

Detection of organophosphate pesticides using a prototype liquid crystal monitor

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The precision and accuracy of a prototype wearable liquid crystal monitor (LCM) for the measurement of airborne organophosphate pesticide concentrations was explored in a series of laboratory experiments. LCM response to vapor-phase and aerosol diazinon was compared to concentrations obtained using a standard reference method (NIOSH 5600) at concentrations ranging from ~8 to 108 ppb (parts per billion) over durations of 2 to 80 hours. Temperature (~25, 30, and 35 °C) and relative humidity (15, 50, and 85%) were varied to estimate the effect of these factors on LCM performance. The LCM response to vapor phase pesticide exposure was linear for concentrations in the range of 8–20 ppb. At exposure concentrations above ~20 ppb, however, there was a decline in monitor response and measurement precision. Elevated temperatures improved diazinon vapor-only measurement precision, while increased relative humidity reduced LCM response at the extremes of tested temperatures. Compared to vapor-only exposures, the LCM was less sensitive to diazinon aerosol concentrations, but displayed reasonable precision over a relatively large range of exposures (29 to 1190 ppb-hr). Further efforts to characterize temperature and humidity effects and improve low-end sensitivity would likely provide a portable personal exposure monitor or environmental sensor for this widely used class of pesticides.

Introduction

Pesticides are widely used to kill pests and improve crop yields but there is increasing concern about their long term human health effects in workers and children.^{1–5} The organophosphate (OP) compound diazinon is one of the most widely used agricultural pesticides in the world, and in the US the residential use of several OPs has been reduced or eliminated due to concerns over exposure and health effects.^{4,6,7} Recent controlled studies in animals suggest that subtle neurodevelopmental effects may be seen at diazinon exposure levels at or below those that cause cholinesterase inhibition.^{8,9}

One of the challenges in assessing the effects of pesticide exposure is that quantitative pesticide measurement is relatively expensive and time consuming.^{10,11} While measurements of environmental media indicate that diazinon is present in soil, water, and air, directly assessing human exposure requires relatively cumbersome equipment and extensive chemical analysis facilities.⁴ It is increasingly clear that small, sensitive, lightweight wearable monitors with direct read outs are needed to assess exposure to a wide variety of chemicals at work, home, and in public places.¹¹ The lack of simple methods that are sensitive, reliable and provide varying measurement durations (hours to

days) restricts our ability to assess exposure in important subpopulations, such as children.^{12,13}

Liquid crystals (LCs) are materials typically composed of rod-like molecules, which possess short-range (liquid-like) positional but long-range (crystal-like) orientational order.¹⁴ This unusual combination of properties, mobility and long-range ordering, permits molecular events at surfaces to be rapidly amplified within micrometre-thick films of LCs.¹⁵ Changes within such films are readily reported through the interaction of light with the LC film. For example, a film of LC supported between two substrates, with molecules oriented perpendicular to surface, will appear dark when viewed between crossed polarizing filters. If the molecules within the LC film are perturbed away from the surface normal, the film will then appear bright when viewed between crossed polarizing filters.

Surfaces decorated with selected metal perchlorates have been demonstrated to promote alignment of LCs perpendicular to the surface *via* coordination interactions between the metal ions on the surface and the nitrile group of the LCs.¹⁶ When a thin film of LC supported between these surfaces is exposed to target analytes, such as OPs, the target analytes diffuse into the LC film and bind competitively to the metal ions, disrupting the coordination interactions between the metal ions and the LCs. These changes are amplified into bulk ordering transitions in the LCs that extend throughout micrometre-thick LC films. The LC response to a cumulative exposure to an analyte, such as the OP pesticide diazinon, can be quantified by measuring the area of the optically anisotropic region (a bright front) on the LC film when it is placed between crossed polarizing filters before and after exposure to the analyte (Fig. 1).

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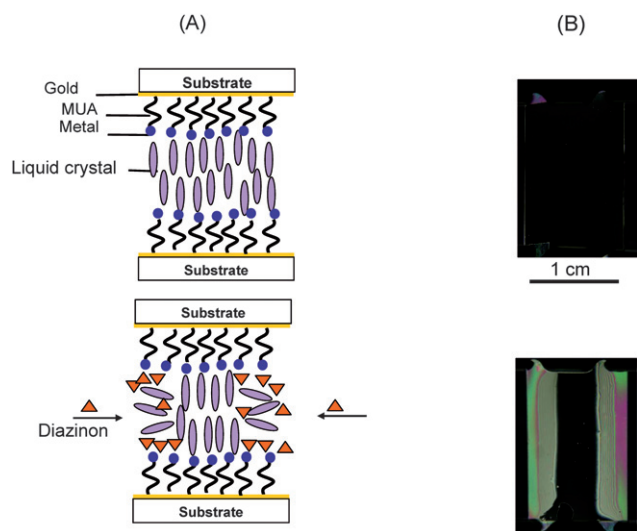


Fig. 1 (A) Schematic of a thin film of LC supported between two chemically functionalized surfaces before (top) and after exposure to diazinon (bottom). (B) The optical image of a LCM between crossed polarizing filters before (top) and after (bottom) exposure to diazinon. Before exposure the liquid crystals align perpendicular to the surface and the LCM appears dark between the crossed polarizing filters. When the LCM is exposed to diazinon, the alignment of liquid crystals is disrupted and two bright fronts develop from the sides of LCM.

