Use of Ammonium or Potassium Dihydrogen Phosphate to Protect Pesticides in Spray Mixtures Prepared with Alkaline Waters

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A practical procedure was developed to reduce the possibility of alkaline hydrolysis of pesticides in spray tanks when naturally alkaline waters are used. Natural alkaline water samples collected from the Holland Marsh area and Niagara Region in Ontario had pH values in the range of 7.60–9.68, and their buffer capacity ranged from 0.21×10^{-3} M to 2.00×10^{-3} M. Adding 0.5 g of $NH_4H_2PO_4$ or KH_2PO_4 per liter of water lowered the pH of all samples tested to 6.7 ± 0.3. The majority of pesticides are most stable at this pH and the probability of alkaline hydrolysis occurring can be reduced by this simple procedure.

Water plays a major role in controlling the rate of decomposition of pesticides and on their environmental impact because most pesticides are applied as emulsions or suspensions in water and some of the applied pesticides eventually end up in streams, rivers, and lakes. Past studies revealed that many organophosphorus pesticides (Eto, 1974), particularly malathion (Wolfe et al., 1975) and carbamate pesticides (Kuhr and Dorough, 1976) are susceptible to hydrolysis under alkaline conditions.

The rate of hydrolysis depends on the concentration and chemical structure of the pesticide and on factors such as solvent used, pH, and temperature. In aqueous solutions, rate of hydrolysis of organophosphorus pesticides increases sharply at pH levels higher than 7 (Eto, 1974). Because hydrolysis is primarily catalyzed by the hydroxide ion under alkaline conditions, the rate increases approximately tenfold with each additional pH unit (O'Brien, 1967).

It is appropriate, therefore, to recommend that pesticide mixtures prepared in alkaline water should be used immediately. Any delay in the use of spray mixtures after preparation—whether because of sickness, equipment breakdown, or unexpected weather conditions—could result in poorer pest control than expected. Consequently, extra pesticide applications are needed, resulting in increased crop production costs (Valk, 1975) and perhaps further environmental pollution.

To prevent pesticide decomposition in alkaline water and to maintain biological activity, Johansen and Eves (1972) attempted to stabilize these chemicals with acids and nutrient spray acidifiers. They were, however, unable to maintain a constant pH and found that some pesticides were hazardous to honey bees if the pH spray mixtures was too low. Some pesticides are also susceptible to acid hydrolysis (Eto, 1974) and highly acidic water may damage plant tissues (Kemp, 1975). It seems reasonable, therefore, to conclude that the water most suitable for preparing pesticide mixtures before application will be neutral or slightly acidic.

This paper reports the values of pH and buffer capacity of certain natural waters in southern Ontario. The effect of $NH_4H_2PO_4$ or KH_2PO_4 in neutralizing naturally alkaline waters and in buffering them at pH 6.5–6.9 is demonstrated. The significance of using these chemicals in a routine procedure for preparing pesticide spray mixtures is discussed.

EXPERIMENTAL SECTION

Samples. Water samples were collected in polyethylene bottles from rivers, wells, ponds, and lakes of the Niagara Region and from several locations along rivers and canals around the Holland Marsh, Ontario. Four collections were made during 1975, 1976, and 1977. These samples were compared to several alkaline and buffer solutions prepared as references.

pH Meter. A Type 45 R/ER pH Controller, Chemtrix Inc., Hillsboro, OR, equipped with a sealed glass electrode (no. 9105), Broadley-James Corporation, was used. To record titration curves, Rustrak recorder Model 288, Gulton Industries, Inc., Manchester, NH, was equipped with the above pH controller. A solenoid actuated burette (Sargent-Welch S-11093-25) was modified to provide a constant flow of titration liquids at 3.5 mL/min. Accuracy of the above system was ±0.05 pH and repeatability was ±0.03 pH.

