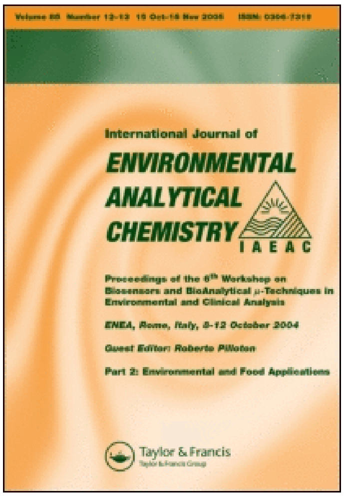

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EVALUATION OF THE FATE OF ALDICARB AND ITS METABOLITES IN ORANGES

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The accumulation, persistence and fate of systemic pesticide aldicarb was melencholy evaluated in orange crops. The concentration of this pesticide and its two toxic metabolites, aldicarb sulfoxide and aldicarb sulfone was determined in leaves, rind and pulp of three orange varieties (*Satsuma, Navelina* and *Clemetina de Nules*) and in the top soil of the orange groves. The groves were located in two different places in the Valencia Community (Spain). The analysis showed that the aldicarb concentration was lower than those of aldicarb sulfoxide and aldicarb sulfone. In all cases, the residues persisted at least 160 days in vegetable samples and between 157 and 227 days in soil samples. Residue concentrations measured in the soil samples were highly variable but a relation with the organic matter content can be observed. The residue levels found in vegetal products were higher in leaves than in rind, and in rind than in pulp. The maximum residue values were obtained between 47 and 70 days after the application. One hundred days after treatment (Security period) the residue levels of total fruit were lower than the maximum residue level of 0.2 mg/kg established by law.

KEY WORDS: Aldicarb, metabolites, oranges, soil, persistence, gas chromatography.

INTRODUCTION

Aldicarb [2-methyl-2-(methylthio)propanal, O-[(methylamino) carbonyl] oxime] is marketed as a 10% granular formulation under the trade name Temik. This broad-spectrum soil-applied pesticide is registered in Spain for the control of nematodes, mites, aphids and a variety of other pests in several crops including citrus, potatoes and ornamentals[1].

Since the introduction of aldicarb for agricultural use many researchers have conducted laboratory and field studies to determine the degradation pathways of this pesticide in soil[2–5]. These studies demonstrate that the aldicarb in soils is oxidized in 7–10 days to aldicarb sulfoxide and then more slowly to aldicarb sulfone. Both aldicarb sulfoxide and aldicarb sulfone are more toxic than the parent compound. They also showed that aldicarb and its metabolites in moist soil translocated upward relative to the capillary action of water and that the movement rate and distance increased with the increase in soil moisture.

Other research[6–8] found groundwater contamination by aldicarb resulting from normal agricultural use. Because of the high water solubility of the pesticide and the porosity of the soil, the chemical might leach out of the root zone into the underlaying aquifer.

The aldicarb and its metabolites were absorbed from the soil by the plants where the metabolism and fate is followed. As a result of the large migration capacity of these compounds in the environment, the concentrations reached in vegetables are highly variable. Researchers have also studied the absorption, metabolism and elimination of aldicarb and its metabolites in several crops, like oranges[9–11], sugar beets[12,13], watermelons[14,15], lemons[16,17] and potatoes[18–20]. These studies have demonstrated that the environment has a strong influence on accumulation and metabolism. Laboratory model validation is important. Field experiments are necessary to ensure that the laboratory data are adequate and that the models accurately depict the field behavior of a chemical. Field exposure may show that a factor not monitored in the laboratory is actually significant.

The aim of the present study is monitor the movement and degradation of the pesticide aldicarb and its two principal toxic metabolites in the fruits and leaves of three different orange varieties *Clementina de Nules, Satsuma* and *Navelina* and in the soils of the corresponding orange groves, using an analytical method validated in a previous work[21].

MATERIALS AND METHOD

Experimental site

The sampling points are located in three orange groves situated in two different places on the coast of the Valencia Community (Spain). The Satsuma crop is located in Torreblanca and the Navelina and Clementina de Nules crops are found in Carcaixent. The fields had not previously been treated with aldicarb.

Some physical and chemical characteristics, the soil type according to the FAO[22] classification for the soil of each citrus crop are reported in Table 1.

Table 1 Soil properties at the three orange crops.

