

Chemistry of King Abdallah Canal Water in the Jordan Valley. II. Effect of Water pH on the Stability of Dimethoate

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ABSTRACT. Chemical analysis of King Abdallah Canal (KAC) water in the Jordan Valley (JV) was conducted for collected samples from ten different sites along the KAC. Water analysis include parameters such as pH, electrical conductivity (E.C.), and major anions and cations.

The chemical stability of dimethoate was studied at different water pH values. Four different treatments were used to study the stability of dimethoate. These treatments were canal water (pH = 8.44), distilled water, phosphoric acid - treated canal water (pH = 6.00), and propionic acid - treated canal water (pH = 6.00). Spray solutions samples were allowed to stand for 1,4 and 24 hrs before extraction. Gas liquid chromatographic (GLC) method was performed in the determination of dimethoate in water samples. Canal water samples caused the highest % of hydrolysis for dimethoate after 24 hrs from treatment, while losses were much lower in distilled water. Phosphoric acid - treated canal water showed almost negligible % of hydrolysis during 24 hrs, while propionic acid - treated canal water was much less efficient compared to distilled water and phosphoric acid - treated canal water.

In Jordan, most of the agricultural land is concentrated in the JV. Farmers use the KAC water for mixing their pesticides (Map 1). This canal is 110.5 km long and feed about 232,460 donums of agricultural land (Jordan Valley Authority, 1988, personal communication).

Dimethoate [O,O-Dimethyl S-(N-methyl carbamoylmethyl) phosphorodithioate; trade names: 'Cygon', 'Perfekthion', 'Rogor', 'Roxion', 'Systoate',

...others] is an organophosphorus insecticide/acaricide introduced by a large number of companies. It is considered as systemic insecticide and acaricide with contact and stomach action on a wide range of crops (Worthing 1987). This compound is widely used in Jordan as general insecticide.

In general, organophosphorus insecticides including dimethoate are unstable under high pH values (Faust and Suffet 1960, Ruzicka *et al.* 1967, Matsumura and Krishna-Murti 1982). They are most unstable under alkaline conditions (Eto 1977), and stable under acidic conditions with pH value of 5.0-6.0. Hydrolysis rate of insecticides is dependent upon their chemical structure and water pH (Ruzicka *et al.* 1967). A pH value in excess of 6.00 is most likely to affect the stability of ester compounds like organophosphorus pesticides (Mason 1985).

Farmers in the JV have complained that certain pesticides are not effective. Some farmers used to double the recommended dose of pesticide in order to increase its efficiency (Farmers 1989, personal communication). No information under the Jordanian conditions is available on alkaline hydrolysis of dimethoate. Therefore, the objective of the present work was to study the KAC water situation chemically, and investigate the stability of dimethoate after 1,4 and 24 hrs at different water pH values.

Experimental

Chemicals and materials

Acetone, dichloromethane, all for residue analysis grade, were obtained from Merk, Dramstadt, Germany. Sodium sulfate anhydrous GR (May and Baker, England), sodium chloride GR (Carlo Erba, Milano 1), glass wool prewashed with petroleum benzene in Soxhlet (Merk no. 605), orthophosphoric acid 85% (B.D.H., England), propionic acid 45% (WBC, England), sulfuric acid 98% (Baker chemicals Co., Germany), EDTA (Riedel-De Haen AG, Germany).

Dimethoate reference standard 99% analysis grade, and dimethoate 40% EC, formulated (w/w).

Apparatus and equipment

Water pH was measured using a digital pH meter with the help of combination electrode, model 8520 (Hanna Instrument, Italy). Electrical conductivity was measured by using EC-meter, model PW 9506 (Philips, England). Chloride (Cl^{-1}) concentration in water was measured directly using the chlorocounter instrument (Marius-Utrecht, Holland). The determination of

carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) concentrations in water samples is based on titration with sulfuric acid, while sulfate (SO_4^{2-}) concentration is determined by titration of water sample with Ethylene Diamine Tetraacetic Acid (EDTA). The concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by using Atomic Absorption Spectrophotometer with wavelengths of 422.7 nm and 285.2 nm, respectively (Perkin-Elmer, U.S.A). Sodium (Na^+) and potassium (K^+) concentrations were determined by using Flame Photometer with wavelengths of 589 nm and 767 nm, respectively (Gallenkamb).

