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Original scientific paper

Impact of water quality on pesticides and fertilizer compatibility

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SUMMARY

Mixtures of two or more pesticides are very common in contemporary agriculture. However, changes in their efficacy or biological activity, such as synergism and antagonism, phytotoxicity, persistence, toxicity to non-target organisms, may occur as a consequence. This study was conducted in order to evaluate the compatibility of insecticides (cyantraniliprole – Exirel, chlorantraniliprole – Coragen 20 SC), a fungicide (captan – Merpan 50 WP) and a foliar fertilizer (Folia Stim Mix TE), as well their mixtures, in spray liquids, depending on water quality (well water from two locations in Serbia – Mala Remeta and Čerević). These products are used to control the most significant peach pests, and as an additional source of nutrients. Water analysis (pH, hardness, electroconductivity, chloride, nitrate, nitrite, ammonia, calcium and iron content) and tests of physico-chemical properties of the spray liquids (pH, suspensibility, dispersibility, surface tension, and electroconductivity) were performed in a laboratory experiment according to standard methods. The physico-chemical properties of the liquids changed depending on water quality and components incorporated in the mixture. However, all tested spray liquids showed consistency and compatibility over a period of 24 hours.

Keywords: pesticides, fertilizer, mixture, water quality, physico-chemical properties, compatibility

INTRODUCTION

Chemical control is the most important tool in integrated pest management (IPM) because it is time-saving, accessible, and often low-cost when appropriately applied (Castro, 2009). Mixtures of plant protection products (PPPs) are commonly and intensively used for broadening the spectrum of activity, slowing down or delaying the appearance of resistant populations, etc., all for the ultimate goal of increasing yield and ensuring high quality of agricultural products. Therefore, they are also essential for resistance management programs. However, inappropriate chemical control can cause irreversible environmental and economic impact (Moraes et al., 2019), e.g. change the efficacy or biological activity (synergism and antagonism, phytotoxicity or persistence). The commonest negative effect on treated plants is phytotoxicity (Vuković et al., 2014). It occurs as temporary or permanent damage of vegetative/generative organs of crops and non-target plants, slows down or completely stops germination, and causes physiological and morphological changes. Phytotoxicity can occur as a result of simultaneous application of two or more PPPs, which are normally used for different target purposes, or due to double amounts of non-pesticidal components (solvents, wetters, emulsifiers, etc.). The main factors that influence phytotoxicity are water characteristics (pH, temperature, hardness), plant species, the sensitivity of varieties and the growth stage of plants (Vuković, et al., 2014). It is also important to note that pesticide mixtures can be highly toxic to non-target species, such as aquatic organisms and mammals (Mihajlović et al., 2019).

This study is based on previous knowledge that the quality of water used in plant protection affects the physico-chemical and biological properties of fungicides, insecticides and other components (fertilizers) in mixtures (Vuković et al., 2013). However, information regarding this subject is still lacking, especially for new active substances.

In this study, the compatibility of liquid sprays of a novel group of anthranilic diamide insecticides (cyantraniliprole, chlorantraniliprole), a fungicide (captan), a foliar fertilizer and their mixtures were analyzed as depending on water quality. These mixtures are intensively used currently for the protection of peach from its most important pest (*Grapholita molesta* Busck) and the causative agent of shot hole disease (*Stigmina carpophila* Lev).

MATERIALS AND METHODS

Well water used in this study was collected from fields at two locations in Vojvodina Province, Serbia (Mala Remeta – location 1 and Čerević – location 2) just prior to treatment. Water analysis (pH, hardness, electroconductivity, and chloride, nitrate, nitrite, ammonia, calcium and iron contents), as well as physico-chemical properties of spray liquids (pH, suspensibility, dispersibility, surface tension, and electroconductivity), were performed according to standard methods in the laboratory. The physico-chemical properties were chosen according to the Manual on the Development and Use of FAO and WHO Specifications for Pesticides (2016), based on their influence on the biological efficacy of pesticides.

The pH value of the spray liquids prepared in well water was determined according to the CIPAC MT 75 method (Dobrat & Martijin, 2007a). For determination of suspensibility, the CIPAC MT 15 method (Dobrat & Martijin, 2007b) was used, while dispersion stability was determined according to CIPAC MT 180 (Dobrat & Martijin, 2007c), both expressed as percentage (%). Surface tension of spray liquids (mJ/m^2 with an accuracy of ±0.1 mJ/m^2) was determined using the tensiometer (Lecomte du Nouy) (Šovljanski et al., 2002). Electroconductivity was determined using the conductometer (WTW pH/cond 740), and the CIPAC MT 32 method (Dobrat & Martijin, 2007c), with pre-calibration in standard hard water at 25 °C, expressed in μS/cm. Analysis of the physico-chemical properties was performed in triplicates, immediately after preparation and after 24 h.