	Navelina	*Clementina de Nules*	*Satsuma*
Soil	*Luvic Calcisol*	*Arenosol*	*Chromic Luvisol*
Colour (Munsell)	*Brown 7.5YR 5/4*	*Yellowish red 5YR 5/6*	*Redish brow 2.5YR 4/4*
Texture:			
% sand	40	92	56.4
% silt	40	6	17.6
% clay	20	2	20
classification	clayey loam	sandy	clayey loam
pH (H_2O)	8.05	8.10	8.15
% organic matter	1.00	1.24	0.96
P assim.[a] (mg/kg)	29	9	80
K assim.[b] (mg/kg)	180	50	441
$CaCO_3$ (%)	40.80	2.95	21.75
EC[c] ($S.m^{-2}$)	0.162	0.132	0.318

[a] assimilable phosphorus
[b] assimilable potassium

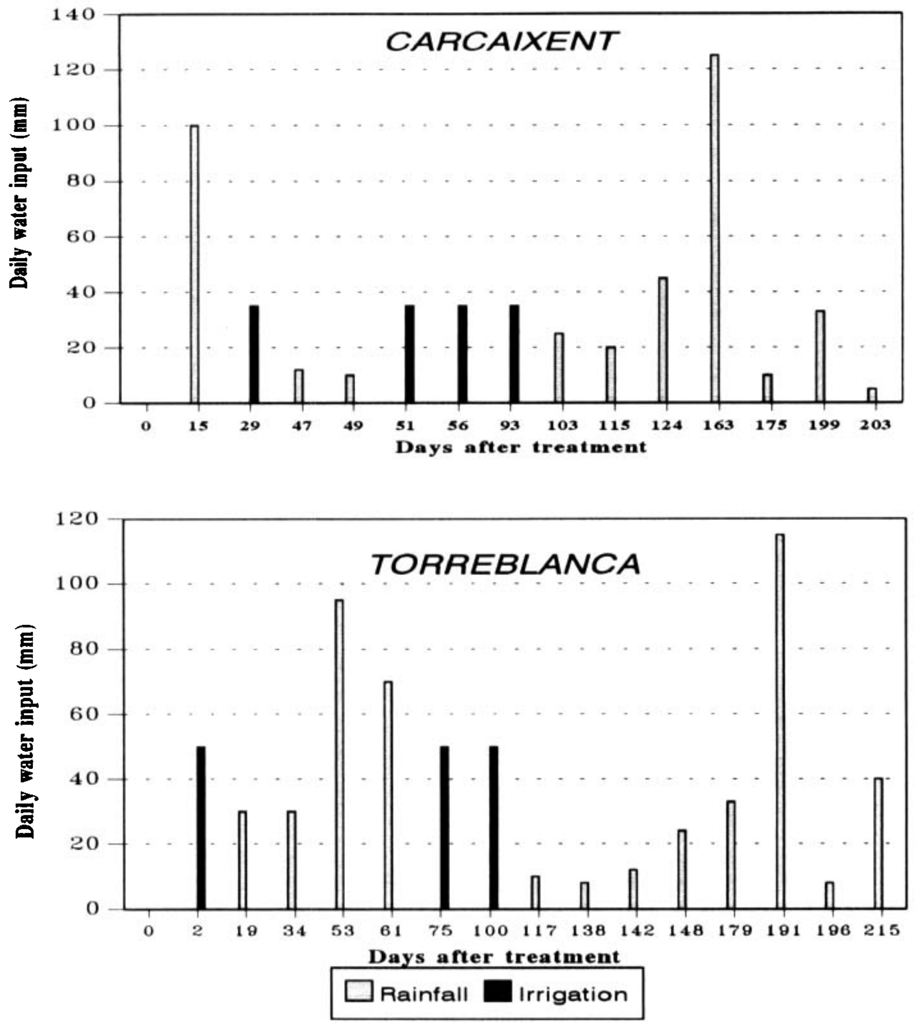

Figure 1 Daily water input at the two field sites.

The orange groves are formed by 6 year-old trees, with a height of 2–3 m and a trunk diameter of 1.5–2.5 m.

The daily water input by rain and irrigation during the studied period on each site is shown in Figure 1. Watering was carried out using the traditional flood-irrigation system.

Treatment

Aldicarb was applied in Torreblanca on 11 September 1991, as a 150 g·kg^{-1} granular material at a rate of 10 kg of a.i. ·ha^{-1}. Four days late, aldicarb was applied to the Carcaixent sites using the same application equipment and at the same rate. At each site, the granules were incorporated into the top 15 cm of soil in a 50 cm wide band along a row at a distance of 1.5 m from each tree trunk (under the canopy).