Gas liquid chromatographic (GLC) analysis of dimethoate residues in water were made on a Dani model 3800 equipped with nitrogen/phosphorus detector and glass column packed with 3% DC-200 on chromosorb W-AW/DMCS, 80-100 mesh.

The injection port, oven, and detector temperatures were 250, 170, and 250°C, respectively. Nitrogen was used as a carrier gas at a flow rate of 15 ml/min. Recorder, model BD 41 (Kipp and Zonen, Holland) was used with the following operating conditions: attenuation: 64; sensitivity: 10mv; chart speed: 5mm/min. In addition, analytical balance, shaker, rotary evaporator with vacuum, micro syringes, and other basic laboratory equipment were used.

Dimethoate Standard Solution

Stock solution (1000 ppm) of dimethoate was prepared by dissolving 0.025 g of active ingredient in 25 ml acetone. Aliquots of stock solution were used to prepare solutions containing 1.0, 5.0, 10.0, 15.0, and 20.0 ppm dimethoate, and to establish a calibration curve.

Recovery test

Recovery test was done by adding 50 μl of the 1000 ppm dimethoate standard (previously prepared) to a 100 ml untreated water sample. Thereafter, extraction procedure was carried out as in the samples.

Treatments preparation

Three grab samples of water were collected from KAC to be used in spray solution preparations. Each sample consisted of about 5L of water. Samples were used by taking water from the three grab samples to ensure good water sampling. Mix them, then use the mixture in treatments preparation. This is to provide more reliable water pH value.

Four different treatments were used to study the effect of water pH on dimethoate stability. These treatments are:

1. Canal water (CW) only, pH of 8.44. This is to determine the stability of dimethoate under alkaline water conditions.
2. Canal water adjusted to a pH of 6.00 by the dropwise addition of orthophosphoric acid 1% (PW).
3. Canal water adjusted to a pH of 6.00 by the dropwise addition of propionic acid 1% (PrW).
4. Distilled water (DW) only.

After treatment with dimethoate, water samples were allowed to stand in darkness for 1,4, and 24 hrs before extraction. Samples were analyzed in duplicate.

Extraction

A modified method based on that described by Zweig (1972) was followed in the extraction of dimethoate from water.

A 100 ml water sample was transferred into a 250 ml separatory funnel with 5g NaCl. The funnel was shaken briefly in order to dissolve the salt. The solution is then extracted three times with 25 ml dichloromethane each. It was shaken 2-3 times after each addition of the solvent (whenever shaking, carefully release pressure by opening the cock each time), then, strongly shaken for about 2 minutes. Leave the solution for few minutes for separation. After separation, dichloromethane phase (lower phase) was passed through a glass funnel filled with anhydrous sodium sulfate into a 250 ml round bottom flask. Wash with several small portions of dichloromethane. Concentrate the extract just before dryness using a rotary evaporator with a bath temperature of 38°C. Add 5 ml of acetone to the concentrate. Evaporate once again to about 1 ml. The residue will then be taken in 5 ml acetone. Samples are ready now for injection. Each sample was injected 2-3 times. The standard solution was injected before and after each sample.

Calculations

Remaining dimethoate after each time interval for each treatment was calculated according to the following formula based on that described by Zweig (1974):

$$\% \text{ Dimethoate Remaining} = \frac{H_s}{h_i} \times \frac{W_i}{W_s} \times P \times F$$

Where H_s , H_i are the average peak heights due to the formulated and standard dimethoate, respectively. While W_s , W_i are the weight of formulated dimethoate added to water sample and the weight of standard dimethoate, respectively. The symbol P refers to the purity of dimethoate standard, while F is the recovery factor = 100% recovery.

Results and Discussion

Chemical analysis of water

Results of chemical analysis of water showed that water pH values of the selected sites along the KAC in the JV were slightly high and ranged between pH 7.90-8.27. This was during July 1988. The electrical conductivity, major anions and major cations showed fluctuation even at the same site. This is due to the non homogenous mixing of water along the KAC. Table 1 summarizes the general inorganic properties of KAC water in which pH, E.C., and major anions and cations are listed. Carbonate (CO_3^{-2}) was not detected in any water sample. This agrees with Brown *et al.* (1970) who noted that carbonates can only occur at a sufficient water pH value of more than 8.30.

