research for
man and environment

RIJKSINSTITUUT VOOR VOLKSGEZONDHEID EN MILIEU
NATIONAL INSTITUTE OF PUBLIC HEALTH AND THE ENVIRONMENT

RIVM report 515004 011

Duplicate 24-hour diet study 1994

organochlorine and organophosphorous pesticides

R.A. Baumann, R. Hoogerbrugge, P. van Zoonen

July 1999

This investigation has been performed by order and for the account of the Inspectorate for Health Protection, Commodities and Veterinary Public Health, within the framework of project 515004, Nutrition and health risks.

RIVM, P.O. Box 1, 3720 BA Bilthoven, telephone: 31 - 30 - 274 91 11; telefax: 31 - 30 - 274 29 71

Abstract

Duplicate diet samples collected in 1994 were analysed for organochlorine and organophosphorous pesticides. For some organophosphorous pesticides it was not possible to evaluate wether dietary intake exceeded the established Acceptable Daily Intake (ADI). For the other organophosphorous compounds as well as for the organochlorine pesticides, the calculated daily intake was well below the ADI.

Contents

Samenvatting

In 1994 namen 123 respondenten deel aan een duplicaat 24-uurs voedingsonderzoek. De verzamelde duplicaat voeding monsters werden geanalyseerd op macro parameters, nutrienten, mineralen, sporenelementen en contaminanten.

Bij aanvang van het onderzoek werd een inschatting gemaakt of de aanwezigheid van pesticiden in deze monsters een mogelijk risico voor de consument opleverde. Hiertoe werd een methodiek ontwikkeld om potentieel verdachte pesticiden te selecteren gebaseerd op gegevens omtrent voedsel consumptie, Acceptabele Dagelijkse Inname (ADI) en Maximum Residu Limiet (MRL).

Een aantal organochloor (9) en organofosfor (25) pesticiden werd geselecteerd voor nader onderzoek. Voor beide groepen pesticiden werd een 20-tal monsters, uit de monsterserie van 123, geselecteerd voor analyse.

Een analysemethode gebaseerd op vloeistof extractie, clean-up met Gel Permeatie Chromatografie en kwantitatieve bepaling met gas chromatografie met selectieve detectie werd ontwikkeld om de genoemde verbindingen te analyseren.

Bij het analyseren van de 20 monsters op organochloor pesticiden werd driemaal een residu aangetroffen (2 x vinclozolin en 1 x dicofol). De berekende gehalten vinclozolin waren resp. 11 en 22 µg/kg, voor dicofol was dit 17 µg/kg. De berekende dagelijkse innames bedroegen slechts een fractie van de vastgestelde ADI's, namelijk resp. 5% en 10% voor vinclozolin, en 28% voor dicofol.

Voor een aantal organofosfor pesticiden was het niet mogelijk om aan te kunnen tonen of een dagelijkse inname de vastgestelde ADI overschreed, omdat de aantoonbaarheidsgrenzen van de analysemethode voor deze verbindingen te hoog waren. Voor de andere geselecteerde organofosfor pesticiden werden geen residuen in de 20 geanalyseerde duplicaat voeding monsters aangetroffen.

Summary

In 1994, 123 respondents participated in a duplicate 24-hour diet study. Each respondent collected one duplicate of the food and drinks, including drinking water he/she consumed in a continuous 24-hour period. The collected duplicate diet samples were analysed on macro parameters, nutrients, minerals, trace elements and inorganic as well as organic contaminants. To evaluate if pesticides present in these samples migh lead to a possible consumers risk, a methodology was developed to select potentially suspect pesticides on the basis of food consumption, Acceptable Daily Intake (ADI) and Maximum Residue Limit (MRL) data. Thus, 9 organochlorine (OC's) and 25 organophosphorous (OP's) pesticides were selected. For both pesticides groups, 20 out of the 123 samples were selected for analysis. These samples were selected in such a way that the chance of detecting the slected pesticides was maximised. This was achieved by identifying for all selected compounds which commodities do have a relatively large contribution to the Theoretical Maximum Daily Intake (TMDI). Information on the duplicate diet samples was screened on this pesticide/commodity combinations, and subsequently a ranking of all samples was made. The top 20 of these rankings, both for OC's and OP's, were selected for analysis.

An analytical method based on liquid extraction, Gel Permeation Chromatography for clean-up and gas chromatography with selective detection for determination was developed to analyse the target compounds.

Applying this method for the detrmination of the organo chlorine pesticides, in 3 duplicate diet samples a residue was measured (2 x vinclozolin and 1 x dicofol). The calculated concentrations for vinclozolin were resp. 11 and 22 µg/kg, and for dicofol 17 µg/kg. The calculated daily intakes were only a fraction of the stablished ADI's, resp. 5% and 10% for vinclozolin and 28% for dicofol.

For some organophosphorous pesticides it was not possible to observe wether a dietary intake exceed the established ADI, because their limits of determination were too high. For the other selected organophosphorous pesticides no residues were measured in the dulicate diet samples.

1 Introduction

In 1994, duplicate portions were collected by 123 volunteers of the food, drinks and drinking water they consumed in a 24-hour period. Participants in this study, reflecting the 18-74 year old Dutch population, were recruted by the food inquiry bureau AGB Fresh Foods from residents living in an area of approximately 30 km around Bilthoven.
Sampling was carried out in two sessions of one week each, starting on monday and ending on sunday. The first session took place in march, the second in september. In march 31 men and 31 women participated, in september 29 men and 32 women. The mean age of all participants was 44 years and the mean body weight 75 kg.
The mean weight of the 123 duplicate diet 24-hour samples was 2603 g, range 1491 to 4449 g. Woman (N=63) collected on average 2452 g, range 1491 to 4160 g. For men (N=60) these numbers were respectively 2761 g, and 1639 to 4449 g. A seasonal effect on the average weight diet intake was not found.
Following homogenisation in a 5 gallon Waring Blender, each duplicate diet sample was split in several sub-samples, of which one portion of approximately 1 kg was lyophilized. The remaining sub-samples were frozen at -20 °C and kept at that temperature until use.
A detailed description of the sampling and sample preparation procedures is given in [1].

The collected samples were analysed on energy content and macro parameters (moisture, fat, protein, carbohydrates, alcohol and fiber content) [2], sterols [3], fatty acids [4], nitrate and nitrite [5], minerals (sodium and potassium) [6], trace elements (iron, selenium, copper and zinc) [7-10], heavy metals (lead and cadmium) [11], polychlorinated biphenyls and dioxins (report in progress) and a selection of pesticides.

This report describes the results of the analysis of a selection of the duplicate diet 24-hour samples for a number of organochlorine (OC) and organophosphorous (OP) pesticides. The criteria applied to the selection of the pesticides as well as the selection of the samples are

described in detail. Developed analytical methods are evaluated on the basis wether they are succesful in answering the question if daily residue intake leads to possible consumers risk.