Sampling

All the samples from the Torreblanca site were collected prior to the treatment and 14, 34, 51, 68, 91, 113, 135 and 157 days after aldicarb treatment. Sampling times at the Carcaixent location were 1 day before and 19, 36, 58, 73, 95, 119, 139 and 165 days after application. In both sites, two more soil samples were collected at 187 and 227 days after treatment.

The soil samples were take at a depth of 15 cm and at a distance of 2.5 m from the trunk of the tree in a semi-circle parallel to the points at which the product was applied. Orange fruits and leaves were picked homogeneously (ca. 100 leaves and 4 fruits from each tree).

Samples were stored in a glass container in the refrigerator until the analysis (about 48 hours). Soil samples were pulverized in a mortar. The fruits were peeled. The leaves, the rind and the pulp were chopped in a Moulinex food processor.

Procedure

The soil (100 g) added to a water/acetone mixture was shaken by sonication. The extract was filtered, concentrated and partitioned with chloroform as previously described[17]. The leaves (50 g), rind (25g) and pulp (100 g) were shaken in the same way. Before the partitioning with chloroform, the extracts were cleaned-up by acidification and partitioned with petroleum ether. The chloroform solution was dried over anhydrous Na_2SO_4 and concentrated to 1 mL.

Aldicarb, aldicarb sulfoxide and aldicarb sulfone were analysed using a Konik 2000-C gas chromatograph, equipped with a nitrogen phosphorus detector (NPD) and 2 m × 4 mm i.d. glass column packed with 6% QF-1 + 4% SE-30 on 100/120 mesh Chromosorb Q.

Injector and detector temperatures were 145 and 200°C, respectively. The oven temperature was programmed starting at 130°C for 5 min and then increasing 30°C min^{-1} to 170°C where it was maintained 8.5 min[21].

RESULTS AND DISCUSSION

Extraction procedure and chromatographic separation

For determination of the efficiency of the analytical method, control samples of soil, pulp and rind were fortified with 0.03 mg/kg of aldicarb and its sulfone and 0.06 mg/kg of aldicarb sulfoxide prior to the extraction and the percent of recovery and relative standard deviation were calculated. The detection limit, determined as three times the peak-to-peak noise level was also calculate. All the data are shown in Table 2.

Table 2 Analytical results of the method.

	aldicarb		*aldicarb sulfoxide*		*aldicarb sulfone*	
Matrix	*($x^1 \pm R.S.D^2$)%*	*LOD^3 (mg/kg)*	*($x^1 \pm R.S.D^2$)%*	*LOD^3 (mg/kg)*	*($x^1 \pm R.S.D^2$)%*	*LOD^3 (mg/kg)*
Pulp	75 ± 12	0.003	100 ± 11	0.004	93 ± 11	0.002
Rind	75 ± 13	0.014	78 ± 11	0.025	89 ± 9	0.020
Leaves	76 ± 10	0.013	81 ± 11	0.020	90 ± 8	0.010
Soil	76 ± 8	0.003	75 ± 11	0.006	92 ± 10	0.002

[1]x: percentage of recovery
[2]R.S.D.: relative standard deviation
[3]LOD: limit of detection

Figure 2 shows a chromatogram of (A) blank (B) non-spiked rind extract, (C) rind extract spiked with the three compounds and (D) real rind sample extract containing the three compounds. The extraction procedure removes most the interferences from the matrix. The peaks corresponding to the three carbamates presented correct peak shape and good reproducibility which allow a correct quantification.