For the analysis, insecticides based on cyantraniliprole (Exirel, 100 g a.i./l, SE [suspo-emulsion]) and chlorantraniliprole (Coragen 20, 200 g a.i./l, SC [suspension concentrate]), a fungicide based on captan (Merpan 50, 500 g a.i./kg, WP [wettable powder]) and a plant nutrition agent (Folia Stim Mix TE, a concentrated liquid formulation with 100% EDTA chelate micronutrients) were applied at application rates shown in Table 1.

The results of the analyzed parameters are expressed as average values. The significance of differences of the test parameters was evaluated using ANOVA for a threshold of 0.05 (statistic software Statistica 12).

Tabela 1. PPPs, foliar fertilizer, their mixtures and application rate

PPPs and fertilizer	Application rate (kg, l/ha)
Exirel	0.6 l/ha
Coragen 20 SC	0.2 l/ha
Merpan 50 WP	2.5 kg/ha
FoliaStim Mix TE	1.5 l/ha
Exirel SE + Merpan 50 WP	0.6 l/ha+2.5 kg/ha
Coragen 20 SC + Merpan 50 WP	0.2 l/ha+2.5 kg/ha
Exirel SE + FoliaStim Mix TE	0.6 l/ha+1.5 l/ha
Coragen 20 SC + FoliaStim Mix TE	0.2 l/ha+1.5 l/ha
Merpan 50 WP + FoliaStim Mix TE	2.5 kg/ha+1.5 l/ha
Exirel SE + Merpan 50 WP + FoliaStim Mix TE	0.6 l/ha+2.5 kg/ha+1.5 l/ha
Coragen 20 SC + Merpan 50 WP + FoliaStim Mix TE	0.2 l/ha+2.5 kg/ha +1.5 l/ha

RESULTS AND DISCUSSION

Water analysis

Water properties, such as pH, electroconductivity and hardness, can affect the quality and efficacy of pesticides and their mixtures in the process of application. It may also happen during mixing pesticides with non-pesticide substances (complex fertilizers, adjuvants, protectants), increasing the risk of undesired effects (Vuković et al., 2013). These water properties can cause accelerated degradation of active substances, changes in suspensibility or biological effect (antagonism, additive effect, synergism), and finally toxicity to plants. The results of chemical analyses of water are shown in Table 2.

Based on the analysis, water samples were classified as slightly alkaline and hard water. The results of the analysis of water samples from both locations showed high concentrations of ammonium (Federal Minister of Labor, 1998). The other tested parameters had values below the prescribed maximum allowable concentration (MAC). Based on a scale for determination of water hardness, both samples (locations 1 and 2) were classified as hard water, with $CaCO_3$ contents of 355 to 361 mg/l, respectively.

pH of spray liquids

The values of pH of well water from location 1 ranged from 7.9 to 8.2 over a period of 24 h (Figures 1 and 2). The spray liquids of insecticides, fungicide and foliar

Tabela 2. The quality of water used in the experiment

Location	Analyzed parameters								
	pH	E* (mS/cm) on 20°C	NO_3^- mgN/l	NO_2^- mgN/l	NH_4+ mgN/l	Chloride mgCl/l	$CaCO_3$ mg/l	Ca mg/l	Fe mg/l
1	8.1	654.0	3.1	0.01	**0.3**	7.1	**355.0**	80.4	<0.1
2	8.2	757.0	1.2	0.01	**0.4**	31.4	**361.0**	115.0	<0.1
MAC**	**6.8-8.5**	**≤1000**	**50**	**0.03**	**0.1**	**200**	***	**200**	**0.3**

* Electroconductivity
** MAC – maximum allowable concentration for II class water quality (Official Gazette SRJ, 1998)
*** water hardness scale (0-4 very soft; 4-8 slightly soft; 8-16 slightly hard; 16-30 hard; over 30 very hard)