Experimental Procedures. A 25-mL water sample, in a 100-mL Erlenmeyer flask, was titrated with 0.01 M HCl with the above system. The initial pH and the pH change during titration were recorded with the automatic end point setting at pH 3.2. From the chart obtained, the buffer capacity (β) was calculated. It is expressed as the number of moles of HCl required to cause 1.00 L of the sample to change from pH 8 to pH 7. The number of moles of HCl, required to adjust the pH of 1.00 L of the sample from its original pH to pH 7.0, was calculated and tentatively expressed as the total buffer capacity (β'). Other acids, $CH_2ClCOOH$, $CHCl_2COOH$ and $(C_2H_5O)_2P(O)OH$, and two phosphates, KH_2PO_4 and $NH_4H_2PO_4$, were also used in lieu of HCl for comparison. After these preliminary experiments, either KH_2PO_4 or $NH_4H_2PO_4$ was added to water samples at rates of 0.5 g/L (0.5 lb/100 gal) and 1.0 g/L (1.0 lb/100 gal); the pH was recorded before and after addition. Further experiments were conducted after lowering the pH of natural water by adding $NH_4H_2PO_4$ at 0.5 g/L; seven formulated pesticides (five insecticides, one fungicide, and one herbicide) were added (at the standard recommended rate) individually to the buffered natural water, and pH change was recorded. A similar experiment was conducted also on a commercial basis (at a high concentrate rate) with 100 gal (455 L) of water.

Water Analyses. Some of the water samples were analyzed for hardness, calcium, conductivity, etc., by staff of the Ontario Ministry of the Environment, Laboratory Service Branch, Water Quality Section, Rexdale, Ontario, by methods currently used in routine water analysis in the laboratory.

RESULTS AND DISCUSSION

Water samples from canals, rivers, and wells, collected at the same locations on four separate occasions in the Holland Marsh area during 1975–1977, showed considerable variation in pH and buffer capacity (Table I). The

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Table I. pH, Buffer Capacity (β) and Total Buffer Capacity (β') of Water Samples Collected during 1975, 1976, and 1977 from the Holland Marsh Area

	June 20, 1975			April 8, 1976			July 14, 1976			April 28, 1977		
sampling site	pH	$\beta \times 10^{-3}$	$\beta' \times 10^{-3}$	pH	$\beta \times 10^{-3}$	$\beta' \times 10^{-3}$	pH	$\beta \times 10^{-3}$	$\beta' \times 10^{-3}$	pH	$\beta \times 10^{-3}$	$\beta' \times 10^{-3}$
canal 1	8.75	0.25	0.35	8.30	0.54	0.76	8.35	0.80	1.06	8.25	1.00	1.24
2	8.73	0.56	0.85	8.45	0.78	1.04	8.45	0.88	1.14	8.05	1.05	1.09
3	8.65	0.47	0.67	8.00	1.04	1.04	8.02	1.03	1.05	8.13	1.18	1.32
4	8.02	0.21	0.21	8.45	0.60	0.89	8.02	1.00	1.02	8.18	1.10	1.30
5	8.63	0.46	0.59	8.35	0.78	0.94	8.35	1.06	1.21	8.35	1.09	1.28
6	8.60	0.49	0.67	7.90	0.96	0.86	8.05	0.92	0.95	8.35	0.93	1.26
river 1	8.72	0.54	0.70	8.20	0.61	0.70	8.08	1.05	1.14	8.10	1.29	1.44
2	8.85	0.68	1.16	8.15	0.80	0.91	7.90	1.48	1.33	8.35	0.97	1.31
3	8.78	0.61	0.87	8.70	0.65	1.06	8.55	1.12	1.42	8.38	1.13	1.41
well 1							8.47	1.02	1.30	8.20	1.12	1.35