Table 1. Inorganic properties of King Abdallah Canal water in the Jordan Valley during July, 1988

Parameter	Range
E.C. (mmho/cm)	0.90-1.60
pH	7.90-8.27
Major Anions (Meq/L):	
Cl^-	1.82-5.36
HCO_3^-	4.40-6.00
SO_4^{2-}	0.60-5.40
Major Cations (Meq/L):	
Ca^{2+}	3.20-6.70
Mg^{2+}	2.00-2.90
K^+	0.10-0.45
Na^+	2.00-6.11

Dimethoate Stability Determination

Recoveries were evaluated six times at a concentration of 10.0 ppm, and were high and ranged between 118-122%. The alkaline hydrolysis of dimethoate is initiated by the nucleophilic attack of the hydroxide ion at the phosphorus atom (Eto 1977). The expected hydrolysis pathway is represented in Fig. (1) (Sanderson and Edson 1964, Menzie 1969). Remaining % of dimethoate after each time

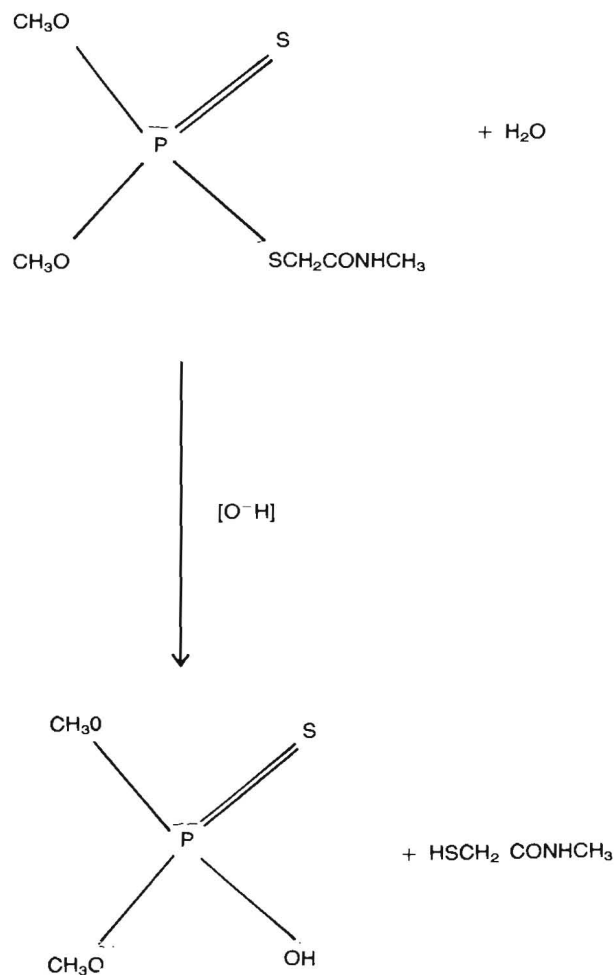


Fig. 1. Hydrolysis pathway of dimethoate in water under alkaline conditions

interval and for each treatment are given in Table 2. Results indicated that we can use canal water (pH = 8.44) in preparing dimethoate spray solution to be used during the first 4 hrs after preparation without modifying the water pH. Low percentage of loss in dimethoate (7.7%) took place during that period of time (Table 2). If the spray solution need to be left for about 24 hrs, as some farmers do, we should modify the canal water pH to 6.00 before preparation. The loss of dimethoate in non treated canal water increased from 7.7% after 4 hrs to 40.5% after 24 hrs. Meanwhile, the loss was only 7.7% after 24 hrs in the case of phosphoric acid-treated canal water.

Dimethoate was found to be almost stable in distilled water during the first 4 hrs, but loss increased to 13.4% after 24 hrs. Dimethoate loss decreased from 40.5% to 7.7% in 24 hrs after lowering the pH using phosphoric acid. Meanwhile, propionic acid treatment was not able to maintain dimethoate stability in canal water as good as phosphoric acid (Table 2).