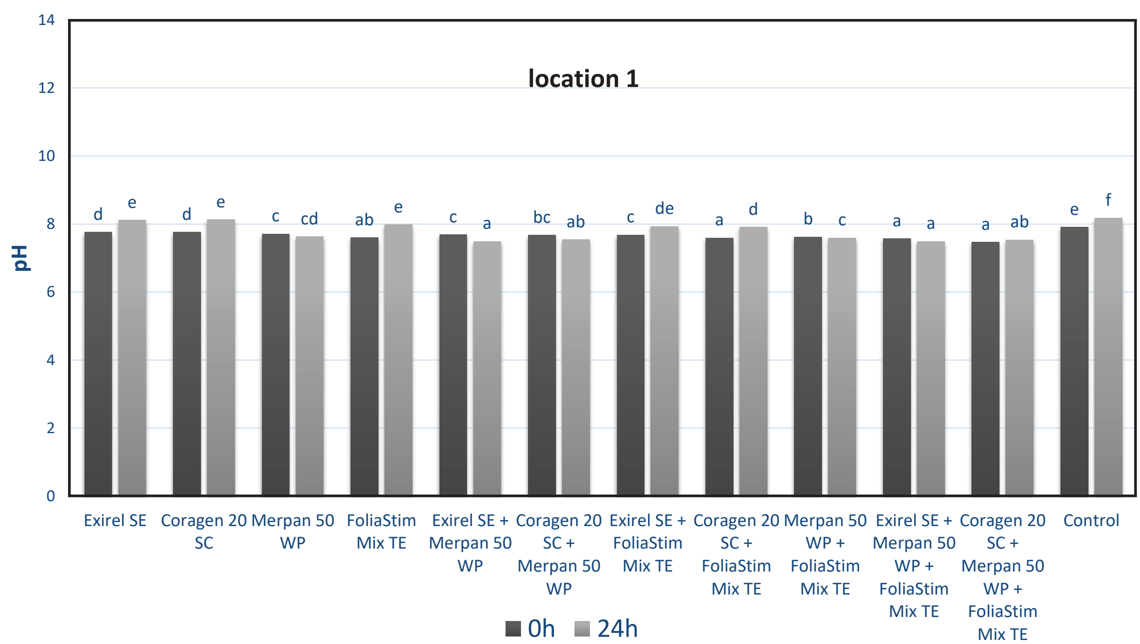

Figure 1. pH values of spray liquids of insecticides, fungicide, foliar fertilizer and their mixtures in well water immediately after mixing and after 24 h (location 1)

fertilizer showed slightly alkaline reaction (7.6-7.7) at the moment of mixing. After 24 h, there was a slight increase in pH values (7.5-8.2), while the mixtures Exirel + Merpan 50 WP, Coragen 20 SC + Merpan 50 WP and Exirel + Merpan 50 WP + Folia Stim Mix TE showed decreasing pH. Most spray liquids of the tested insecticides, fungicide, foliar fertilizer, and their mixtures showed increasing pH from the moment of preparation until the expiry of 24 hours. Based on the pH of spray liquids made with water from location 1, it is evident that the medium reaction changed depending on the components and age of spray liquids.

The pH values of well water from location 2 ranged between 7.7 and 7.8 over 24 h (Figures 1 and 2).

Spray liquids of Exirel, Coragen 20 SC, Merpan 50 WP and FoliaStim Mix TE showed slightly alkaline reaction (7.5-7.9), while only with the spray liquid of Merpan 50 WP fungicide had decreasing pH after 24 h (7.5). Spray liquids of Exirel + Merpan 50 WP and Coragen 20 SC + Merpan 50 WP showed decreasing pH, while it increased in the other mixtures after 24 h. All insecticide and fungicide mixtures with foliar fertilizer displayed neutral to slightly alkaline reaction (7.3-7.7) right after mixing, and all mixtures showed