2 Materials and methods

2.1 Selection of pesticides

Because the number of pesticides that might possibly be present in composite food samples accounts to several hundreds, selection criteria for compounds that may lead to a relatively large possible risk for the consumer are needed. For this reason, a selection method based on available information from International Organisations concerned with food safety/health protection of consumers as the Food and Agriculture Organisation (FAO) of the United Nations, the Codex Alimentarius Commision (CAC) and the Global Environment Monitoring System - Food Contamination Monitoring and Assessment Programme (GEMS/Food) of the World Health Organisation (WHO) was applied, leading to a selection of target compounds. In this selection process, a number of parameters described in this chapter plays a role.

The Acceptable Daily Intake (ADI) of a specific pesticide (mg/kg bodyweight), is the estimate of the amount of substance in food and/or drinking water that can be ingested daily over a lifetime without appreciable health risk to the consumer. The ADI is established by the FAO/WHO Joint Meeting on Pesticide Residues (JMPR) taking into account all available information (biochemical, metabolic, pharmacological and toxicological) derived from animal studies as well as observations in humans [12]. To estimate the ADI for humans, a safety factor depending on which specific information is used for the calculation, is taken into account.

The Maximum Residue Limit (MRL) (mg/kg) represents the maximum concentration of a specific pesticide residue that is allowed to be present on a specific commodity. The MRL is established by the CAC (after recommendation by the JMPR), taking into account data from field trials and the use of Good Agricultural Practice (GAP) [13].

Neither the ADI nor the MRL is permanently fixed. As new information/data becomes available, the ADI or MRL may be reconsidered by the JMPR.

An estimate of dietary residue intake can be made by calculating the Theoretical Maximum Daily Intake (TMDI) (mg/day x person) for a specific pesticide. The TMDI is calculated using the MRL and the average daily consumption of each food commodity for which an MRL has been established. The MRL is multiplied by the average food consumption for each commodity and these products are then summed, resulting in a value for the TMDI. The average daily food consumption for a large number of commodities can be derived from World and Regional diets established by WHO, National diets or food consumption studies [14]. The current approach used for TMDI calculations in The Netherlands is described in [15]. Because the definition of the TMDI assumes that in every food commodity the pesticide is present at the MRL, it is a gross over-estimate of dietary residue intake. Furthermore, food processing and/or food preparation (peeling, cooking etc.) often leads to reduction of pesticide residues in the diet, compared to residues present in the primary agricultural products.
A more realistic approach to estimate dietary intake can be reached by calculating the Estimated Daily Intake (EDI) (mg/day x person). The EDI is a prediction of the long-term daily intake of a pesticide based on the assumptions of average daily food consumption, median residues from supervised field trials and changes in residue levels resulting from food processing and/or food preparation [14].
A first insight whether the intake of food may lead to a possible risk for the consumer, for a certain pesticide, can be obtained by comparing the ADI and TMDI values calculated for that pesticide. When the TMDI is smaller than the ADI, the risk may be considered very low or negligible. In the case that the TMDI is larger than the ADI, it cannot be ruled out that a certain risk may occur.

In the study described in this report, selection of pesticides was focussed mainly on insecticides (organochlorine and organophosphorous compounds). TMDI calculations carried out by WHO based on ADIs established by JMPR, Codex MRLs and the WHO global diet or when available the WHO European diet, are used for the risk assessment of pesticide residues. Based on evaluations made by the JMPR [16], a number of compounds for which the TMDI > ADI or the TMDI represented a substantial part of the ADI, was identified for closer investigation. This selection of compounds, together with ADI, TMDI and

TMDI/ADI ratio, is given in Appendix 2. The list is extended with compounds that were frequently found on primary agricultural products as analysed by the Dutch Food Inspection Service during the years 1994-1996 [17], e.g. iprodione and vinchlozolin. Finally, compounds were added to the list because of their very low ADI values (several organophosphorous pesticides).
As additional information, the residue definition (to be determined as), and the year in which the JMPR reviewed the compound are also incorporated in the table.

To investigate acute health risk by dietary residue intake for a consumer, another approach is used. EDIs and meal sized portions or individual pieces of fruit or vegetables are important input parameters for this assessment.
A clear description on the estimation of dietary intake of pesticides, for the evaluation of chronic as well as acute risks, is given in [18].

2.2 Selection of samples

When the data on the occurrence of pesticides in primary agricultural products of the Dutch market (1994-1996) as provided by the Dutch Food Inspection Service [17] are evaluated, it is expected that pesticide residues in the 1994 duplicate diet samples are present at a low concentration level, e.g. in the low µg/kg range or less. Duplicate diet studies carried out in the USA [19,20] also point in this direction.
At the start of the study, the question was raised wether pooled samples or single samples should be analysed. On statistical grounds there is no driving force to choose either single or pooled samples. Firstly, there is not enough information on the distribution of single pesticides over the samples. Secondly, there is no reason to assume that the distribution of the pesticides over the samples is correlated. However, by pooling samples a dilution of a pesticide present in a single sample may occur. Because residues at a relatively low concentration level are to be expected, pooling may lead to not identifying residues originally present in a single sample. For this reason, we choose to analyse single samples. In Chapter

3.1 the influence of pooling samples on the distribution of pesticide residues is discussed in some detail.

In order to work efficiently with the limited amount of frozen sample material and also taking into account the expected low concentration levels, a selection of samples from the collected 123 samples was made in such a way that the chance of detecting a pesticide was maximised. This can be achieved by identifying in the JMPR calculation sheets, for all the selected pesticides given in Appendix 2, which commodity/commodities has/have a relatively large contribution to the calculated TMDI. This resulted in a list of commodities that do have a large contribution to the TMDI of each single OC and OP. Also information of the Food Inspection Service on the specific occurrence of pesticides in primary agricultural products was taken into account. The commodities listed from TMDI calculation sheets were compared with the commodities as described in the enquiry data sheets for the collected duplicate 24-hours diet samples. Hereafter, a ranking was made for the samples based on the matching of commodities.

For the organochlorine pesticides two routes of dietary intake can be distinguished. One route for the classical OC's (for instance heptachlor and dieldrin) is via fatty food (meat, fish, fats and oils present in processed foods). The other route for the more modern OC's (vinchlozolin and iprodione) is via leafy vegetables as lettuce, spinach and endive, grape and tomato. For both routes 10 samples were selected. A typical example of an extract of an enquiry data sheet from a selected sample, both for the classical and the modern OC's, is given in Appendix 3.

For the organohosphorous pesticides the route of dietary intake is via fruits (for instance citrus, grape and apples), cereals (bread), rice and potato. The samples that were selected for analysis contained 2-4 of these different commodities. Also within this serie of selected samples, all commodities that were identified as significantly contributing to the intake of each single OP were present [16]. A typical example of an extract of an enquiry data sheet from a selected sample for the OP's is also given in Appendix 3.

Thus, a selection of 20 samples to be analysed for the OC's, and 20 samples to be analysed for the OP's was made. For both selections, 10 samples were taken form the March 1994 and the September 1994 sampling session, respectively.

2.3 Analytical methods

The applied analytical method for the determination of organochlorine as well as organophosphorous pesticides is a modified version of Multi Residue Method 1 as described in the 6th edition of the Dutch manual 'Analytical Methods for Pesticide Residues in Foodstuffs' [21]. The methods both comprise an extraction step with ethyl acetate, clean up of the extract by Gel Permeation Chromatography (GPC), and analysis of the cleaned extract with capillary gas chromatography with selective detection. In Appendix 4, a description of both methods is given.