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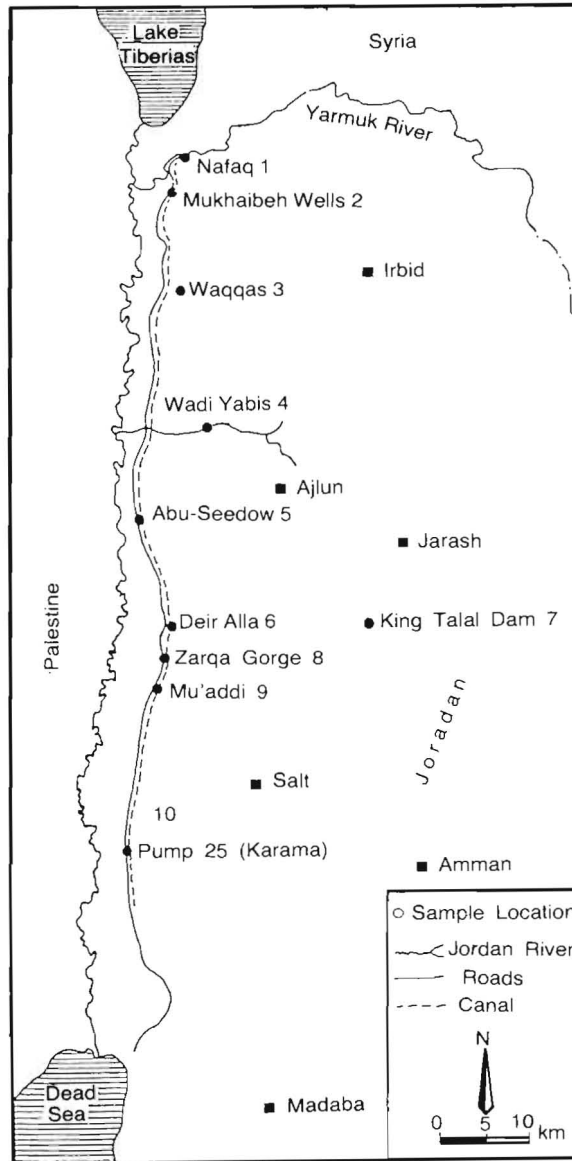
Table 2. Comparison of remaining dimethoate % in the four different water treatments after 1,4 and 24 hrs from preparation

Time after treatment (hrs)	Remaining dimethoate (%)			
	Canal water (pH = 8.44)	Distilled water	PW ^a (pH = 6.00)	prW ^b (pH = 6.00)
1	99.30*	100.00	100.00	89.00
4	92.30	098.20	100.00	86.70
24	59.50	086.60	092.30	78.00

^aPhosphoric acid-treated canal water.

^bPropionic acid-treated canal water.

*Average value of two replicates. Each replicate is an average of the closest two injections.



Map 1. Water collection sites in the Jordan Valley along the King Abdallah Canal.

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٢ - تأثير الرقم الهيدروجيني (pH) للمياه على ثبات مبيد الدايمثويت

خليل إسحق المغربي و إبراهيم خالد الناظر

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تم إختيار عشر مناطق مختلفة على إمتداد قناة الملك عبدالله في وادي الأردن وذلك لجمع عينات المياه منها من أجل دراسة خواصها الكيميائية . وتشتمل عملية التحليل على دراسة خواص المياه من حيث الرقم الهيدروجيني (pH) ، التوصيل الكهربائي (E.C) والانيونات والكاتيونات السائدة .

أما ثبات مبيد الدايمثويت فقد تمت دراسته على قيم رقم هيدروجيني (pH) مختلفة، حيث استخدمت أربع معاملات لدراسة ثبات المبيد فيها، هذه المعاملات هي مياه قناة الملك عبد الله (pH = 8.44) ، الماء المقطر، مياه القناة المعاملة بحامض الفسفوريك (pH = 6.00) ومياه القناة المعاملة بحامض البروبيونيك (pH = 6.00) . وقد تمت دراسة ثبات المبيد في المعاملات المختلفة بعد ثلاث فترات زمنية من تحضير محلول الرش وهي ١ و ٤ و ٢٤ ساعة . اتبعت طريقة الكروماتوجرافي السائل الغازي (GLC) في تحديد ثبات مبيد الدايمثويت في الماء . دلت النتائج على أن مياه قناة الملك عبد الله ذات الرقم الهيدروجيني العالي تسببت في حدوث أعلى نسبة فقدان (تحلل مائي) للدايمثويت بعد ٢٤ ساعة من المعاملة ولكن هذه النسبة كانت أقل بكثير في حالة استخدام الماء المقطر . أدت معاملة مياه القناة بحامض الفسفوريك إلى المحافظة على ثبات المبيد خلال ٢٤ ساعة، أما معاملة مياه القناة بحامض البروبيونيك فقد أظهرت كفاءة أقل من تلك المعاملة بحامض الفسفوريك في المحافظة على ثبات المبيد في الماء .