Table II. pH, Buffer Capacity (β), and Total Buffer Capacity (β') of Water Samples from the Niagara Region and of Alkaline and Buffer Solutions

sample		pH	$\beta \times 10^{-3}$, pH 8-7	$\beta' \times 10^{-3}$, initial pH-pH 7
well	1	7.60	1.85	1.11
	2	7.80	1.32	1.06
	3	7.85	1.26	1.07
	4	7.70	2.00	1.80
	5	8.00	0.64	0.64
pond	1	7.95	1.08	1.03
	2	7.98	0.60	0.59
	3	9.68	0.25	0.79
stream	1	8.20	0.89	1.09
	2	8.05	0.74	0.76
Lake Ontario	1	7.90	0.54	0.49
	2	8.15	0.53	0.58
	3	8.70	0.24	0.44
rain	1	8.00	0.61	0.58
0.00001 M NaOH		8.65[a]	0.17	0.29
0.005 M $NaHCO_3$		8.40[a]	1.64	1.97
0.001 M $NaHCO_3$		7.95[a]	0.56	0.52
0.005 M $(NH_4)_2HPO_4$ 0.0005 M $NH_4H_2PO_4$		7.95[a]	2.84	2.70
0.002 M $(NH_4)_2HPO_4$ 0.0002 M $NH_4H_2PO_4$		7.88[a]	1.35	1.19
0.001 M $(NH_4)_2HPO_4$ 0.0001 M NH_4HPO_4		7.85[a]	0.64	0.54

[a] Measured values. (They deviate slightly from calculated values.)

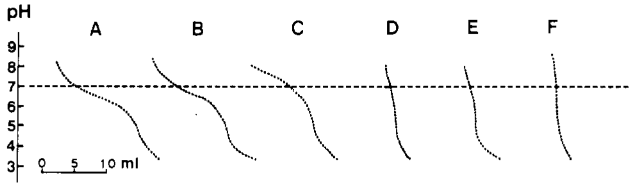

Figure 1. Titration curves with 0.01 M HCl for 25-mL samples of natural water, alkaline solutions, and a buffer solution: (A) a natural water sample with a reasonable buffer capacity; (B) 0.005 M $NaHCO_3$ solution; (C) a buffer solution consisting of 0.005 M $(NH_4)_2HPO_4$ and 0.0005 M $NH_4H_2PO_4$; (D) a natural water sample with a small buffer capacity; (E) 0.001 M $NaHCO_3$ solution; (F) 0.00001 M NaOH.

total buffer capacity (β') also differed markedly even though the water samples were collected from the same locations; these values increased consistently over the period of the experiment.

The values of pH, buffer capacity (β), and total buffer capacity (β') of water samples from the Niagara Region as well as prepared alkaline solutions and buffer solutions are shown in Table II.

These results indicate no correlation between pH values and buffer capacities. Although pH is a good indicator of the possibility of alkaline hydrolysis of pesticides (McNall, 1974; The Fruit World and Market Grower, 1975), it does not indicate the magnitude of buffer capacity. For example, a pure NaOH solution of 10^{-5} M has a high pH (ca. 9.0), but its buffer capacity is very small (Table II). If an organophosphorus pesticide is dissolved in a 10^{-5} M NaOH solution, some of the pesticide will be hydrolyzed. The acid produced as a result of hydrolysis, would neutralize the NaOH and the pH of the solution would be reduced. Accordingly, the rate of hydrolysis of the remaining pesticide will slow down substantially. Browett (1976) illustrated this effect in his study on hydrolysis of malathion. In contrast, the buffer capacities of most of the water samples in the present study are sufficient to permit decomposition of the common pesticides when used at recommended rates in agriculture (Browett, 1976) as well as in the natural environment (Chemistry in Canada, 1977).

The pH change during titration with 0.01 M HCl of most water samples was rather slow until pH 6 (Figure 1A). The slope of the titration curve, however, became quite steep after pH 6 with the inflection point near pH 5. This titration curve is very similar to that recorded with a 0.005 M $NaHCO_3$ solution (Figure 1B). A curve with a typical buffer solution consisting of $(NH_4)_2HPO_4$ (0.005 M) and $NH_4H_2PO_4$ (0.0005 M) is also shown (Figure 1C) for comparison. The three other curves in Figure 1 are for a water sample with a low buffer capacity (Figure 1D), 0.001 M $NaHCO_3$ solution (Figure 1E), and 0.00001 M NaOH solution (Figure 1F).