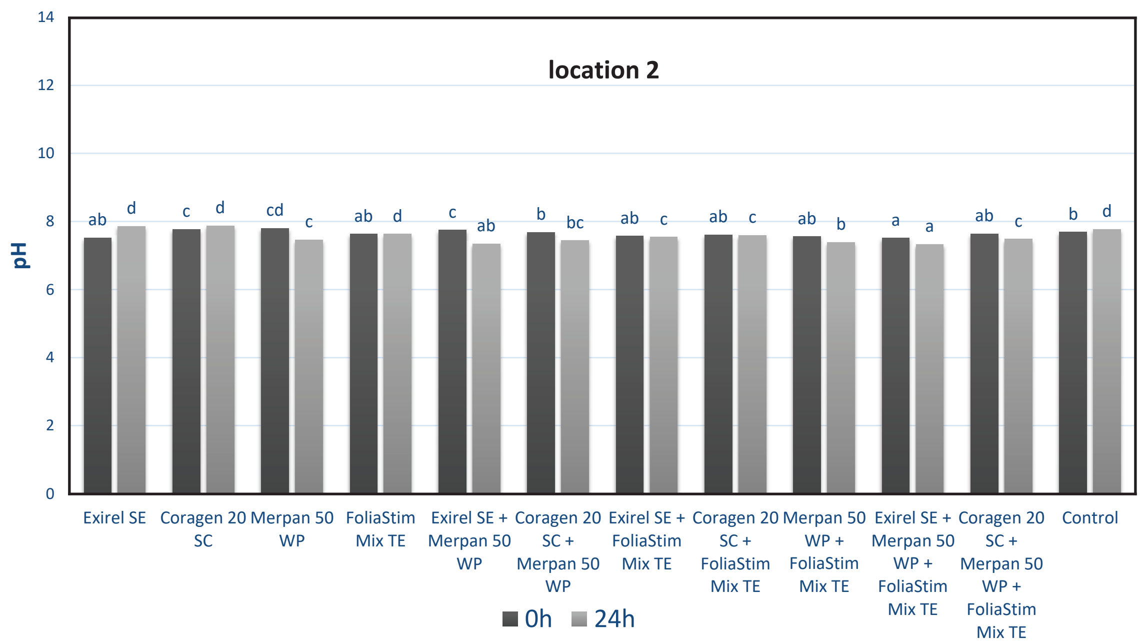

Figure 2. pH values of spray liquids of insecticides, fungicide, foliar fertilizer and their mixtures in well water immediately after mixing and after 24 h (location 2)

Table 3. Suspensibility of spray liquids of insecticides (SC), fungicide (WP) and foliar fertilizer

Insecticides, fungicide, foliar fertilizer and their mixtures	Suspensibility (%)	
	Location 1	Location 2
Coragen 20 SC	99.9	99.9
Merpan 50 WP	54.4	56.3
Exirel + Merpan 50 WP	54.1	60.0
Coragen 20 SC + Merpan 50 WP	90.5	88.2
Coragen 20 SC + FoliaStim Mix TE	99.9	99.9
Merpan 50 WP + FoliaStim Mix TE	88.8	88.4
Exirel + Merpan 50 WP + FoliaStim Mix TE	85.8	88.4
Coragen 20 SC + Merpan 50 WP + FoliaStim Mix TE	96.4	95.1

decrease in pH after 24 h. In general, spray liquids of fungicides (azoxystrobin, mancozeb) and insecticides (thiamethoxam, cypermethrin) insignificantly changed pH, compared to control water, during the 24 h test period. However, the presence of the complex fertilizer, regardless of other components and water pH, changed the medium reaction in all variants from slightly alkaline to neutral and slightly acid (Vuković et al., 2013).

Suspensibility depending on water quality

Suspensibility of the SC, WP and WG formulations of PPPs dissolved in water shows that the persistence of active substances and other components in spray liquids over a specific time has an acceptable value of 60% (Federal Minister of Economy, 2001). In this study, the suspensibility of the pesticides, fertilizer and their mixtures ranged from 54.1 to 99.9%. The suspensibility of the insecticide Coragen 20 SC was very high in both tested waters (99.9%), as well as its mixture with Folia Stim Mix TE. However, the fungicide Merpan 50 WP, formulated as a wettable powder, showed reduced suspensibility with values below the limit (54.4-56.3%), and its mixture with the insecticide Exirel had the same result (54.1-60%) (Table 3).

The rate of coagulation is the most important property for evaluation of components in mixtures. Mixtures with rapid precipitation trend involve a risk in their use as precipitates contain high concentrations of non-pesticide ingredients and active substances that are phytotoxic. Over 2/3 of unstable products coagulate and precipitate within 5-15 minutes (Hrlec, 1999). The stability of most insecticides (pyrimifos-methyl and imidacloprid) and fungicides (propineb and mancozeb) in spray liquids prepared with well water is reduced, compared to the same suspensions in tap water, which indicates the dependence of pesticide stability on water quality and on the choice of tank-mix. This further indicates changes in suspensibility caused by the quality of water for treatment and the choice of ingredients in a mixture (Vuković et al., 2013).

