide industry in rivers and into soil [21]. According to earlier publications [8], the main source of the OCPs in pumpkin seeds and the oil respectively, were persistent residues in the soil. To ensure these findings, in field-trials pumpkin plants were grown on different types of soil (sand, clay) and different degree of HCB-contamination (0.05–5 ng HCB per g soil) distributed all over the typical growing area of Styria. Table III presents the HCB content of pumpkin seed samples and the corresponding soil samples over two consecutive years. A clear positive correlation between the HCB contamination in soils and seeds could be shown with an enrichment factor in the majority ranging between 5 and 25, depending on location, climate, rain fall and soil type. Though, HCB-concentrations in soil presented in Table III are averages of fields with sizes of about 1 to 2 hectares and may vary greatly on individual sections of the field (as is shown later in Table V), which may be an explanation for the dispersion of the enrichment factors in the second year to values as high as 520. In addition, one has to take into account that growing pumpkin on the same field over two consecutive years is unusual in practise, as pumpkin planting has to follow a strict rotation principle to ensure high yield and a low rate of diseased plants. Nevertheless, via this field-trial it could be proved that the HCB content of the soil is the determining factor for the HCB content in pumpkin seeds. In cultivation experiments with other plants, as e.g. sunflowers, rape or puppy on contaminated fields no OCP uptake into the seeds could be detected for these plants (data not published). Growth experiments with sunflowers and radiolabelled HCB confirmed these results [22]: the ^{14}C-HCB content of the pumpkins was up to twenty times higher than in the sunflowers. The Styrian oil pumpkin can thus be regarded as a special indicator for the presence or absence of OCPs in the environment. However, the exact pathway of HCB from the soil via the roots into the seeds or via the vapour through the foliage has still to be elucidated.

TABLE III HCB concentrations in pumpkin seed samples and in corresponding soils (ng/g) over two consecutive years

Field No.	*HCB-Conc. in soil, year 1*	*HCB-Conc. in seed, year 1*	*Enrichment-factor, year 1*	*HCB-Conc.in soil, year 2*	*HCB-Conc. in seed, year 2*	*Enrichment-factor, year 2*
57	2.2	40	18.2	0.05	10	200.0
131	1.3	33	25.4	0.8	9	11.2
909	1.5	14	9.3	0.6	11	18.3
96	2.6	38	14.6	2.5	23	9.2
764	2.1	15	21.7	0.9	15	16.7
857	2.0	93	46.5	2.0	162	81.0
866	1.6	3	1.9	0.2	5	25.0
242	4.4	35	7.9	0.7	26	37.1
204	2.7	23	8.5	2.4	16	6.7
822	3.6	68	18.8	3.8	65	17.1
562	5.7	52	9.1	4.4	116	26.4
559	1.3	3	2.3	0.1	6	60.0
732	1.7	29	17.0	0.05	26	520.0
81	0.4	16	40.0	0.05	3	60.0

Concept for the reduction of the HCB-contamination

Reductions of the concentration of heavy metals as cadmium and lead in soils have been achieved with the cultivation of plants accumulating metals [23,24]. No such possibility has been taken into account for the reduction of the soil OCP contamination so far. Similar experiments were carried out during this study with the Styrian oil pumpkin, but its capability proved to be too limited to achieve a significant reduction of the soil HCB contamination [25].

Another approach for the reduction of the HCB concentration was the application of activated carbon on the agriculturally used areas. HCB showed a great tendency for adsorption onto lipophilic sites in agricultural soils as proved by low recovery values especially when using supercritical fluid extraction (SFE) for real-life samples [16]. Powdered activated charcoal is known for its high adsorptive capacity and carbon sorbents with non-polar, inert and hydrophobic properties are gaining popularity as alternative sorbents in solid-phase extraction of pesticides in water or liquids in general [26,27].