According to Stumm and Morgan (1970), although the dissolved or homogeneous carbonate system gives a strong effect on buffer action in natural water, it is not solely responsible for pH regulation because many heterogeneous chemical, biochemical, and geochemical processes contribute significantly to the buffering of these waters. The values for carbonate and bicarbonate, and possibly for conductivity (which are obtained in ordinary water analyses), probably give a fairly good indication of the approximate level of buffer capacity of waters (Table III).

The titration curves of typical water samples titrated with 0.01 M HCl (Figure 2A,D) are compared with those titrated with other acids. The curve (Figure 2B), with 0.01 M $CHCl_2COOH$ (pK = 1.48) is very similar to that with HCl but the high pK value of $CH_2ClCOOH$ (pK = 2.85) was reflected on the curve after the inflection (Figure 2C). The titration curve (Figure 2E) with 0.01 M $(C_2H_5O)_2P(O)OH$ (pK = 1.49) appears very similar to those of HCl

Table III. Composition of Assorted Waters from the Holland Marsh and the Niagara Region

sample		Ca^{2+}, mg/L	Mg^{2+}, mg/L	Na^+, mg/L	K^+, mg/L	chloride as Cl, mg/L	sulfate as SO_4, mg/L	hardness as $CaCO_3$, mg/L	total carbonate, mg/L	total bicarbonate, mg/L	pH	conductivity, µmho/cm
canal	1[a]	41	14	12	0.6	25	12	159	131	131	8.2	346
	2[a]	72	17	24	0.9	42	6	248	235	235	8.1	545
	3[a]	93	14	22	2.8	46	10	289	255	255	7.9	605
	4[a]	98	17	27	3.6	57	29	315	257	257	8.0	680
	5[a]	98	15	28	3.9	56	30	307	252	252	7.9	682
	6[a]	67	15	10	1.8	22	32	228	183	183	8.0	468
river	1[a]	88	18	21	2.1	44	9	292	253	253	7.8	600
	2[a]	125	21	25	2.7	66	38	399	307	307	7.7	805
	3[a]	82	16	15	1.5	36	23	271	227	176	8.8	525
well	1[a]	48	23	9	1.5	7	1	215	229	229	7.7	425
	4[b]	167	101	72	81.0	88	435	835	392	392	7.7	1850
	5[b]	40	9	13	1.5	33	31	136	86	86	7.8	334
pond	1[b]	88	35	32	9.1	100	146	364	157	157	2.5	860
	3[b]	30	25	8	2.8	30	70	178	75	66	8.7	390
rain	1[b]	30	5	7	3.0	7	57	97	48	48	7.9	234
distilled water	1[c]	<1	<1	<1	<0.1	2	<1	1	4	4	5.7	4.6
tap water	1[c]	41	8	13	16.0	32	30	136	88	88	7.5	329

[a] From Holland Marsh. Samples collected on June 22, 1977. [b] From Niagara Region. Samples collected on May 31, 1977. [c] From the Research Station, Agriculture Canada, Vineland Station, Ontario.

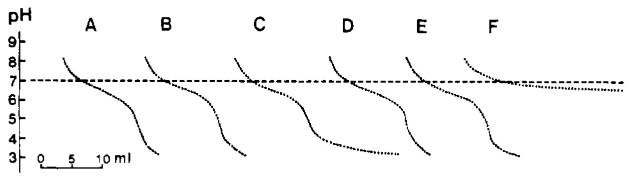

Figure 2. Titration curves for 25 mL of two typical water samples (samples 1 and 2) with different kinds of 0.01 M acids and 0.01 M $NH_4H_2PO_4$. Sample 1 was used for titrations A, B, and C, and sample 2 was used for titrations D, E, and F: (A and D) HCl, (B) $CHCl_2COOH$, (C) $CH_2ClCOOH$, (E) $(C_2H_5O)_2P(O)OH$, (F) $NH_4H_2PO_4$.