3 Results and discussion

3.1 Distribution of pesticides in single and pooled samples

In a way, duplicate diet samples themselves are pooled samples. They are constituted of primary agricultural products, processed foods, drinks and drinking water. The primary products may be consumed raw or processed (e.g. peeled, cooked or fried). For these reasons, the distribution of pesticide residues in duplicate diet samples will be different from their distribution in primary products. To clarify this phenomenon a model for the distribution of pesticide residues in duplicate diet samples was made. This model is illustrated by applying it to a specific pesticide, viz. iprodione. Iprodione was chosen because it scores the highest number of positive results in primary products [17], thus generating the highest possible amount of information about its distribution in raw agricultural commodities. In the model, a number of assumptions were made. Firstly, the distribution of iprodione residues in primary products (partly making up the duplicate diet samples) was the same as the distribution of iprodione residues in primary products of the Dutch market during the years 1994-1996 [17]. While screening the enquiry data sheets of the samples, it was observed that not a single duplicate diet sample contained more than 4 commodities that could possibly carry an iprodione residue that would significantly contribute to the total residue, assuming allowed use. As the second assumption, this number of 4 commodities was chosen as upper limit. A further screening of the enquiry data sheets made clear that this is also a valid assumption for the other OC's as well as for the OP's. Furthermore, it was assumed that these commodities in total comprise 40% (w/w) of the duplicate diet sample, and that no breakdown or disappearance of pesticide residues occurred, going from primary product to duplicate diet. These last two assumptions result in an overestimation (upper limit) of the amount of iprodione residue present in the duplicate diets.

In fig. 1 a number of curves are depicted. These curves describe the probability density as function of the iprodione concentration (mg/kg). The numbers n = 1, 2 and 4 refer to a single duplicate diet sample in which respectively 1, 2 and 4 commodities are present that may carry a significant iprodione residue. Data on iprodione from ref. [17], e.g. percentage of

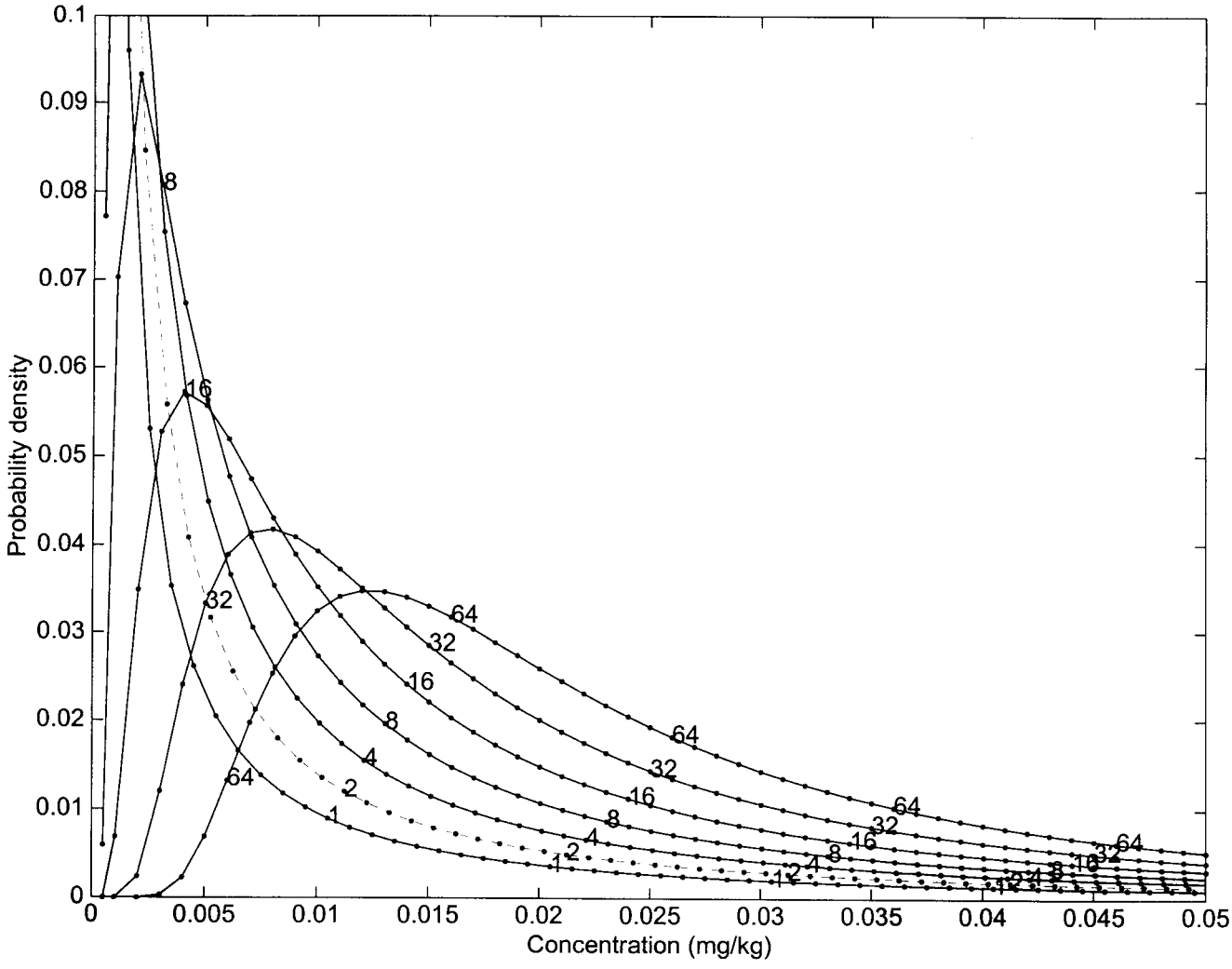

Fig. 1. Probability density vs. iprodione concentration (mg/kg), for n = 1 - 64. For explanation of this figure see text.

positive results, median value etc., have been used to construct the curve (n=1) in the figure. The curve is based on a lognormal distribution with the parameters fitted on the data of [17]. All the other curves are derived by convolution from this (n=1) curve. The curves with numbers n = 8, 16, 32 and 64 describe the probability density function for pooled duplicate diet samples (resp. 2, 4, 8 and 16 samples pooled). The curves of fig. 1 can be integrated over the concentration interval from the limit of determination (LOD) to infinity. This integration gives the relation between the fraction of samples above the LOD and the LOD (for n = 1, 2, 4 etc.) depicted in fig. 2.

