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Kinetics of Maneb Residues Reduction by Washing and Peeling in Three Varieties of Open Air Stored Tomatoes

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Abstract: Maneb (Plantineb 80) is a fungicide widely use in the control of tomato diseases in Ngaoundéré. Its use is known to be abusive. The present study was carried out in tomatoes cultivated during interseasonal period (September-November) and harvested in January. The objectives are to assess the rate of mane b decay in raw commodities stored in open air during 12 days; to determine the effect of peeling and washing on the rate of decrease of mane b residues in three tomatoes varieties: Roma VF, Rio Grande and Rossol VFN. The colorimetric method was used to determine the CS₂ concentration at 302 nm wave length. As results, reduction of 92% (max.) from initial mane b residues occurred after 12 days of storage; peeling decreases more residues (max. 69%) than running tap water washing (max. 38%).

Key words: Open air, washing, peeling, mane b, varieties, tomatoes, kinetics

INTRODUCTION

Dithiocarbamates belongs to pesticide family widely used in the control of vegetable diseases. They may be used as fungicides, herbicides or insecticides (EPA, 2001). They are divided in to 3 subclasses: Ethylene bis-Dithiocarbamates (EBDC) such as mane b and mancozeb, DimethylDithiocarbamates (DMDTC) like ziram and ferbam and Mono-Methyl-Dithiocarbamates (e.g., metam sodium) (EPA, 2001). Another common mechanism of toxicity is the regeneration of CS₂ and Ethylene Thiourea; which have neuropathic, teratogenic and antithyroidic properties (EXTONET, 1993).

In Ngaoundéré town, country men practice market-gardening. The production of three main varieties of tomatoes (Rio Grande, Roma VF and rossol VFN) spreads out throughout the year. The control of tomatoes diseases is done by a homologated pesticide known as mane b at more than 93% (MINAGRI, 2002). This fungicide PLANTINEB 80 as trade name is known to be abusively used (Sonchieu, 2004; CPI, 2004). The misuse is characterized by: repeated sprayings, high doses and high concentration employed. The time lapse between last spraying and harvest is very short (0 to 3 days) and treatments begin early and end lately. These factors induce the important remainder of mane b residues in the raw harvested fruits (Ismene *et al.*, 1993). Despite this risk, pesticides residues control in food to consume or to be marketed in the country is still absent.

In this region, consumers have the habits to eat ripe raw fruits after washing or not and in cooked meal. Some people buy tomatoes and store in open air for a time. In the other hand, sometime, the producers, due to the rambling of animals, harvest raw-fruits and store them in open air at room temperature before sale.

The objectives of this study are to determine whether air exposition has some impacts in mane b residues degradation after washing or not before storage; also to assess the influence of peeling and washing after this mode of conservation in the above cited tomatoes varieties.

MATERIALS AND METHODS

Origin, sampling and treatment of samples: The tomatoes fruits varieties Rio Grande, Roma VF and Rossol VFN are used. These tomatoes planted in September 2003, have been harvested in the agricultural farms where spraying has been done by the mane b (PLANTINEB 80). The spraying has been done according to farmer's habits (4 days intervals with 139 mg L⁻¹ and 2500 l ha⁻¹). At the final synchronized spraying, at the same conditions, the initial amount of mane b residues is determined for each variety. After the final synchronized spraying (noted day zero), 7 kg of ripe tomatoes are sampled, wrapped in 1 kg mass in the polyethylene bag and immediately forwarded in the laboratory for conservation.

Treatment of samples

- Storage and sampling: It's done at room temperature ($\approx 25^{\circ}\text{C}$) during 12 days; the sampling for analysis is done every 2 days for each variety
- Washing: It was done by running tape water during 2 min
- Peeling: sheet of ripe fruit is separated from the fruit by nipper after scission with the knife
- The blending is done by the small blender, ROBOT.

One kilogram of the sample is blended and 250 g are sampled for the extraction.

Extraction and determination: The determination of EBDC in general is done after CS_2 regeneration (FAO, 1995). In the case of this study, method described by Henriett *et al.* (1980) and modified by Schwack *et al.* (1999) has been used. The concentrated sulphuric acid is used for the CS_2 regeneration and released by the plumbic acetate (1%) after heating. The recuperation is done with the mixed solution of methanol (98%) and potassium hydroxide (1%) (3:4).

After obtaining CS_2 , the concentration is defined by spectrophotometric method with Spectronic Genesys™ 2PC apparatus at 302 nm wave length. The results giving here are the mean of 2 analyses.