Table IV. Effect of Adding $NH_4H_2PO_4$ or KH_2PO_4 at 0.5 g/L and 1.0 g/L on pH of Samples of Water Collected in the Holland Marsh[a]

sample		initial pH	$NH_4H_2PO_4$ 0.5 g/L	$NH_4H_2PO_4$ 1.0 g/L	KH_2PO_4 0.5 g/L	KH_2PO_4 1.0 g/L
canal	1	8.25	6.85	6.65	6.80	6.59
	2	8.05	6.90	6.70	6.73	6.54
	3	8.13	6.85	6.66	6.80	6.58
	4	8.18	6.83	6.66	6.78	6.59
	5	8.35	6.87	6.66	6.78	6.56
	6	8.35	6.82	6.62	6.78	6.57
river	1	8.10	6.90	6.75	6.80	6.62
	2	8.35	6.82	6.61	6.75	6.55
	3	8.38	6.80	6.60	6.73	6.56
well	1	8.20	6.78	6.60	6.78	6.57

[a] Collected April 28, 1977.

and $CHCl_2COOH$. $(C_2H_5O)_2P(O)OH$ is one of the typical acids produced from organophosphorus pesticides as a result of alkaline hydrolysis.

Titration curves were markedly different with KH_2PO_4 or $NH_4H_2PO_4$. As shown in Figure 2F, the pH of water was reduced fairly rapidly as titration proceeded with 0.01 M $NH_4H_2PO_4$ solution until it reached pH 7.0 and then slowed down. Even with the addition of excess amounts, pH essentially stayed constant around pH 6.8 (Figure 2F).

Because individual waters have many different components, their pH and buffer effects are different; accordingly the values of buffer capacity (β) are not necessarily proportional to the values of total buffer capacity (β') (Tables I and II). Since the prime purpose of this study was to devise a practical means of reducing the alkalinity of natural waters to slightly below pH 7.0, the values of total buffer capacity (β') rather than the values of buffer capacity (β) may be more indicative of the amount of acid that will be required.

From the above information, a simple practical procedure was developed to stabilize the pH of natural waters when preparing pesticide mixtures. Either $NH_4H_2PO_4$ or KH_2PO_4 lowered the pH of the majority of water samples to 6.6–6.9 when added to water at the rate of 0.5 g/L. Examples of this effect are shown in Table IV. This level of pH control was expected because the dissociation constant (K) for $H_2PO_4^-$ is 6.23×10^{-8} (pK = 7.21), and the pH of the phosphate solutions at 0.5 g/L was 5.15 for KH_2PO_4 and 5.12 for $NH_4H_2PO_4$.

The concentrations of $NH_4H_2PO_4$ and KH_2PO_4 at 0.5 g/L were 4.35×10^{-3} M and 3.68×10^{-3} M, respectively. Since the highest buffer capacity and the highest total buffer capacity of natural water samples examined in this study were 2.00×10^{-3} M and 1.80×10^{-3} M, respectively, the concentration suggested (0.5 g/L) is adequate to reduce and stabilize the pH of these waters. After pH was reduced by adding the phosphate, the further change in pH values caused by adding the formulated pesticide was insignif-

Table V. Effect of Formulated Pesticides When Added at the Standard Recommended Rate on Stability of pH of Buffered Natural Water (pH = 6.70)[a]

pesticides	formulated products	rate, g/L	pH value after adding
azinphos-methyl	Guthion, 50% WP Chemagro Ltd.	0.625	6.65
carbaryl	Sevin, 50% WP Pfizer Chemicals Genetics Ltd.	2.00	6.65
dimethoate	Cygon, 4E Cyanamid of Canada	1.00	6.64
malathion	Malathion, 25% WP Pfizer Chemicals Genetics Ltd.	2.00	6.65
phosmet	Imidan, 50% WP Stauffer Chemicals	1.25	6.66
metiram	Polyram, 80% WP BASF Canada Ltd.	2.00	6.64
paraquat	Gramoxone, 2 EC Chipman Chemicals Ltd.	5.00	6.65

[a] The initial pH value of natural water used was 8.55. When $NH_4H_2PO_4$ was added at 0.5 g/L to this water, the pH value dropped to 6.70. Pesticide formulations were added individually to this buffered water at the rate shown above.