Dispersion stability

Dispersion stability of the test PPPs and foliar fertilizer, as well as their mixtures, was observed immediately after mixing and after 0.5 h, 1 h, 2 h and 24 h (Table 4). After 24 h, redispersion was also evaluated (0.5 h). During observation, all spray liquids in the tested waters exhibited stability without any separation.

Surface tension of spray liquids

Surface tension depends on the treated surface, temperature of spray liquids, intermolecular forces of fluid whereby polar liquids (water) have higher surface tension than non-polar ones (Šovljanski et al., 2002).

Surface tension of well water (location 1) was 48 mJ/m^2 and 46.3 mJ/m^2 immediately after sampling and after 24 h, respectively. Surface tension of all spray liquids ranged from 34-45 mJ/m^2 after mixing, while 24 h later it was 35-41 mJ/m^2 (Figures 3 and 4). The obtained results on surface tension of Exirel and Coragen 20 SC spray liquids indicate a decrease in analyzed values after 24 h. The foliar fertilizer had a high surface tension (47 mJ/m^2) after mixing, while its value after 24 h matched the control.

Table 4. Dispersion stability of insecticides, fungicide, and their mixtures with foliar fertilizer

Insecticides, fungicide, foliar fertilizer and their mixtures	Dispersion stability				
	0 h*	0.5 h	1 h	2 h	24 h
Location 1					
Exirel	s	s	s	s	s
Exirel + Merpan 50 WP	s	s	s	s	s
Exirel + FoliaStim Mix TE	s	s	s	s	s
Exirel + Merpan 50 WP + FoliaStim Mix TE	s	s	s	s	s
Location 2					
Exirel	s	s	s	s	s
Exirel + Merpan 50 WP	s	s	s	s	s
Exirel + FoliaStim Mix TE	s	s	s	s	s
Exirel + Merpan 50 WP + FoliaStim Mix TE	s	s	s	s	s

*- immediately after preparation; s-stable

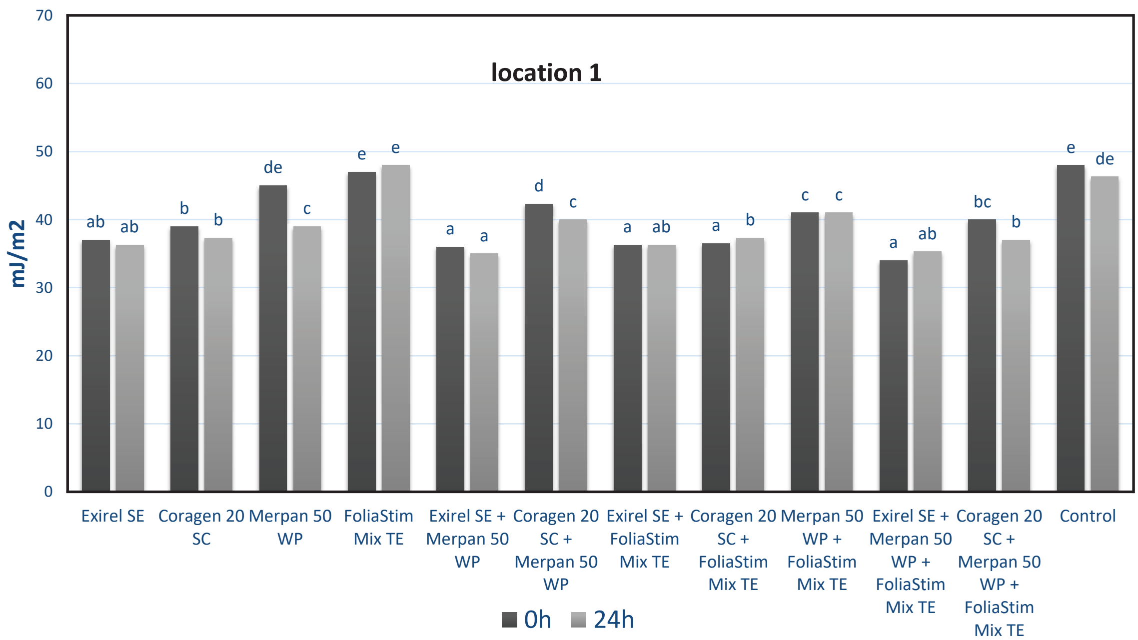

Figure 3. Surface tension of spray liquids of insecticides, fungicide, foliar fertilizer and their mixtures in well water immediately after mixing and after 24 h (location 1)