Starting with controlled experiments in pots and in the green house led to encouraging results [28], so in 1996 0.04 % activated carbon (upper layer of the soil: 20 cm, dimension of each section 10 m × 33 m length) were brought out as an aqueous suspension on a field (for exact scheme, see Table IV). A statistical design of the field was necessary to take into account the inhomogenity of the field with respect to the HCB contamination as presented in Table V. Soil samples were taken at this field before and two weeks after the application of the charcoal powder (corresponding the seed of the pumpkin) and during the harvest and were analysed for their content of extractable HCB. As stated earlier, soil HCB-concentration varied over a broad range (see Table VI), but despite this inhomogenity trends could still be extracted due to the statistical design of the field (see also Figure 1). A small but not significant shift of the contaminant concentration in soil could be monitored along the season from average 15.5 ng/g (all 36 sections) at seed to 14.7 ng/g at harvest. Several other soil parameters were determined (as e.g. the content of organic carbon, content of NO_3, NH_4, water and pH), but no influence of the activated carbon application on the soil could be found.

TABLE IV Experimental design of field Ilz 2, divided into 18 sections treated with activated charcoal powder (marked with AC) and 18 non-treated control sections (marked with 0)

section	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
1	AC	0	AC	0	0	AC	AC	0	AC	AC	0	0
2	AC	0	AC	0	0	AC	AC	0	AC	AC	0	0
3	AC	0	AC	0	0	AC	AC	0	AC	AC	0	0

TABLE V Concentration of HCB in the soil sections of field Ilz 2 before application of activated carbon (ng/g)

section	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
1	2	5	17	23	28	17	11	14	12	12	16	26
2	10	17	22	17	10	12	10	14	14	18	23	18
3	31	11	10	11	23	17	34	14	26	16	3	3

TABLE VI Soil HCB concentrations of sections of field Ilz 2 treated (AC) or non-treated (0) with activated charcoal powder, before application

sections	*Minimum (ng/g)*	*Maximum (ng/g)*	*Average (ng/g)*	*Median (ng/g)*
0 (n=18)	3 (section 12/1)	28 (section 5/1)	15.3 ± 7.5	15.0
AC (n=18)	2 (section 1/1)	34 (section 7/3)	15.6 ± 7.2	15.0

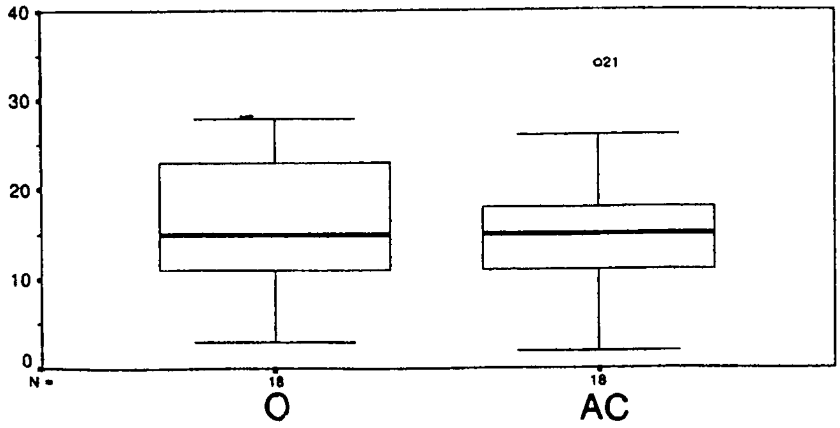

FIGURE 1 Soil HCB concentration before application of activated charcoal powder, divided in sections to be treated (AC) or not treated (O) with activated charcoal powder

Corresponding pumpkin seeds analysed for their HCB concentration showed an average of 244.7 ± 115.6 ng/g HCB (n=36), but as positive result a clear reduction of the contamination in the sections treated with activated carbon with an average of 198.2 ng/g versus 291.1 ng/g in the non-treated control sections could be monitored (enrichment factor reduced from 19 to 12.7 in sections treated). Data are illustrated in Table VII and Figure 2, although the 18 sections treated with activated charcoal powder originally had a higher HCB content in soil (as depicted in Figure 1 and Table VI), HCB-concentrations in the pumpkin seeds grown thereon were as much lower as one third and thus under the Austrian intervention level of 250 ng/g. The success of this method could be attributed to the adsorptive capacity of the activated carbon: highly polar and lipophilic HCB may be adsorbed onto the sorbent surface and therefore is only partially available for the uptake of the plant. Exact data of this equilibrium is not obtainable by now, but at the best (irreversible adsorption) a single application of activated carbon on agriculturally used areas might be sufficient for a reduction of the HCB content of the oil seed for some years. In contrast to the soil samples analysed earlier with an average HCB-contamination of 0.05–5 ng/g, this fields average HCB-concentration was extremly high (15.3–15.6 ng/g), leaving open the possibility of even greater HCB-reductions on originally lower contaminated fields; this will be studied in the next two years field-trials.