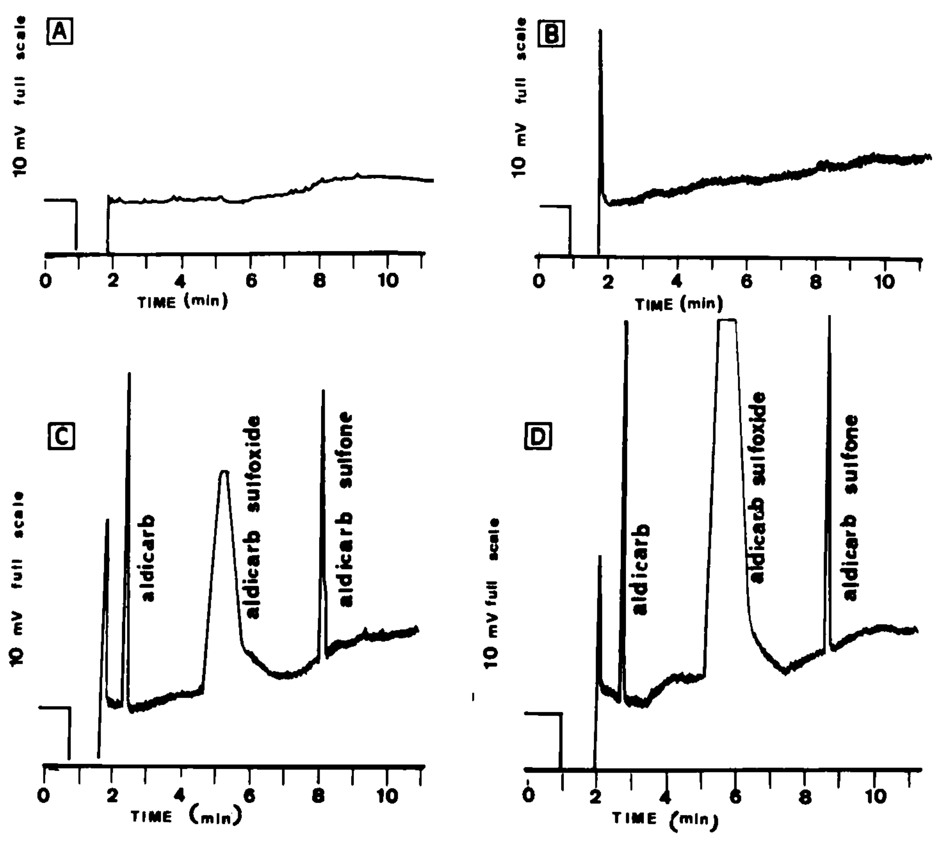

Figure 2 Packed column gas chromatography of (A) Blank, (B) unspiked rind extract, (C) extract from a spiked rind with 0.02 mg/kg for aldicarb and its sulfone and 0.04 mg/kg of rind for the sulfoxide and (D) real rind sample containing 0.03 mg/kg of aldicarb, 0.50 mg/kg of aldicarb sulfoxide and 0.06 of aldicarb sulfone.

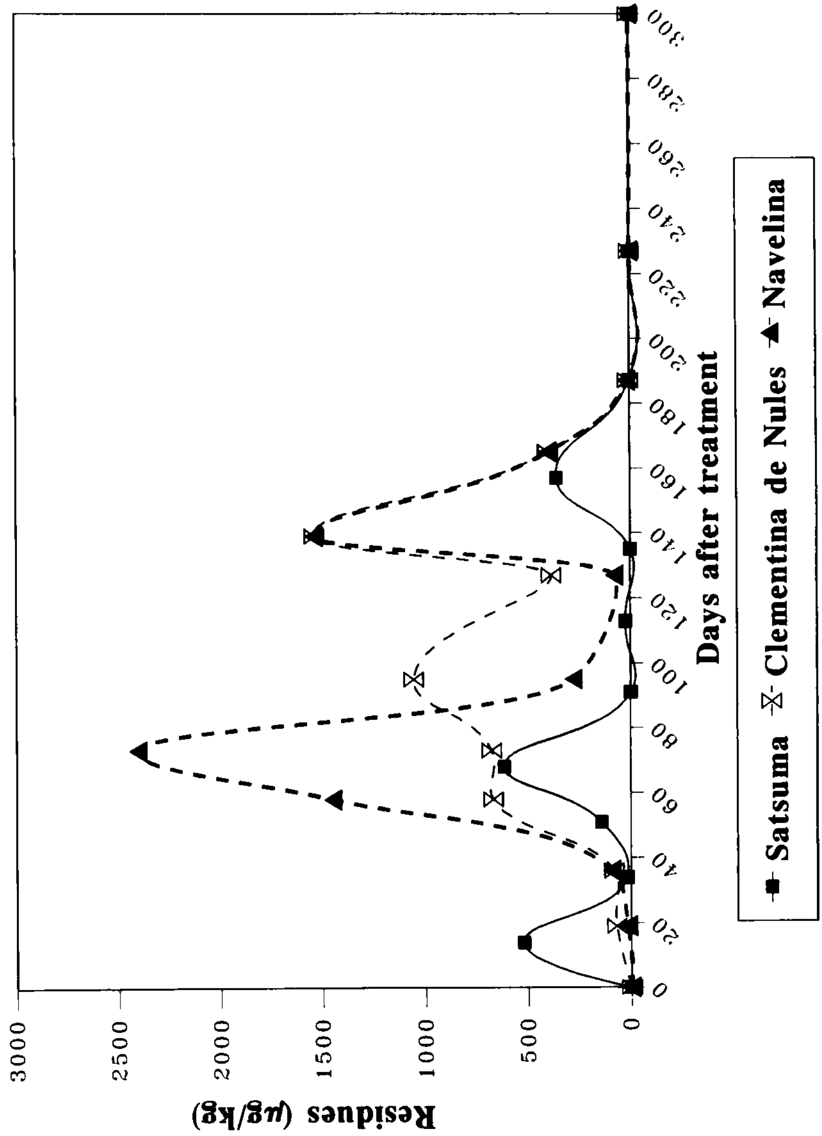

Figure 3 Total carbamate residues found in the top soil samples of the three varieties.