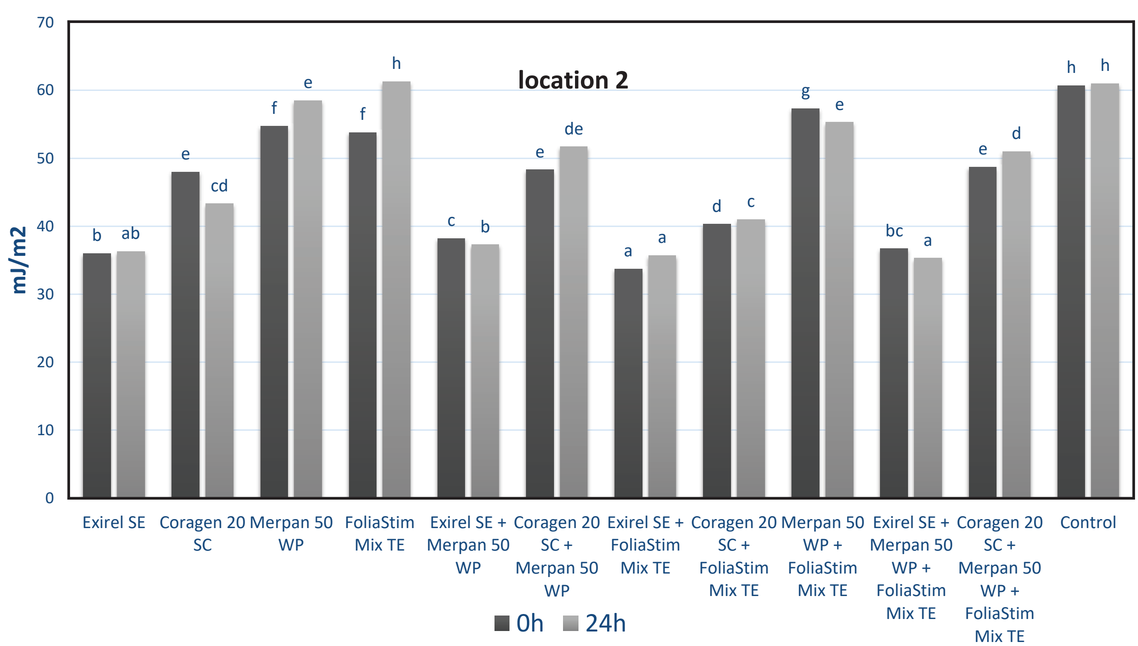

Figure 4. Surface tension of spray liquids of insecticides, fungicide, foliar fertilizer and their mixtures in well water immediately after mixing and after 24 h (location 2)

The surface tension of mixtures of insecticides and fungicide slightly decreased after 24 h. The surface tension of insecticides, fungicide, and foliar fertilizer mixtures was almost the same 24 h after preparation. Finally, surface tension of spray liquids decreased in comparison with control liquid, and the changes depended on components and the expiration time of 24 h.

The surface tension of well water from location 2 slightly increased 24 h after sampling. The value of surface tension of the spray liquid containing the fungicide Merpan 50 WP and FoliaStim Mix TE increased, in contrast to the other spray liquids. An analysis of surface tension data shows that the Exirel insecticide data were 36 mJ/m^2 and 36.3 mJ/m^2 after mixing and after 24 h, respectively. Coragen 20 SC produced surface tension of 48 mJ/m^2, which decreased down to 43.3 mJ/m^2 after 24 h. In the case of foliar fertilizer, initial surface tension (53.8 mJ/m^2) increased after 24 h (61.3 mJ/m^2). All insecticide and fungicide spray liquids manifested a slight decrease in surface tension 24 h after preparation, compared to the values measured immediately after mixing, except the Coragen 20 SC + Merpan 50 WP mixture, which showed a slight increase in surface tension after the resting period of 24 hours.

Surface tension of the tested spray liquids increased in value after 24 h, except for the Merpan 50 WP + Folia Stim Mix TE mixture. Spray liquids of Coragen 20 SC + Merpan 50 WP + Folia Stim Mix TE mixtures showed an increase in surface tension after 24 h, when it was 51 mJ/m^2. Based on the obtained results, it is evident that the surface tension of spray liquids depends on the quality of water, components and its expiration after 24 h.