Table VI. Effect of $NH_4H_2PO_4$ on Stabilizing pH of a Spray Mixture Prepared with Alkaline Water and Malathion on a Commercial Basis

procedures and description	pH reading
100 gal (455 L) spray tank was filled with well water	7.85
added 0.5 lb (227 g) of $NH_4H_2PO_4$, stirred, and dissolved	6.78
added 6 lb (2722 g) of 25% malathion WP (FMC) and stirred	6.90
added 4 fl. oz. (114 mL) of super spred (FMC, pH 8.0) and stirred	6.93
added extra 0.5 lb of $NH_4H_2PO_4$[a]	6.75
added extra 4 fl. oz. of super spred[a]	6.78

[a] Optional procedure.

icant in the laboratory experiment (Table V) and also in the commercial scale experiment (Table VI).

Once pH is lowered to 7 or lower, the rate of hydrolysis of alkaline susceptible pesticides becomes markedly slower (Eto, 1974; MacNeil et al., 1973; O'Brien, 1967); accordingly, the delay in using the prepared spray mixtures becomes substantially less critical. Since many natural waters in the world are alkaline with very high salt contents, (CIPAC Monograph, 1972), it could be expected that some of them would have high buffer capacities. If those waters are used for preparing pesticides, it may be necessary to increase the quantity of the phosphate, possibly to 1 g/L, to obtain satisfactory control.

NaH_2PO_4 showed the same effect, but the recommendation was confined to $NH_4H_2PO_4$ and KH_2PO_4 because these two are well-recognized fertilizers and may contribute as foliar nutrients when applied. When water-soluble fertilizers are used along with pesticides as a tank mixture, 0.5 g/L of the phosphate is not sufficient to lower the pH. Although most dry fertilizers are acidic, the majority of water-soluble fertilizers being used routinely in the Holland Marsh area are strongly alkaline. They are used at a rate of 3.0 g/L or higher and the resultant buffer capacity of the water exceeds the capability of the phosphate added.

Since the cost of the phosphates is extremely small relative to pesticides (approximately $0.40 vs. as much as $30 per 100 gal of water), it is worthwhile using either one of them routinely as cheap insurance. Because users will not need to increase the amount of pesticides to cover losses due to hydrolysis, or the number of spray applications, a saving in pesticide consumption is highly probable. Also, it is clear that any reduction in total pesticide use will contribute to a cleaner environment.

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LITERATURE CITED

Browett, W. R., B.Sc. Thesis, Chemistry Department, Brock University, St. Catharines, Ontario, May 1976.

Chem. Can. **29**(8), 20 (1977).

CIPAC Monograph 1, "Standard Waters", Collaborative International Pesticides Analytical Council, W. Heffer & Sons Ltd., Cambridge, U.K., 1972, pp 41–52.

Eto, M., "Organophosphorus Pesticides: Organic and Biological Chemistry", CRC Press, Cleveland, OH, 1974, pp 1–387.

Johansen, C., Eves, J., *J. Econom. Entomol.* **65**, 546 (1972).

Kemp, W. G., Research Station, Agriculture Canada, Vineland Station, Ontario, 1975.

Kuhr, R. J., Dorough, H. W., "Carbamate Insecticides: Chemistry, Biochemistry and Toxicology", CRC Press, Cleveland, OH, 1976, pp 1–301.

MacNeil, J. D., Frei, R. W., Frei-Hausler, M., Hutzinger, O., *Int. J. Environ. Anal. Chem.* **2**, 323 (1973).

McNall, L. R., *Am. Veg. Grower* **22**(4), 35 (1974).

O'Brien, R. D., "Insecticides; Action and Metabolism", Academic Press, New York, 1967, pp 1–332.

Stumm, W., Morgan, J. J., "Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters", Wiley-Interscience, New York, 1970, pp 1–577.

The Fruit World and Market Grower, Vol. 76, Fruit World PTY, Ltd., Carlton South, Victoria, Australia, 1975, p 9.

Valk, M., Muck Research Station, Ontario Ministry of Agriculture and Food, Kettleby, Ontario, 1975.

Wolfe, N. L., Zepp, R. G., Baughman, G. L., Gordon, J. A., *Bull. Environ. Contam. Toxicol.* **13**, 707 (1975).

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