Soil samples

Figure 3 shows the total carbamate residues in the soils treated with aldicarb. In the three soils the carbamate residues persist more than 227 days. The results of these experiment were inconclusive. This variation is probably due to the fact that the aldicarb application points were not uniformly spaced.

Many factors are involved in the degradation rate of aldicarb in soils: temperature, pH, microbial oxidation in the surface soil, permeable soils and irrigation. The data obtained by other authors are as irregular as the results of this study. Maitlen and Powell[2] took soil samples at two depths to determine whether the residues were greater in the top soil or at lower depths. Residues were found in samples from the top and from the deeper-lying soils.

Jones[4] note that the variability in the total carbamate residue levels yielded coefficients of variation ranging from 80 to 210%.

Soil samples probably should have been taken from greater depths, as researchers do not entirely agree on the degree of movement of aldicarb and its metabolites in soil. Wyman and Jensen[3] found than there was a little lateral movement of residues in soil in irrigated and non-irrigated fields and that the residues moved up and down (leaching).

Vegetables samples

There were detectable residues of aldicarb and its sulfoxide and sulfone metabolites in all the vegetable samples of the crops treated with Temik.

Figure 4 shows the persistence curves obtained by direct interpolation of the points for aldicarb, aldicarb sulfoxide and aldicarb sulfone, as well as the curve of total aldicarb residues (sum of the three compounds expressed as aldicarb) in (A) pulp, (B) rind and (C) leaves of the variety Navelina.

Figure 5 and 6 show the same curves for the varieties Clementina of Nules and Satsuma, respectively.

In the first sample analyzed the concentrations of aldicarb sulfoxide and aldicarb sulfone were higher than the concentration of aldicarb. This indicates the rapidity of transformation of the aldicarb into its oxidation products.

The residue values are in all cases higher in leaves than in rind, and in rind than in pulp. This corroborates the results obtained in oranges of the Valencia Late variety by Iwata *et al.*[9] who, after comparing the results of 4 plots treated with increasing doses, always detected higher residue levels in leave that in rind and in rind than in pulp. This also agrees with the data of a previous study[11] in which the persistence of aldicarb and its toxic metabolites was determined in a crop of oranges of the Valencia Late variety.

Maximum residue values in the leaves are observed approximately 35 days after the application of Temik and are maintained without much variation until day 90. Expressed as total residue these values fluctuate between 7 and 5 mg of aldicarb/kg of leaf. Being the highest value for the Clementina variety and the lowest for the Satsuma.

The maximum concentration in rind for the variety Clementina de Nules is 1.226 mg/kg and appears 73 days after application. For the variety Navelina, it is 0.568 g/kg and appears