Electroconductivity of spray liquids

Electroconductivity of the slightly alkaline well water from location 1 remained the same after 24 h (624.3-624 µS/cm). Electroconductivity values of the PPPs Exirel, Coragen 20 SC and Merpan 50 WP increased after 24 h (Figures 5 and 6), while electroconductivity of the fertilizer ranged 1004.3-1029 µS/cm. Electroconductivity values in mixtures of the tested insecticides and fungicide ranged from 700-709 µS/cm after mixing, and increased (726.3-737 µS/cm) after 24 h. Electroconductivity in mixtures of the foliar fertilizer with fungicide, and fertilizer with insecticides increased as well. It can be inferred that electroconductivity depends primarily on the liquid components and partially on the standstill time.

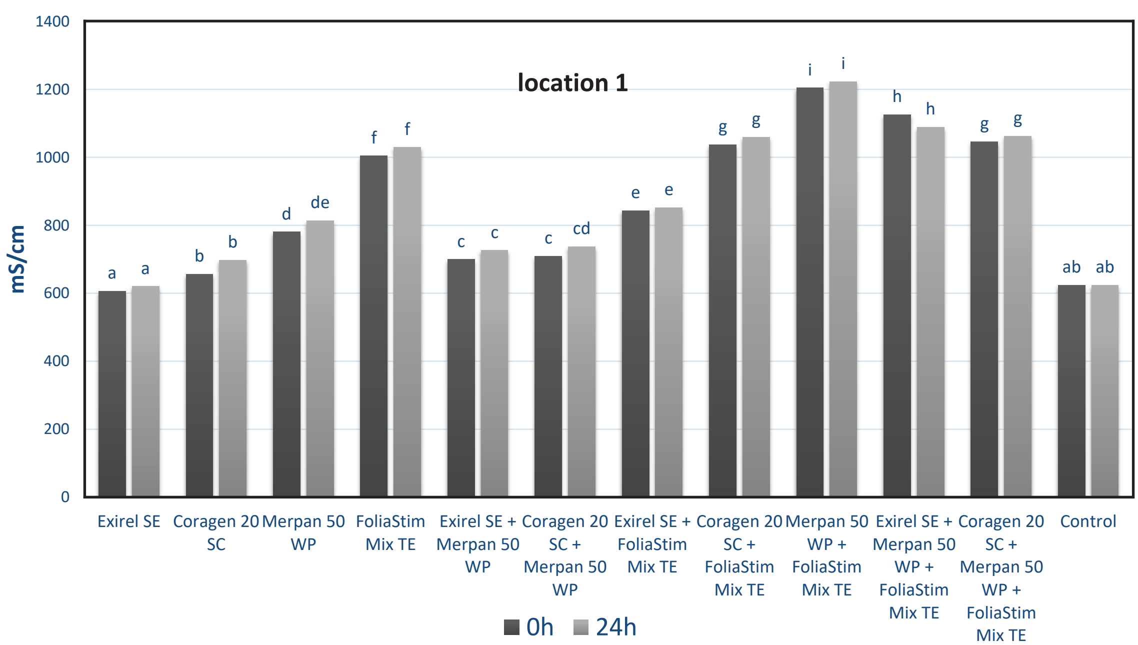

Figure 5. Electroconductivity of insecticides, fungicide, foliar fertilizer and their mixtures in well water immediately after preparation and after 24 h (location 1)