With a limit of determination of 34 µg/kg for iprodione, for the method of analysis applied in this study, it can easily be read from the figure which part of the distribution can be measured

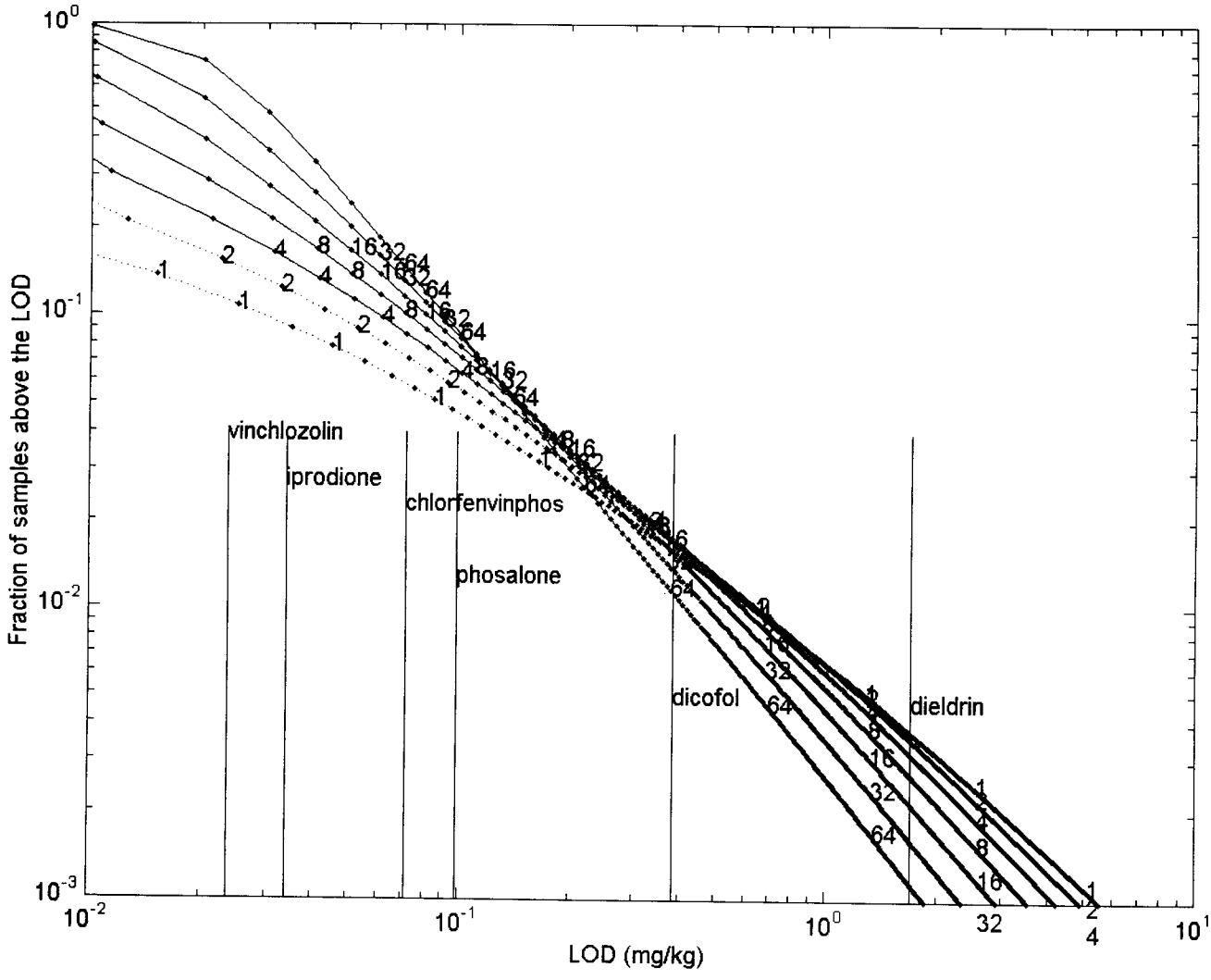

Fig. 2. Fraction of samples above the LOD vs. LOD, for n = 1 - 64. For explanation of this figure see text.

as positive, for single as well as pooled duplicate diet samples. Beside iprodione, also for some other pesticides that were incorporated in this study, after scaling of the LOD by the ratio between the median of the distribution of iprodione and the median of the other pesticide, the same approach as described above was followed. The results obtained for these compounds are also given in fig. 2. The expected upper limit of positive results for iprodione in single duplicate diet samples (n = 4 curve) is approximately 15%, e.g. 3 out of the 20 samples that were selected for analysis in this study. For vinchlozolin and dicofol, 20% and 1.5% are the expected upper limits, respectively.

3.2 Organochlorine pesticides

In order to evaluate the performance of the analytical method a recovery experiment was carried out. Total diet samples were spiked with OC's at the concentration level of the established limit of determination and at 5x the limit of determination. The results of this experiment are given in Appendix 5 (Table I) as recovery low and recovery high (both n=5), respectively. These results were eventually corrected for residues that were present in the sample material that was used for spiking.

With the exception of tecnazene and dicofol, recoveries for the OC's at the low level ranged from 87 - 130% with Relative Standard Deviations (RSD's) of 8 - 22%, and at the high level from 94 - 130% with RSD's of 5 - 12%.

For tecnazene the recoveries at the low and high level were 62% and 67% with RSD's of 27% and 30%, respectively. Dicofol could not be detected at the low recovery level, the recovery high was 42%, with an RSD of 3%. This low recovery was caused by breakdown of dicofol in the spiking standard solution. However, it is possible to analyse dicofol in the samples at the recovery low level.

The results for the analysis of the OC's in the 20 selected total diet samples are given in Table II of Appendix 5. The LOD for the individual compounds (reported as <) is set at or about the recovery low concentration level. In 3 samples a pesticide residue was found. In two samples vinchlozolin was detected (sample no. 96M3054, concentration 22 µg/kg and sample no. 96M3085, concentration 11 µg/kg). In 1 sample dicofol was detected (sample no. 96M3129, concentration 17 µg/kg).

The total weight of the collected duplicate 24-hour diet samples no. 96M3054, 96M3085 and 96M3129 is 2697, 2733 and 1948 g, respectively [1]. The calculated residue intake of vinchlozolin for the two samples (96M3054 and 96M3085) is 59 and 30 µg, the calculated residue intake of dicofol (sample 96M3129) is 33 µg.

The ADI for vinchlozolin is 0.01 mg/kg body weight or 0.6 mg/person (1995 JMPR evaluation). The calculated intakes of 59 and 30 µg comprise 10% and 5% of the ADI,

respectively. The ADI for dicofol is 0.002 mg/kg body weight or 0.12 mg/person (1994 JMPR evaluation). The calculated intake of 33 µg comprise 28% of the ADI.

The LOD established for heptachlor/beta-hepo and dieldrin (Appendix 5), enables quantitation of these compounds in samples in which their concentration is at least 3 times the established PTDI values. Applying another method of analysis, it is possible to analyse these OC's at a lower concentration level in food samples. However, the method to be used in that case would make it very difficult to analyse all the OC's selected in this study in one analytical run. Thus, for efficiency reasons the method as described in section 2.3 was chosen. Inspection of the chromatograms did not reveal concentrations of heptachlor/beta-hepo and dieldrin in the samples at the 1-6 µg/kg concentration level. In this way it was secured that these compounds were not present in the duplicate diet samples at an amount corresponding to 100% or more of the PTDI's. In a study carried out in Finland in 1993 [22], the estimated average daily intake of dieldrin was 0.03 µg/person. This comprises 0.5% of the PTDI of this compound.