RESULTS

Impact of washing and peeling on maneb residues decreases during tomatoes air exposition

Roma VF variety: Figure 1a shows the effect of washing and peeling on maneb residues is at a decrease. The diagrams representing maneb reduction in washed tomatoes are about the same in unwashed one. This is characterized by the Fig. 1b, where regression curves representating the both varieties of tomatoes are almost similar: $Y = -0.3825X + 10.612$ and $Y = -0.3732x + 10.272$ for unwashed and washed tomatoes respectively. The percent of reduction varies from 2 to 5%.

Meanwhile, peeling regression curve shows high degradation slope: $Y = -0.497X + 9.4689$. The percentage of reduction by peeling ranges from 12 to 41%.

Rio grande variety: The diagrams presented in Fig. 2a and b show the variation of maneb residues levels after washing and peeling. According to these diagrams, washing reduce the amount of maneb residues. This is characterized by the regression curves with $Y = -0.4604X + 8.2907$ for washed tomatoes and $Y = -0.3318X + 9.1264$ for the unwashed one. On the other hand, peeling removes

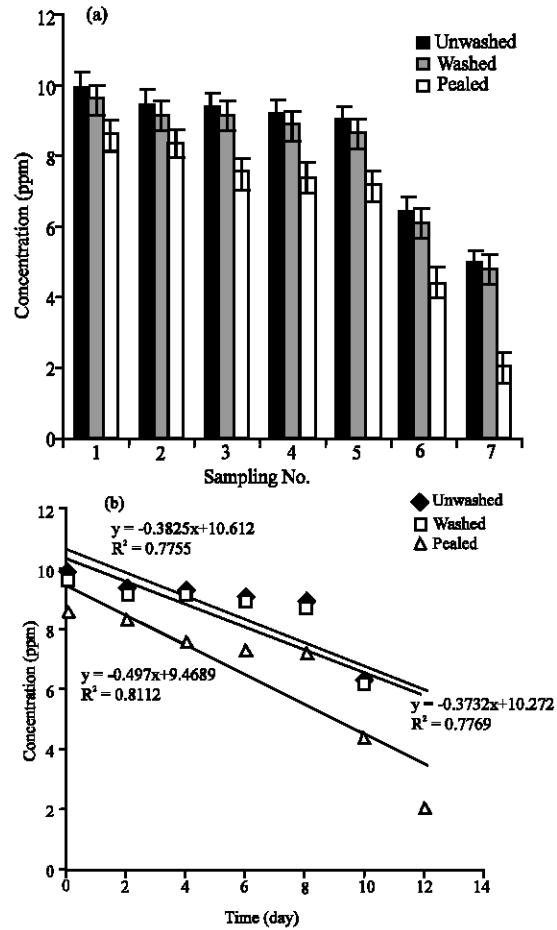


Fig. 1: Impact of washing and peeling on maneb on Roma VF tomato variety during open air storage. a): Compared diagram and b): Regression curve

considerably the residues than washing. This removal rate ranges from 46 to 69% for the former and from 8 to 38% for the later. The representative peeling regression curve has fewer slopes: $Y = -0.2616 X + 4.5954$.

Rossol VFN variety: Maneb residues decrease after washing it varies from 14 to 22%. Figure 3a represents these variations. Figure 3b presents curves regression with $Y = -0.389X + 9.287$ and $Y = -0.338X + 7.6625$ before washing and after washing respectively. The third curve represents peeling effect: $Y = -0.4459X + 7.0654$ is the corresponding equation. The diagram of Fig. 3a shows that, peeling has more effect, reducing the total amount in wide range: 19 to 64%.

Comparative study of unwashing, washing and peeling on maneb residues decrease in open air stored tomatoes

Unwashing: Concentrations presented on Table 1 show variation of degradation in different varieties. Although

Table 1: Effect of time, peeling and washing on maneb residues reduction in open air stored tomatoes
Concentration (mg kg⁻¹)