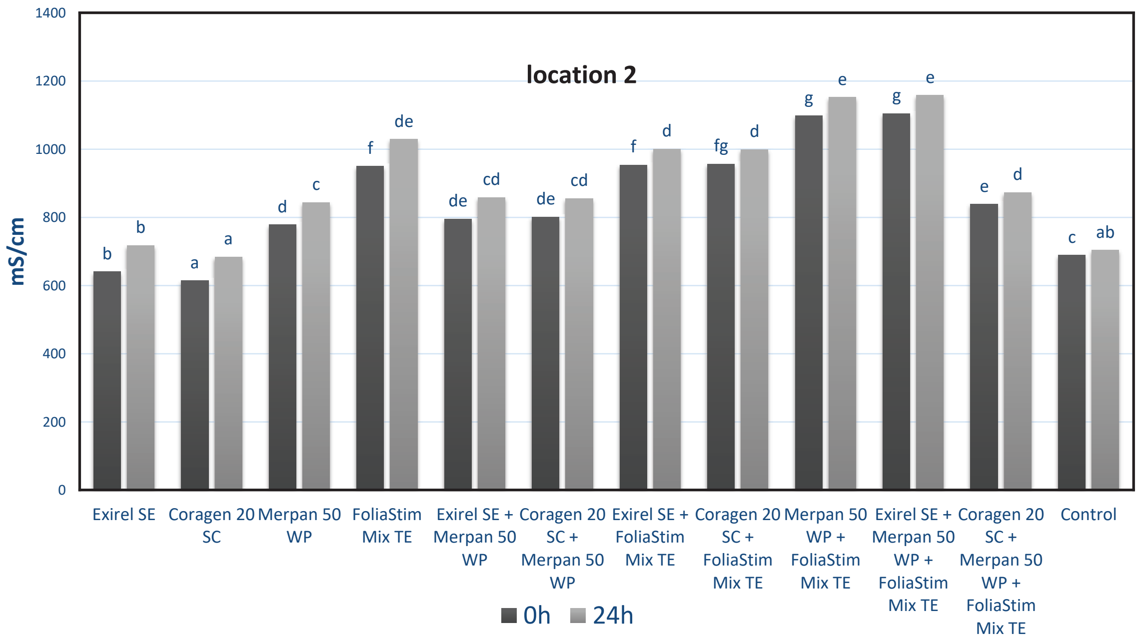

Figure 6. Electroconductivity of insecticides, fungicide, foliar fertilizer and their mixtures in well water immediately after preparation and after 24 h (location 2)

Electroconductivity of the alkaline well water from location 2 was 689.3 μS/cm, and it slightly increased over 24 h (704.3 μS/cm). Electroconductivity of the tested insecticides, fungicide, foliar fertilizer and their mixtures in water from location 2 increased after 24 h (Figure 6).

The lowest electroconductivity was measured in the spray liquid of Coragen 20 SC (614.6-684 μS/cm), while the highest was in the triple mixture of Exirel + Merpan 50 WP + FoliaStim Mix TE, which ranged from 1100-1172 μS/cm, similar to the results obtained in the water test at location 1.

CONCLUSION

Changes in physicochemical properties of pesticide mixtures can cause different consequences for crops and other plants, as well as the environment. However, most researchers focus on the effects of individual substances.

This study analyzed the influence of water quality on spray liquids of individual substances (cyantraniliprole, chlorantraniliprole, captan and foliar fertilizer), and their mixtures, testing the most important properties. Based on the obtained results, it could be concluded that the physico-chemical properties of spray liquids of insecticides, fungicide, fertilizer, their dual and triple mixtures, vary depending on the quality of water and the components included in their composition. However, all tested spray liquids exhibited consistency, and compatibility, over 24 h.

ACKNOWLEDGMENT

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Uticaj kvaliteta vode na kompatibilnost pesticida i đubriva

REZIME

Smeše dva ili više pesticida vrlo su česte u savremenoj poljoprivredi. Međutim, promene u efikasnosti ili biološkoj aktivnosti preparata, poput sinergizma i antagonizma, fitotoksičnosti, postojanosti, toksičnosti za neciljane organizme, mogu se javiti kao posledica primene takvih smeša. Ovo istraživanje je sprovedeno u cilju procene kompatibilnosti radnih tečnosti insekticida (cijantraniliprol - Exirel, hlorantraniliprol - Coragen 20 SC), fungicida (kaptan - Merpan 50 WP) i folijarnog đubriva (Folia Stim Mix TE), kao i njihovih smeša, u zavisnosti od kvaliteta vode (bunarska voda sa dva lokaliteta u Srbiji - Mala Remeta i Čerević). Navedeni preparati se koriste za suzbijanje najznačajnijih štetnih organizama breskve i kao izvor hranljivih sastojaka za biljku. Analize vode (pH, tvrdoća, elektroprovodljivost, hloridi, nitrati, nitriti, amonijak, sadržaj kalcijuma i gvožđa) i fizičko-hemijskih svojstava radnih tečnosti (pH, suspenzibilnost, disperzibilnost, površinski napon i elektroprovodljivost) izvedene su u laboratorijskom uslovima prema standardnim metodama. U zavisnosti od kvaliteta vode i komponenti koje su uključene u smešu, došlo je do promene fizičko-hemijskih svojstava radnih tečnosti. Međutim, sve testirane radne tečnosti su pokazale konzistentnost i kompatibilnost tokom 24 sata.

Ključne reči: pesticidi, đubrivo, smeše, kvalitet vode, fizičko-hemijska svojstva, kompatibilnost