3.3 Organophosphorous pesticides

In order to evaluate the performance of the analytical method a recovery experiment was carried out. Total diet samples were spiked with OP's at a concentration level of the expected limit of determination and at 10x the limit of determination. The results of this experiment are given in Appendix 6, Tables I and II, as recovery low and recovery high (both n=3), respectively. The samples that were used for the spiking experiments were first analysed for OP residues; no residues were found.

Phorate-oxon and phorate-sulfon could not be spiked at the recovery high level, because the solutions of these compounds purchased from the manufacturer were too diluted. The compounds could not be obtained in their solid form. Due to analytical problems disulfoton, the demeton-S-methyl complex and monocrotophos could not be detected at the recovery low level. Monocrotophos breaks down in the standard solution.

Recoveries for the OP's at the low level (except phorate) ranged from 92 - 122% with RSD's of 2 - 22%, and at the high level (except demeton-S-methyl-sulfoxide) 69 - 103% with RSD's of 2 - 22%. For phorate, the recovery low level was 47%, with an RSD of 65%. For demeton-S-methyl-sulfoxide, the recovery high level was 91%, with an RSD of 39%.

The results for the analysis of the OP's in the 20 selected total diet samples are given in Appendix 6, Table III. The limit of determination for the compounds (reported as <) is defined as the concentration of an OP that gives a peak in the chromatogram equivalent to 3 times the baseline noise level. Not a single OP could be detected in the analysed samples at or above the LOD level. To evaluate the homogeneity of subsamples, 4 out of the 20 samples were analysed in duplo, results are also given in Appendix 6, Table III as samples nos. 96MxxxxD. No contradictory results compared to the original analyses were observed.

In order to evaluate if a dietary intake > ADI could be observed for the OP's with the developed analytical method, an approach taken into account ADI's, weight of duplicate 24-hour diet samples and LOD values was used. For the collected 123 duplicate diet samples, an average weight of 2.6 kg was calculated and a maximum weight of 4.4 kg was found. If a weight of 3 kg is used in the following calculation, it is certain that for 80% of the samples in this study, a dietary intake > ADI can be observed, for a given LOD.
To illustrate the applied approach, the calculation is carried out for azinphos-methyl as an example. In Appendix 6, Table III an LOD for azinphos-methyl of 0.02 mg/kg is given. The ADI for this compound is 0.3 mg/person. In order to detect an amount of azinphos-methyl in a 3 kg sample equivalent to 100% of the ADI, an LOD of 0.3 mg / 3 kg = 0.1 mg/kg should be attained. The LOD of 0.02 mg/kg is lower than 0.1 mg/kg. This means that for azinphos-methyl (in a 3 kg sample) it is possible to detect down to 20% of the ADI with the developed analytical method.
When this calculation is made for all the OP's that were studied it is observed that for chlorfenvinphos, the demeton-S-methyl complex, disulfoton, monocrotophos and phorate complex it is not possible to observe wether a dietary intake > ADI. Chlorfenvinphos and phorate complex can be analysed quite sensitively with the developed method. The main

reason that it is not possible to observe if a dietary intake > ADI, is the very low ADI value for these compounds. Applying a modified analytical method might well solve this problem. For phorate the situation is even worse than for chlorfenvinphos because its residue is defined as the sum of phorate, phorate-O-analogon, their sulfoxides and sulfones, expressed as phorate. The LOD for phorate is the sum of the LOD's of the compounds incorporated in the residue definition, leading to a relatively high LOD value of 0.06 mg/kg (as given in Appendix 6, Table III). The demeton-S-methyl complex, disulfoton and monocrotophos give problems mainly due to their instability, even when they are analysed in samples spiked at the recovery low level. This, combined with the fact that the ADI's established for these OP's are also very low, makes it difficult to imagine an analytical method that can be successfull in evaluating wether a dietary intake > ADI is the case. On the other hand, because of the inherent instability of the compounds, it may be worth while to generate additional information on them through processing studies in order to establish reduction factors. With these reduction factors, a more reliable estimation can be made concerning possible daily intake.

Finally, visual inspection of the chromatograms of the analysed selection of 20 samples gave no evidence for the presence of OP's other than the selected group, at the recovery low level.

3.4 Discussion

The last RIVM duplicate diet study was carried out in 1984-1985. The results obtained for a number of pesticides (organochlorine, N-methylcarbamates, pentachlorophenol, systemic fungicides and profam/chloroprofam) are described in 6 sub-reports [23-28]. Although a number of pesticides were present in the analysed samples, all calculated intakes were well below the established ADI's. The most important conclusion that could be drawn from this study was that residue intake of the investigated pesticides did not lead to an appreciable consumers risk.

Comparison of the results obtained from the 1984-1985 study and the 1994 study is hampered by the fact that only 3 organochlorine pesticides (heptachlor, beta-hepo and

dieldrin) were selected in both studies. Moreover, different analytical methods with a different performance were applied to measure them. However, the results obtained for both duplicate diet studies are not contradictory. Information from other studies e.g. OC's in mothers' milk [29] and fatty food products, all point to decreasing concentration levels of classical OC's in the food chain for over 20 years.

4 Conclusions and suggestions for further research

Evaluating the results of the 1994 duplicate 24-hour diet study, there is no evidence that residue intake of the selected OC's exceeds established ADI's. For a number of the selected OP's it is not possible to evaluate exceedance of residue intake of the established ADI's. For the other selected OP's, there is no evidence that residue intake exceeds established ADI's. Presumabely, because measured residue intakes are lower than TMDI's for the relevant pesticides, reduction factors play a role. Reduction factors can be estimated for pesticides that give measurable residues in foodstuffs.

Measurements of sumparameters in duplicate diet samples, as for instance cholinesterase inhibition and total organic tin, may be carried out in order to estimate if analysis of individual cholinesterase inhibitors or organic tin compounds is feasible.

Evaluation of acute risks may be important in view of possible consumers risk, especially for risk groups like for instance children under 6 years of age and large consumers. In this respect, cholinesterase inhibitors e.g. organophosphorous esters and N-methylcarbamates are suspect groups of pesticides. In view of US legislation (Food Quality Protection Act of 1996), the outcomes of the International conference on pesticide residues variability and acute risk assessment (York, UK, dec. 1998) and the ongoing discussion at the international level about how to evaluate pesticides that have a common mode of action, it might also be interesting to measure sumparameters such as cholinesterase inhibition for the assessment of acute risks.

In order to be able to evaluate chronic as well as acute risks, the availability of sensitive and selective methods of analysis that are able to quantitate pesticides at or below the ADI and/or the acute reference dose, is indispensable.