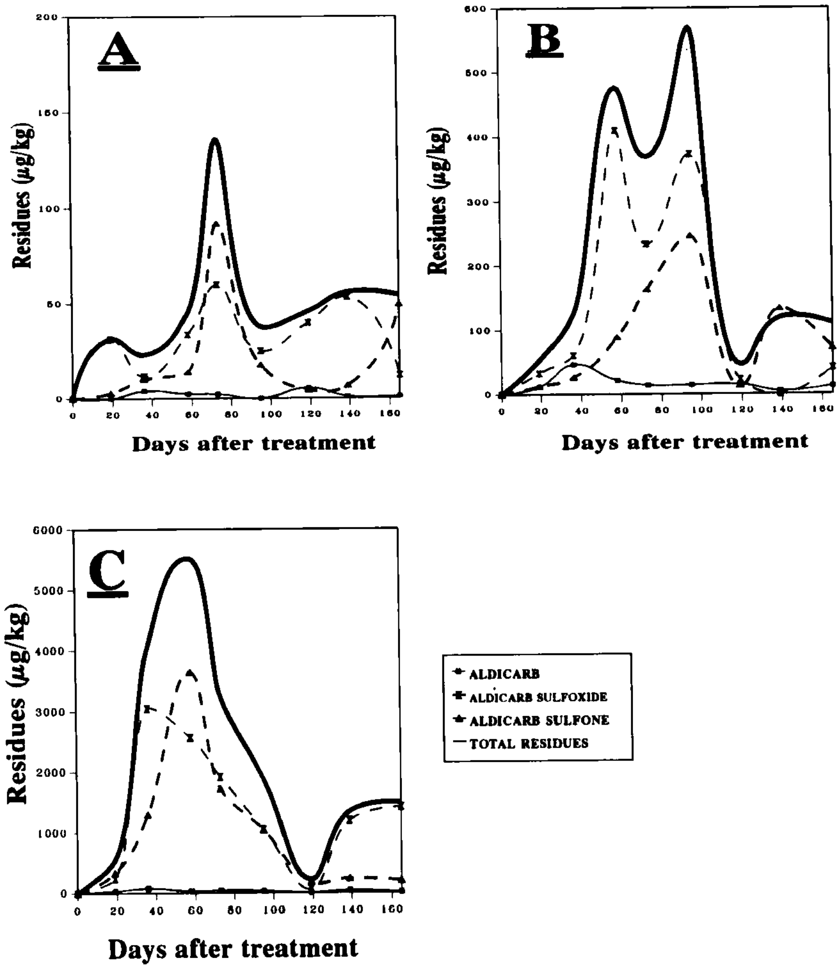

Figure 4 Persistence curves obtained in (A) pulp, (B) rind and (C) leaves of the variety Navelina.

95 days after application, but residue values of 0.475 mg/kg are found from day 58 after soil treatment. In the variety Satsuma, the maximum residue in rind is 0.837 mg/kg and appears 34 days after the application; After 91 days this value is 0.319 mg/kg and diminishes abruptly after 116 days to 0.044 mg/kg.

The highest quantity of residues in pulp appears on day 90 in the varieties Satsuma and Navelina with amounts of 0.808 mg/kg and 0.136 mg/kg, respectively, and a little before day 73 in Clementina of Nules, where a value of 0.455 mg/kg is reached.

Iwata *et al.*[9] detected the maximum values in fruit and leaves between days 45 and 65, with concentrations of 0.25 mg/kg in rind, 0.05 mg/kg in pulp and 12 mg/kg in leaf.

Picó *et al.*[11] found the highest levels of residues 90 days after the soil treatment. The concentration was 0.112 mg of aldicarb /kg in pulp, 0.298 mg /kg in rind and 7.980 in leaf.