Problems arose during the analyses of the soil samples: Soil itself is a highly adsorptive matrix [29], but with addition of activated carbon extraction yields of HCB further decreased, this could be the explication for the varying results of the HCB concentration in soil. Selected samples were also extracted with supercritical fluid extraction (SFE), but no difference could be found between the results taking into account the variance in residue analysis (data not published). Another fact to consider is the presence of soil compounds with high affinity to carbon surface as these humic acids may lead to a competitive adsorption process with HCB.

TABLE VII HCB concentrations in pumpkin seeds of field Ilz 2, divided in sections treated (AC) or non- treated (0) with activated charcoal powder

sections	*Minimum (ng/g)*	*Maximum (ng/g)*	*Average (ng/g)*	*Median (ng/g)*
0 (n=18)	49	527	291.1 ± 132.5	292.5
AC (n=18)	52	347	198.2 ± 73.5	205.5

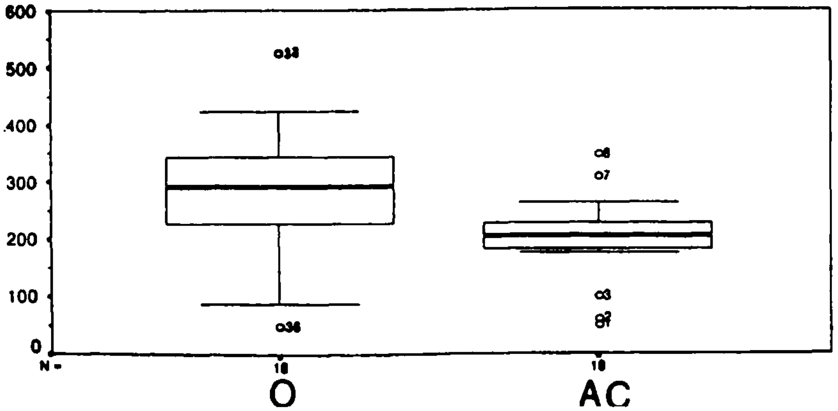

FIGURE 2 HCB concentration in pumpkin seeds, divided in sections treated (AC) or non-treated (O) with activated carbon

CONCLUSIONS

In this comparative study a large number of environmental samples from various sources in Styria have been analysed for their OCP content over a period of almost 10 years. A significant correlation of the OCP content of pumpkin seed samples and the corresponding soils could be established. The results indicate that the determining factor for the HCB concentration in the pumpkin seeds is the HCB concentration in the soil. Although the agricultural use of HCB is banned since 1987, it is still found as the major OCP contaminant in soils due to its stability towards biodegradation. Today, further pollution can not be ruled out because HCB occurs often as by-product in various chemical production processes. Due to its high environmental half-life time, HCB will still be present in Styrian soils in the decades to come. From the results obtained yet we can conclude that the application of activated charcoal powder as an adsorbent on contaminated agricultural areas is one possibility to reduce the HCB-content in foodstuffs. HCB contamination in soil can not be modified or decreased, but due to the binding of highly lipophilic HCB onto the carbon surface, it is no longer available for the plant. Further studies will have to be carried out to enlighten this process and equilibrias involved and to evaluate the costs and further potential of this method. As the concentration factor of HCB found in the soil and in the pumpkin seeds varies between 5 and 25 (average value 15), one must conclude that the average contamination of a field must not exceed 4 ppb in order to harvest seeds with an average contamination not exceeding the German intervention level of 50 ppb HCB. By reducing the bioavailability of HCB in soil due to its strong adsorption onto charcoal, pumpkins can still be cultivated safely on high HCB-contaminated fields or alternatively, significantly lower HCB levels in seeds will be achieved by cultivation on charcoal-treated soils with already initially low contamination levels.