References

[1] H.A.M.G. Vaessen et. al., Duplicaat 24-uurs voeding onderzoek 1994 - Verzamelen en bewerken van het monstermateriaal, RIVM report no. 389101 008, december 1995 (in Dutch, English summary)

[2] H.H.S. Roomans, Inspectorate for Health Protection, in preparation

[3] R.C. Schothorst and A.A. Jekel, Food Chemistry 64 (1999), 561-566

[4] R.C. Schothorst, internal RIVM report 1102/97 ARO Sch/sch

[5] H.A.M.G. Vaessen and R.C. Schothorst, Food Additives and Contaminants, Vol. 16, no. 5 (1999) 181-188

[6] J.W. van Loon, A. van Ooik en R. Ritsema. Duplicaat 24-uurs voedingen 1994 - inname aan natrium en kalium, RIVM report no. 515004 004, december 1996 (in Dutch, English summary)

[7] A. van Ooik, G. van den Burg, R. Ritsema, J.W. van Loon en H.A.M.G. Vaessen. Duplicaat 24-uurs voedingen 1994 - ijzerinname, RIVM report no. 515004 001, march 1996 (in Dutch, English summary)

[8] J.W. van Loon, A. van Ooik en R. Ritsema. Duplicaat 24-uurs voedingen 1994 - seleeninname, RIVM report no. 515004 002, june 1996 (in Dutch, English summary)

[9] J.W. van Loon, A. van Ooik en R. Ritsema. Duplicaat 24-uurs voedingen 1994 - koperinname, RIVM report no. 515004 006, december 1996 (in Dutch, English summary)

[10] J.W. van Loon, A. van Ooik en R. Ritsema. Duplicaat 24-uurs voedingen 1994 - inname aan zink, RIVM report no. 515004 005, december 1996 (in Dutch, English summary)

[11] J.W. van Loon, P. de Joode, A. van Ooik en R. Ritsema. Duplicaat 24-uurs voedingen 1994 - inname aan lood en cadmium, RIVM report no. 515004 007, july 1998 (in Dutch, English summary)

[12] Principles for the toxicological assessment of pesticide residues in food, Environmental Health Criteria (EHC) 104, WHO, Geneva, 1990

[13] Codex Alimentarius Commision, Procedural manual, 10th ed., FAO/WHO, Rome, 1997

[14] Guidelines for predicting dietary intake of pesticide residues (revised), GEMS/Food, WHO/FSF/FOS/97.7, WHO, Geneva, 1997.

[15] M.M.H. Dooren-Flipsen, J.D. van Klaveren and G. van Donkersgoed, Theoretical maximum daily intake of pesticide residues in The Netherlands - a model for risk assessment, RIKILT-DLO report 96.28, 1996

[16] International Programme on Chemical Safety (ICPS), JMPR Evaluations through 1998, WHO/PCS/99.1, WHO, Geneva, 1999; and cited references.

[17] H.A. van der Schee, The presence of pesticide residues in primary agricultural products of the Dutch market during the years 1994-1996, Inspectorate for Health Protection, report no. AM9609GF7, aug. 1997

[18] D.J. Hamilton et.al., Optimum use of available residue data in the estimation of dietary intake of pesticides, IUPAC Reports on Pesticides (39), Pure & Appl. Chem., Vol 69, No. 6, pp. 1373-1410, 1997

[19] Food and Drug Administration (FDA) 1996 FDA Pesticide Program, Residue Monitoring 1995. Available at HTTP://VM.CFSAN.FDA.GOV

[20] Food and Drug Administration (FDA) 1998 FDA Pesticide Program, Residue Monitoring 1996. Available at HTTP://VM.CFSAN.FDA.GOV

[21] Analytical Methods for Pesticide Residues in Foodstuffs, sixth edition, Chief Inspectorate for Health Protection, Dutch Ministry of Public Health, Welfare and Sport, The Netherlands, 1996

[22] P.L. Penttilä and K. Siivinen, Food Additives and Contaminants, Vol. 13, no. 6 (1996) 609-622

[23] P.A. Greve et.al., Bestrijdingsmiddelen in duplicaat 24-uurs voedingen (deelrapport 1: organochloorbestrijdingsmiddelen), RIVM report no. 388474001, march 1987 (in Dutch)

[24] C.E. Goewie en E.A. Hogendoorn, Bestrijdingsmiddelen in duplicaat 24-uurs voedingen (deelrapport 2: carbaryl, carbofuran en propoxur), RIVM report no. 388474002, november 1987 (in Dutch)

[25] P.A. Greve et.al., Bestrijdingsmiddelen in duplicaat 24-uurs voedingen (deelrapport 3: pentachloorfenol), RIVM report no. 388474003, july 1987 (in Dutch)

[26] P.A. Greve et.al., Bestrijdingsmiddelen in duplicaat 24-uurs voedingen (deelrapport 4: captan/folpet/captafol), RIVM report no. 388474004, september 1987 (in Dutch)

[27] P.A. Greve et.al., Bestrijdingsmiddelen in duplicaat 24-uurs voedingen (deelrapport 5: carbendazim/thiabendazool), RIVM report no. 388474007, february 1988 (in Dutch)

[28] P.A. Greve et.al., Bestrijdingsmiddelen in duplicaat 24-uurs voedingen (deelrapport 6: profam en chloorprofam), RIVM report no. 388474001, march 1987 (in Dutch)

[29] A.K.D. Liem et.al., Organohalogen Compounds, Vol 26, pp. 69-74, 1995

Appendix 1 Mailing list

1-5 Hoofdinspecteur voor de Gezondheidsbescherming, Waren en Veterinaire zaken (W&V)
6 Directeur Gezondheidsbevordering
7 Directeur-Generaal van de Volksgezondheid
8 Voorzitter van de Gezondheidsraad
9 Regionaal Inspecteur Noord-West van de Inspectie W&V te Amsterdam
10 Regionaal Inspecteur Oost van de Inspectie W&V te Zutphen
11 Regionaal Inspecteur Zuid van de Inspectie W&V te 's-Hertogenbosch
12 Hoofdinspectie voor de Gezondheidszorg
13 Redactie "De Ware(n)-Chemicus"
14 Dr. W. van Eck, directie GZB
15 Drs. J.W. Dornseiffen, directie GZB
16 Drs. H. Jeuring, Inspectie W&V
17 Dr. G. Kleter, Inspectie W&V
18-25 Werkgroep OVR tav de secretaris Dr. R.A. Baumann
26 Depot Nederlandse Publikaties en Nederlandse Bibliografie
27 Directie RIVM
28 Dr. ir. G. de Mik
29 Prof. dr. ir. D. Kromhout
30 Dr. R.W. Stephany
31 Ir. H. van de Wiel
32 Dr. W.H. Könemann
33 Dr. ir E. Lebret
34 Dr. A. Opperhuizen
35 Dr. ir. J. C. Seidell
36 Ir. H.P. van Egmond
37 Dr. T. Visser
38 Drs. E.G. van der Velde
39 Dr. A.K.D. Liem
40-42 Auteurs
43 SBD/Voorlichting & Public Relations
44 Bureau Rapportenregistratie
45 Bibliotheek RIVM
46-65 Bureau Rapportenbeheer
66-75 Reserve exemplaren

Appendix 2 List of target pesticides with ADI, TMDI and TMDI/ADI ratio.