Time (Day)	0	2	4	6	8	10	12
Var. Rossol VFN:							
Unwashed	9.3±0.5 (0)	7.9±1.0 (15)	7.4±0.1 (20)	7.0±0.2 (25)	6.4±0.2 (31)	5.7±2.0 (39)	4.5±0.2 (52)
Washed	7.7±0.1 [17]	6.6±0.3 (14)	6.3±2.0 (19)	6.1±0.5 (22)	5.0±0.2 (35)	4.8±0.6 (37)	3.5±1.0 (54)
Peeled	6.3±0.3 (0) [33]	6.4±0.3 (2)* [19]	5.9±1.3 (7) [21]	5.8±2.0 (8) [18]	2.3±0.6 (63) [64]	2.1±0.4 (68) [35]	2.0±0.2 (69) [58]
Var. Roma VF:							
Unwashed	9.9±1.6 (0)	9.4±0.7 (17)	9.3±0.3 (18)	9.2±0.2 (19)	9.0±0.7 (21)	6.4±1.7 (45)	4.9±0.5 (56)
Washed	9.6±1.6 (0)	9.1±1.7 (20)	9.1±2.1 (20)	8.9±0.2 (21)	8.6±1.7 (24)	6.1±0.7 (46)	4.8±1.6 (57)
Peeled	8.6±1.0 (0) [4]	8.3±0.7 (11) [3]	7.5±0.9 (20) [2]	7.4±1.3 (21) [3]	7.1±0.9 (24) [4]	4.2±0.9 (55) [6]	2.0±0.2 (78) [2]
Var. Rio grande:							
Unwashed	9.5±1.31 (0)	8.1±0.7 (14)	7.7±1.4 (18)	7.1±1.2 (25)	6.6±1.9 (30)	5.8±0.7 (38)	4.78±0.9 (49)
Washed	8.72±1.0 (0)	7.3±1.2 (16)	6.1±0.3 (30)	5.9±0.7 (33)	4.3±0.2 (50)	3.64±1.0 (58)	2.9±0.2 (66)
Peeled	4.5±0.5 (0) [53]	4.3±0.7 (4) [47]	3.5±0.3 (30) [21]	2.8±0.7 (37) [55]	2.5±0.2 (43) [60]	2.0±0.2 (55) [66]	1.5±0.3 (67) [69]

() = Percentage of reduction by time, [] = Percentage of reduction by peeling or washing, * = Minor increase observed

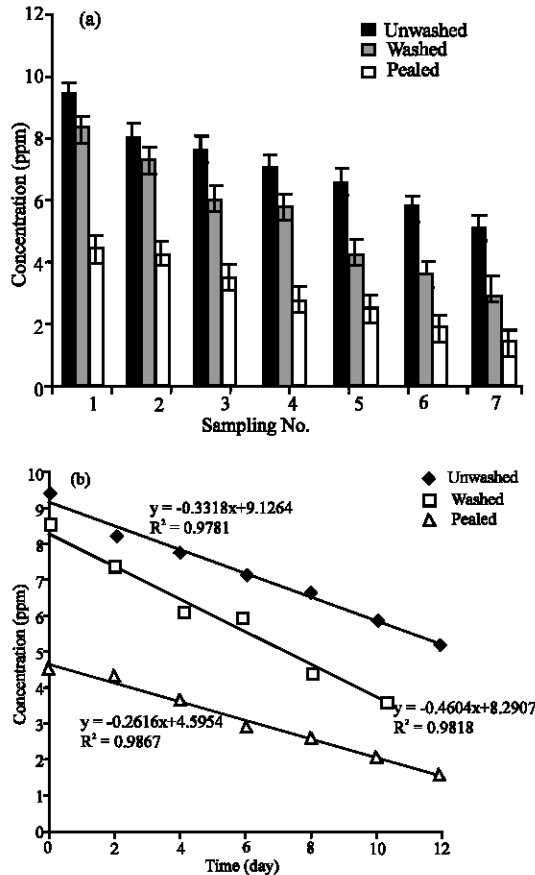


Fig. 2: Impact of washing and peeling on maneb in Rio grande tomato variety during open air storage. a): Compared diagram and b): Regression curve

the initial concentration is about the same, the storage time influences the rate of decay. In Roma VF variety, degradation is slower during 8 first days of storage.

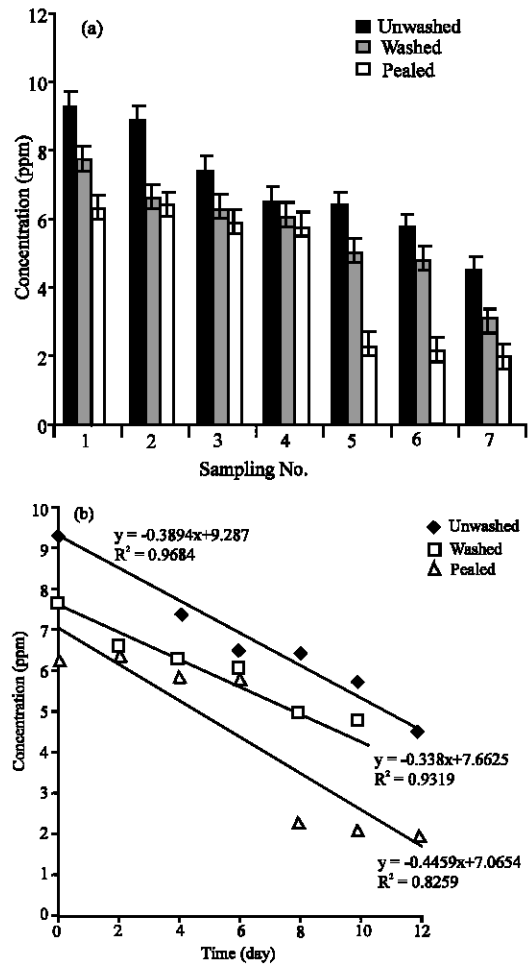


Fig. 3: Impact of washing and peeling on maneb in Rossol VFN tomato variety during open air storage. a): Compared diagram and b): Regression curve