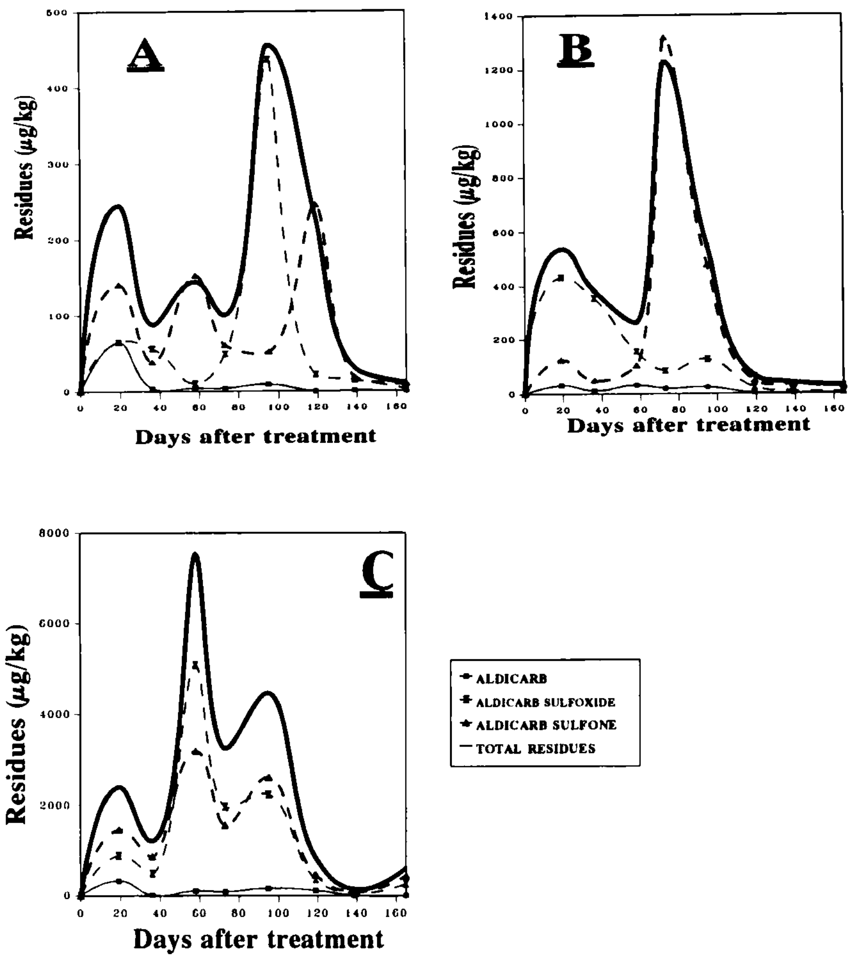

Figure 5 Persistence curves obtained in (A) pulp, (B) rind and (C) eaves of the variety Clementina de Nules.

Although in the same interval of time, the highest residues appeared earlier and were somewhat lower in the work of Iwata *et al.*[9], this could be due to the use of a system of continuous watering (leak) front to the discontinuous system utilized in this work.

The data shown by Picó *et al.*[11] are similar at those obtained in this study, since the study was carried out in it same zone, although the maximum levels appear later. This is probably due to the fact that the study was carried out in a much drier year.

The data do not show a clear relationship between the humidity and the concentration of residues throughout the study. However, more elevated levels are observed after the crops have been thoroughly watered.

The values exposed by Batista *et al.*[10] for aldicarb in Valencia and Navel Late oranges employing doses of 20 and 40 grams of active ingredient per plant oscillate between 0.03

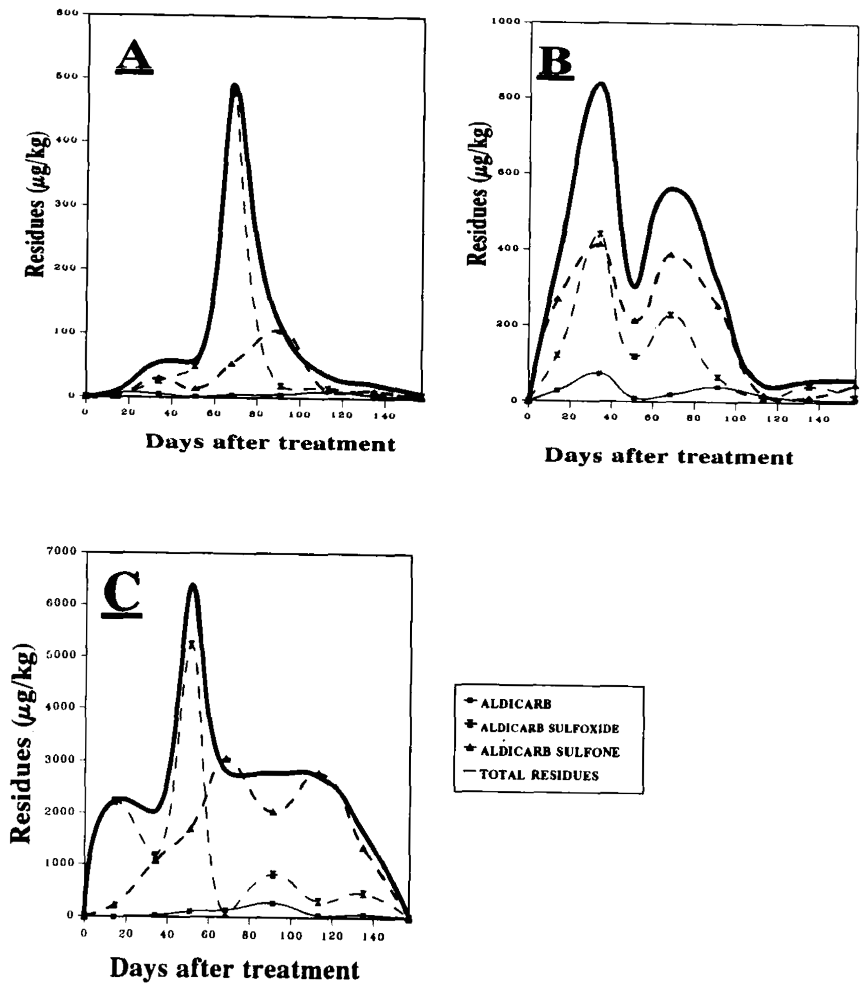

Figure 6 Persistence curves obtained in (A) pulp, (B) rind and (C) leaves of the variety Satsuma.

mg/kg to the sixty days after the application with the dose of 20 g and 0.13 twenty days after treatment with the dose of 40 g. These quantities are lower, but not enough data are available to define a possible cause.