Compounds	To be determined as	ADI (mg/person)	TMDI (mg/person)	TMDI/ADI (x100%)	JMPR
organochlorine					
dicofol	sum of p,p' and o,p' isomers	0.12	1.8958	1580	1994
dieldrin	dieldrin	0.006#			1994
endrin	sum of endrin and delta-keto-endrin	0.012#			1994
heptachlor	sum of heptachlor and beta-hepo	0.006	0.0214	357	1994
iprodione	iprodione	3.6	1.5409	43	1995
tecnazene	tecnazene	1.2	2.2509	188	1994
vinchlozolin	vinchlozolin	0.6	0.822	137	1995
organophosphorous					
azinphos-methyl	azinphos-methyl	0.3	0.2911	97	1995
chlorfenvinphos	chlorfenvinphos	0.03	0.0693	231	1994
chlorpyrifos-methyl	chlorpyrifos-methyl	0.6	2.6476	441	1994
demeton-S-methyl	sum of demeton-S-methyl, its sulfoxide and its sulfon	0.018	0.0152##	84	1998
demeton-S-methylsulfon	demeton-S-methylsulfon	0.018	0.0152##	84	1998
oxydemeton-methyl*	sum of demeton-S-methylsulfon and oxydemeton-methyl	0.018	0.0152##	84	1998
diazinone	diazinone	0.12	0.2451	204	1994
dichlorvos	dichlorvos	0.24			1993
dimethoate	dimethoate	0.6			1987
disulfoton	sum of disulfoton, its sulfoxide and its sulfon	0.018	0.2797	1554	1994
ethion	ethion	0.12	0.1505	125	1994
isofenphos	isofenphos	0.06			1986
methacrifos	methacrifos	0.36			1990
methidathion	methidathion	0.06	0.1202	200	1994
monocrotophos	monocrotophos	0.036			1995
phorate	sum of phorate, its oxygen analog and their sulfoxides and sulfons	0.03	0.038	127	1994
phosalone**	phosalone	0.06			1993
phosmet	phosmet	0.6	0.9321	155	1994
pirimiphos-methyl	pirimiphos-methyl	1.8	1.9844	110	1994
triazophos	triazophos	0.06			1993

*oxydemeton-methyl = demeton-S-methylsulfoxide
**all uses recommended for withdrawal
#PTDI (Provisional Tolerable Daily Intake)
##IEDI (International Estimated Daily Intake) as reviewed by the 1998 JMPR

Appendix 3 Information on the contents of selected samples

The information given in this appendix is extracted from the orginal enquiry data sheets filled in by the volunteers participating in the duplicate diet study.

Typical example of a duplicate diet sample selected for (classical) OC analysis.

Male, age 58, length 178 cm, weigth 92 kg.

Bread, wholemeal: 3 slices
bread, rye: 1 slice
margarine: on all 4 slices of bread
cheese: 1 serving
meat products: 2 servings
icecream vanilla/walnut: 1 serving
kiwi: 1
apple: 2
sauerkraut: 1 serving
smoked sausage: 80 g
bacon: 75 g
bouillon: 2.5 cups
cookie: 1
chocolate: table spoon
black coffee: 5 cups
milk (2% fat): 1 cup
grapefruit juice: 1 glass
tap water: 1 glass
gin: 2 glasses

Typical example of a duplicate diet sample selected for (modern) OC analysis.

Female, age 60, length 162 cm, weigth 56 kg.

Bread, wholemeal: 2 slices
butter: on 2 slices
cheese: 2 servings
yoghurt: 1 bowl
grapes: 1 bunch
pasta: 1 serving
parmezan cheese: 1 serving
tomato, courgette, mushrooms, onion, stir fried: 1 serving
lettuce: 1 serving
biscuit: 1
coffee: 2 cups
tea: 2 cups
tap water: 1 glass
orange juice: 1 glass
herbal extract: 2 spoonsfull
herbal/fiber tablets: 6

Typical example of a duplicate diet sample selected for OP analysis.

Female, age 66, length 149 cm, weigth 60 kg.

Bread, wholemeal: 1 slice
margarine: 25 g
cheese: 1 serving
apple: 2
orange: 1
tomato: 1
kiwi: 2
potato, cooked: 1 serving
endive, cooked: 1 serving
minced meat: 100 g
liver sausage: 20 g
meat balls: 20 g
gravy: 4 table spoons
tomato soup: 2 cups
biscuit: 1
coffee, black: 3 cups
coffee, white: 5 cups
tap water: 3 glasses
mineral water: 1 glass
red wine: 2 glasses

Appendix 4 Analytical methods

Organochlorine pesticides

Extraction of the OC's took place by shaking 2 g of a defrosted and homogenised duplicate diet sample with 4 ml ethyl acetate for 1 minute. The organic extract was centrifuged during 5 min at 3000 rpm. About 2 ml of the clear supernatant was dried over sodium sulfate.
An aliquot of 62 µl of the dried extract was injected onto a Plgel 5 µm 100A, 300 mm x 7.5 mm GPC column. The applied mobile phase was ethyl acetate/cyclohexane (50/50, v/v), the flow rate 1 ml/min. The first 9.2 ml of the eluate was discarded, the next 4.3 ml fraction, containing the analytes, was collected. The collected fraction was concentrated under a nitrogen flow to 4 ml.
Quantitation of the OC's was carried out by capillary Gas Chromatography-Electron Capture Detection (GC-ECD) equipped with an autosampler with a large volume introduction option. An aliquot of 80 µl of the cleaned extract was injected onto a 25 m x 0.32 mm x 0.17 µm HP-Ultra 2 column.

Organophosphorous pesticides

Extraction of the OP's took place by shaking 2 g of a defrosted and homogenised duplicate diet sample with 4 ml ethyl acetate for 1 minute. The organic extract was centrifuged during 5 min at 3000 rpm. About 2 ml of the clear supernatant was dried over sodium sulfate.
An aliquot of 62 µl of the dried extract was injected onto a Plgel 5 µm 100A, 300 mm x 7.5 mm GPC column. The applied mobile phase was ethyl acetate/cyclohexane (50/50, v/v), the flow rate 1 ml/min. The first 9.1 ml of the eluate was discarded, the next 5.9 ml fraction, containing the analytes, was collected. The collected fraction was evaporated until dry under a nitrogen flow, and reconstituted with 1 ml hexane.
Quantitation of the OP's was carried out by capillary Gas Chromatography-Pulsed Flame Photometric Detection (GC-PFPD) equipped with an autosampler with a large volume introduction option. An aliquot of 60 µl of the cleaned extract was injected onto the 50 m x 0.32 mm x 0.20 µm CP-Sil 13 CB column.

Appendix 5 Analytical results obtained for the organochlorine (OC) pesticides.

Table I. Recovery data of OC's added to different samples at two concentration levels.