Where as, Rossol VFN variety presents more rapid degradation. Finally, in Rio Grande variety degradation is about the same as Rossol VFN variety. At the two last day of storage (10th to 12th), all concentrations are sensitively the same; but slopes of regression are still different.

Washing: Table 1 shows evolution of different concentrations affected by washing during storage. During which, maneb residues degradation between Rio Grande and Rossol VFN is sensitively the same. Where as reduction in Roma VF variety remains more constant. Despite this behaviour, at the last day (12th) of storage, all concentrations are more near. Washing affects concentrations by reducing from 2 to 38%.

Peeling: There are more differences in concentration between varieties (Table 1). Degradation in all samples is so different before 8 days. After which, concentrations between Rio Grande and Rossol VFN are almost similar. At the end of the storage, there is confusion in all three concentrations. Peeling maximum effect varies from variety to other day 8 to Rossol VFN and day 12 for Roma VF and Rio grande.

DISCUSSION

Maneb residues concentrations are expressed in term of CS₂ concentrations (FAO, 1996). The duration between applications varies from 3 to 10 days under conditions of normal use (Fournier, 1988). Therefore, at harvest, the residue level must be less than the Maximal Residue Limits (MLR) established at 5 ppm (FAO, 1996), 10 days after final application. Then after final application, harvest and storage in the open air, degradation is accelerated. The long half-life observed is due to the high initial concentration observed at day 0 (Ismene *et al.*, 1993; Matthews *et al.*, 2003; Mara *et al.*, 2003). These differences observed in the different varieties of commodities are based on their aptitude to maintain maneb in the pericarp or in the inner part (Gunther and Blinn, 1970).

The amount of decrease of maneb residues could be due to its instability in air (oxidation) (EXTOXNET, 1993). On the other hand, maturation phenomenon accelerates maneb degradation because, which is itself accelerated after harvesting of fruit (Gautier, 1993).

The washing resistance presented by Roma VF variety may be due to the presence of wax; compared to the green bean, which releases more residues by washing (Gunther and Blinn, 1970; Fontem and Bouda, 1998).

Peeling removes more residues than washing. This behavior may be due to the accumulation of residues in the pericarp observed by some authors (Gunther and Blinn, 1970; Fontem and Bouda, 1998; Sgarbiero *et al.*, 2003). The penetration of maneb as well as pyrimiphos-methyl (Sgarbiero *et al.*, 2003), is indicated by a slight increase of concentration at day 2 for Rossol VFN. According to Gunther and Blinn, 1970, due to the movement of pesticides in foodstuffs, peeling removes residues more quickly with time than washing. Meanwhile, washing removes more residues compared to unwashed tomatoes. This reduction is so high if a detergent is added (Abou-Arab, 1999; Radwan *et al.*, 2005).

The storage effect observed in this study has already been evoked both in cereal grains and vegetables (Holland *et al.*, 1994). Therefore, open air storage presents less obstacles for population in developing countries and is obviously correlated to environmental factors such as temperature, aeration, But this degradation yields a degradation product (ETU) which is more stable and more toxic than the parent compound (EPA, 2001). Then, simultaneous analysis should permit to well appreciate risk of relative intoxication.

This investigation argues with previous observations on pesticides degradation during conservation or cultivation. Theses concentrations are the results of misuse of pesticides practiced in the region (Sonchieu, 2004) and in developing countries in general (Matthews, 2003).

In all cases, peeling removes significantly maneb residues. But this result shows that Rio Grande variety concentrates more residues than others on its pericarp. The rapid decrease of maneb residues should be attributed to maneb movement in the fruit: from internal part (endocarp) to external part (pericarp) which contains much waxes (Adrian and Potus, 1995). However, this practice should not be recommended because fruit pericarp contains high amounts of carotene; a substance known to be deficient in the region (40.5%) (Côme and Corbineau, 1999; Anonymous, 2001). Maneb is then a surface pesticide.

Storage for 12 days conveniently preserved the quality of the fruits. It is concluded that this mode of storage may be recommended to reduce maneb residues in the tomato fruit; of course is considered as a procedure for the non-biological detoxication of pesticides, as those enumerated by Marshall (1978) and Radwan *et al.* (2005).

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