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References

[1] Das neue Österreichische Chemikaliengesetz (1990).
[2] E. Heinisch, *Hercynia*, **20,** 99–116 (1983).
[3] H. Steinwandter, *Chemosphere*, **2,** 119–122 (1976).
[4] N.W. Van den Brink, *The Science of the Total Environment*, **198,** 43–50 (1997).
[5] K.H. Domsch (Ed.), *Pestizide im Boden*(VCH, 1992).
[6] P.K. Fida, *Nutrition*, **6,** 2pp (1982).
[7] G. Puchwein, A. Eibelhuber, W. Brodacz, J. Müller, J. Gölles and M. Unger, *Die Bodenkultur, Zeitschrift für Landwirtschaftliche Forschung*, **41,** 153–175 (1990).
[8] S. Ecker and O. Horak, *Chemosphere*, **29,** 2135–2145 (1994).
[9] Ch. Wentzel, *Nutrition*, **11,** 752–755 (1987).
[10] M. Murkovic, A. Hillebrand, J. Winkler and W. Pfannhauser, *Z. Lebensm. Unters. Forsch.*, **202,** 275–278 (1996).
[11] H. Schilcher and H.-J. Schneider, *Urologe*, **30,** 62 (1990).
[12] S. Ecker, Die Aufnahme von Hexachlorbenzol durch den Ölkürbis, Ph. D. Thesis, University of Vienna (1992).
[13] G. Filek and W. Lindner, *Z. Lebensm. Unters. Forsch.*, **202,** 19–23 (1996).
[14] V. Seidel and W. Lindner, *Anal. Chem.*, **65,** 3677–3683 (1993).
[15] V. Seidel, I. Tschernuter-Meixner and W. Lindner, *J. Chromatogr.*, **642,** 253–262 (1993).
[16] V. Seidel and W. Lindner, *Intern. J. Environ. Anal. Chem.*, **59,** 1–13 (1995).
[17] S.T. Likens and G.B. Nickerson, *Am. Soc. Brew. Chem. Proc.*, 5 (1964).
[18] M. Godefroot, P. Sandra and M. Verzele, *J. Chromatogr.*, **203,** 325–335 (1981).
[19] M. Godefroot, M. Stechele, P. Sandra and M. Verzele, *J. High Resolut. Chromatogr. Commun.*, **5,** 75–79 (1982).
[20] G. Filek, M. Bergamini and W. Lindner, *J. Chromatogr. A*, **712,** 355–364 (1995).
[21] I. Mukherjee and M. Gopal, *J. Chromatogr. A*, **754,** 33–42 (1996).
[22] S. Ecker and O.Horak, in: 13th International Symposium on Chlorinated Dioxins and Related Compounds, *Organohalogene Compounds* (H. Fiedler, H. Frank, O. Hutzinger, W.Parzifal, A. Riss and S.Safe, eds., Vienna 1993) Vol 12: pp 373–376.
[23] W. Hachtel, *Spektrum der Wissenschaften*, **5,** 19–20 (1997).
[24] H. Schilcher and H. Peters, *Pharm. Ind.*, **52,** 916–918 (1990).
[25] Volker Seidel, Rückstandsanalytik von Pestiziden und Toxinen in komplexen Matrices, Ph. D. Thesis, University of Graz (1993).

[26] E. Matisova, L. Kakalikova, J. Lesko and J. de Zeeuw, *J. Chromatogr. A*, **754**, 445–454 (1996).
[27] A. Di Corcia, R. Samperi, A. Marcomini and S. Stelluto, *Anal. Chem.*, **65**, 907–912 (1993).
[28] Gerda Filek-Wittinghausen, Rückstandsanalytik von Organochlorpestiziden und des Mycotoxins Moniliformin in Lebensmitteln und Umweltproben, Ph. D. Thesis, University of Graz (1995).
[29] J. R. Dean, *J. Chromatogr. A*, **754**, 221–233 (1996).