	Spike at low level (µg/kg)	Mean recovery low (%) (n=5)	RSD (%)	Spike at high level (µg/kg)	Mean recovery high (%) (n=5)	RSD (%)
Tecnazene	3.12	67	27	15.6	62	30
Heptachlor	3.04	87	8	15.2	94	7
Vinchlozolin	6.95	96	11	34.7	104	12
beta-hepo	4.63	93	9	23.1	100	8
Dieldrin	6.05	113	22	30.3	130	11
Endrin	8.33	110	15	41.6	120	11
delta-keto-endrin	6.28	94	8	31.4	109	7
Iprodione	34.2	130	20	171	108	5
Dicofol	7.54	n.a.	-	37.7	42	3

Table II. Concentration of OC's in analysed duplicate diet samples (µg/kg)

LOC-LIMS I.D.	96M3054	96M3055	96M3063	96M3065	96M3087
Respondent I.D.	6	7	15	17	39
Tecnazene	<3	<3	<3	<3	<3
Heptachlor	<3	<3	<3	<3	<3
Vinchlozolin	22	<7	<7	<7	<7
beta-hepo	<3	<3	<3	<3	<3
Dieldrin	<6	<6	<6	<6	<6
Endrin	<6	<6	<6	<6	<6
delta-keto-endrin	<6	<6	<6	<6	<6
Iprodione	<34	<34	<34	<34	<34
Dicofol	<8	<8	<8	<8	<8

LOC-LIMS I.D.	96M3104	96M3108	96M3133	96M3135	96M3153
Respondent I.D.	56	60	123	125	143
Tecnazene	<3	<3	<3	<3	<3
Heptachlor	<3	<3	<3	<3	<3
Vinclozolin	<7	<7	<7	<7	<7
beta-hepo	<3	<3	<3	<3	<3
Dieldrin	<6	<6	<6	<6	<6
Endrin	<6	<6	<6	<6	<6
delta-keto-endrin	<6	<6	<6	<6	<6
Iprodione	<34	<34	<34	<34	<34
Dicofol	<8	<8	<8	<8	<8

Table II, continued.

LOC-LIMS I.D.	96M3066	96M3068	96M3076	96M3081	96M3085
Respondent I.D.	18	20	28	33	37
Tecnazene	<3	<3	<3	<3	<3
Heptachlor	<3	<3	<3	<3	<3
Vinchlozolin	<7	<7	<7	<7	**11**
beta-hepo	<3	<3	<3	<3	<3
Dieldrin	<6	<6	<6	<6	<6
Endrin	<6	<6	<6	<6	<6
delta-keto-endrin	<6	<6	<6	<6	<6
Iprodione	<34	<34	<34	<34	<34
Dicofol	<8	<8	<8	<8	<8

LOC-LIMS I.D.	96M3112	96M3115	96M3129	96M3140	96M3142
Respondent I.D.	102	105	119	130	132
Tecnazene	<3	<3	<3	<3	<3
Heptachlor	<3	<3	<3	<3	<3
Vinchlozolin	<7	<7	<7	<7	<7
beta-hepo	<3	<3	<3	<3	<3
Dieldrin	<6	<6	<6	<6	<6
Endrin	<6	<6	<6	<6	<6
delta-keto-endrin	<6	<6	<6	<6	<6
Iprodione	<34	<34	<34	<34	<34
Dicofol	<8	<8	**17**	<8	<8

Appendix 6 Analytical results obtained for the organophosphorous (OP) pesticides.

Table I. Recovery data of OP's added to different samples at or about the LOD level.

Component	Spike level (mg/kg)	Recovery (%)	RSD (%)	n=
Dichlorvos	0.17	118	2	3
Methacrifos	0.03	101	19	3
Phorate-oxon	0.02	121	11	3
Demeton-S-methyl	0.02	nd	nd	3
Phorate	0.03	46	65	3
Monocrotofos	0.03	nd	nd	3
Dimethoate	0.68	101	9	3
Diazinon	0.12	108	12	3
Disulfoton	0.02	nd	nd	3
Chlorpyrifos-methyl	0.53	91	6	3
Demeton-S-methyl-sulfon	0.02	104	22	3
Phorate-sulfoxide	0.02	115	8	3
Pirimiphos-methyl	1.53	103	3	3
Phorate-sulfon	0.02	111	3	3
Isofenphos	0.06	104	10	3
Chloorfenvinfos	0.03	102	2	3
Methidathion	0.06	102	4	3
Ethion	0.13	94	4	3
Triazophos	0.07	115	2	3
Phosmet	0.67	113	8	3
Phosalone	0.06	98	4	3
Azinphos-methyl	0.33	117	3	3

nd : not detectable

Table II. Recovery data of OP's added to different samples at the 10* LOD level.

Component	Spike level (mg/kg)	Recovery (%)	RSD (%)	n=
Demeton-S-methyl-sulfoxide	0.30	90	39	3
Dichlorvos	2.11	91	14	3
Methacrifos	0.42	96	12	3
Demeton-S-methyl	0.26	69	3	3
Phorate	0.36	73	22	3
Monocrotofos	0.42	25	11	3
Dimethoate	8.52	87	7	3
Diazinon	1.53	87	8	3
Disulfoton	0.21	71	3	3
Chloorpyrifos-methyl	6.64	92	5	3
Demeton-S-methyl-sulfon	0.25	103	8	3
Phorate-sulfoxide	0.30	89	4	3
Pyrimifos-methyl	19.12	94	4	3
Isofenfos	0.71	87	7	3
Chloorfenvinfos	0.39	91	3	3
Methidathion	0.76	88	4	3
Ethion	1.58	92	6	3
Triazofos	0.91	95	4	3
Phosmet	8.39	94	8	3
Phosalone	0.72	97	2	3
Azinfos-methyl	4.15	90	3	3

Table III. Concentration of OP's in analysed duplicate diet samples (mg/kg).

LOC-LIMS I.D.	Respondent I.D.	Azinphos-methyl	Chloorfen-vinfos	Chlorpyrifos-methyl	Demeton-S-methyl	Diazinon	Dichlorvos
96M3053	5	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3056	8	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3063	15	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3072	24	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3072 D		< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3076	28	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3080	32	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3085	37	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3097	49	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3105	57	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3109	61	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3109 D		< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3110	62	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3113	103	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3120	110	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3121	111	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3127	117	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3127 D		< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3132	122	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3139	129	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3140	130	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3143	133	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3143 D		< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3153	143	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04
96M3165	155	< 0.02	< 0.02	< 0.01	< 0.2	< 0.01	< 0.04

Table III, continued.

LOC-LIMS I.D.	Respondent I.D.	Dimethoate	Disulfoton	Ethion	Isofenphos	Methacrifos	Methidathion
96M3053	5	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3056	8	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3063	15	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3072	24	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3072 D		< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3076	28	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3080	32	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3085	37	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3097	49	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3105	57	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3109	61	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3109 D		< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3110	62	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3113	103	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3120	110	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3121	111	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3127	117	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3127 D		< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3132	122	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3139	129	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3140	130	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3143	133	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3143 D		< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3153	143	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01
96M3165	155	< 0.01	< 0.04	< 0.01	< 0.01	< 0.02	< 0.01

Table III, continued.

LOC-LIMS I.D.	Respondent I.D.	Monocroto-phos	Phorate	Phosalone	Phosmet	Pirimiphos-methyl	Triazophos
96M3053	5	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3056	8	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3063	15	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3072	24	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3072 D		< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3076	28	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3080	32	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3085	37	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3097	49	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3105	57	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3109	61	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3109 D		< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3110	62	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3113	103	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3120	110	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3121	111	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3127	117	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3127 D		< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3132	122	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3139	129	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3140	130	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3143	133	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3143 D		< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3153	143	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02
96M3165	155	< 0.1	< 0.06	< 0.02	< 0.01	< 0.01	< 0.02