Figure 7 illustrates the curves of total residues (sum of the residuals of aldicarb, aldicarb sulfoxide and aldicarb sulfone expressed as aldicarb) obtained for the entire fruit in the three varieties of oranges.

The highest quantity of pesticide is observed in the fruits of the Satsuma variety, followed by Clementina de Nules and Navelina.

The legislation set a residue limit of 0.20 mg/kg in total fruit expressed as aldicarb for aldicarb and its metabolites in oranges.

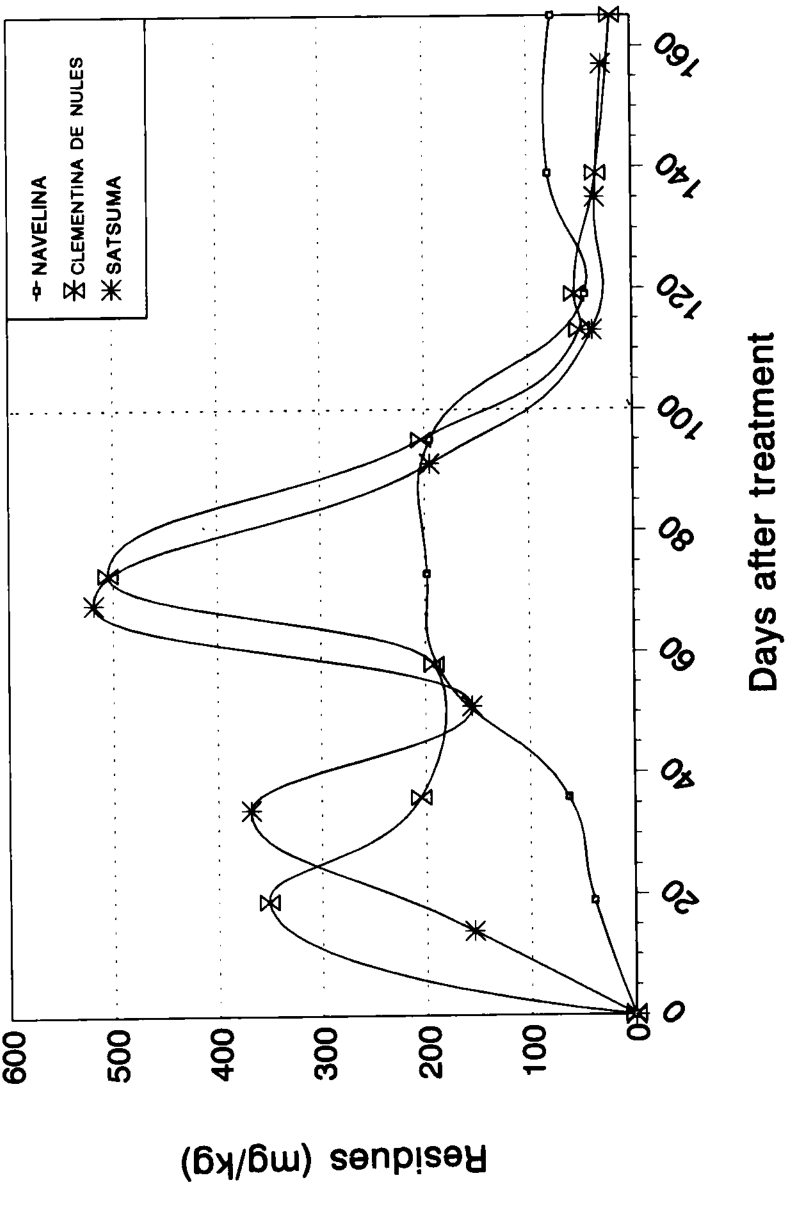

Figure 7 Persistence curves of the total aldicarb in entire fruit of the three varieties.

Nineteen days after the application, this limit has already been surpassed in Clementina de Nules although the values falls and rises again between days 75 and 93.

The Satsuma variety passes this limit from day 34 after the application of the aldicarb until day 68.

The Navelina variety, does not pass the maximum limits in any case. However, the descent in the concentration of residuals is much smaller that in the other cases.

This work demonstrates that Temik application at a rate recommended by the marketers, does not leave quantities of residues higher than the Legislated Tolerances after the Safety period of 100 days in fields that have not been treated with it before. However enough aldicarb persisted to produce detectable residues five month after the treatment in crops and 7 month after treatment in soil.

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