This manuscript reports the response of a prototype liquid crystal monitor (LCM) when exposed to a commonly used pesticide compound, diazinon. The precision and accuracy of OP-sensitive prototype LCMs exposed in the laboratory to known diazinon vapor and aerosol concentrations at varying levels of temperature and relative humidity are also assessed.

Materials and methods

Fabrication of monitors

Large (10.2 × 7.6 cm) glass substrates (Eagle 2000, Corning Inc. NY) were pre-scribed using a glass scribe (Villas Precision Instruments, AZ) and cleaned using a plasma asher (MCF LS-5 Plasma System). The substrates were coated with 20 Å thick titanium layer followed by a 100 Å thick semi-transparent film of gold using e-beam evaporation (Temescal - FC 1800, CA). The coated substrates were cleaned using a UV ozone cleaner (Jelight Company, CA) to remove any organic films. A self assembled monolayer of 11-mercaptoundecanoic acid (MUA) was formed by immersing the substrates in a 1 mM ethanolic solution for 2 hrs with 5% acetic acid in a controlled environment (23 °C and 50% relative humidity). The substrates were then spin-rinsed using a 5% acetic acid solution in ethanol and dried at 2000 rpm for 30 secs. A thin film of gallium(III) perchlorate was then formed by spin coating a 1 mM ethanolic solution for 20 secs at 2000 rpm. Each substrate was then fragmented into sixteen 2.54 × 1.9 cm smaller pieces. Two substrates with functionalized surfaces (randomly selected) were paired face-to-face, separated by ~25 μm thick mylar film forming a cavity between them, and held together using binder clips. The cavity between the substrates was filled at room temperature with commercially available LC E7

(EM Industries, NY) using capillary action. The alignment of LC perpendicular to the substrate was confirmed by the dark appearance of the monitor viewed between two crossed polarizers.

Study design

The study design used three sets of experiments to explore the variability in the response of 6 LCMs within each experimental group to diazinon vapors and aerosols under a wide range of conditions. The first set of twelve experiments measured LCM responses by varying diazinon vapor concentrations (range: 8 to 108 ppb) and exposure durations (2 to 80 hrs) at fixed temperature (T) and relative humidity (RH) levels (~ 30 °C, 50% RH). Ten additional experiments examined LCM responses by varying T (25, 30, and 35 °C) and RH (~ 15, 50, and 85%) at vapor concentrations ranging between 6 and 9 ppb over 20 hrs. The final four experiments explored LCM response to pesticide aerosol at 25 °C and 50% RH for four hours at concentrations ranging from 7.3 to 298 ppb. A standard condition, in which six LCMs were exposed to 80 ppb diazinon vapor at 25 °C and 50% RH, was repeated within all sets of experiments and was used to estimate and correct for lot-to-lot variability in mean LCM response.

Experimental setup

Experiments were conducted in a stainless steel test chamber fitted with humidity, temperature, and flow controls, vapor and aerosol generation systems, LCM monitor hangers, and ports for air sampling (Fig. 2). Relative humidity was controlled by mixing water-saturated air (generated by passing air through a water-filled impinger) with dry air. A removable heating jacket (HTS/Amptek Company, Stafford, TX) was used to provide heat to the system as needed to achieve the desired temperature. A temperature and relative humidity sensor (HH314, Omega, Stamford, CT) with data logging capability was used to continuously monitor these parameters.

All experiments were performed using a commercial formulation of diazinon (AG500, 48% active ingredient, Makhteshim Agan of North America, New York, NY) in either the vapor phase or mixed vapor and aerosol. Vapor phase diazinon was generated by diluting the AG500 formulation with water to a 5% solution and loading it on a 47 mm diameter glass fiber filter (Millipore, AP1504700, Billerica, Massachusetts). The filter was soaked to saturation by submerging it in 1 mL of the dilute diazinon solution. The solvent on the filter was allowed to evaporate by running air through it for 2 hours after which the air passing through the loaded filter was effectively saturated with diazinon vapor.¹⁷ The filter was then placed in a holder attached to the exposure chamber, and diazinon-saturated air was diluted with diazinon-free air to achieve desired concentrations using flow rates determined by mass flow meters (TSI, Model 4143, Shoreview, MN).

Diazinon aerosols were generated by nebulizing a 5% solution of commercial diazinon AG500 in water using a Collison nebulizer (BGI Inc., Waltham, MA). High pressure air was supplied at 10 psi to the nebulizer, which operated in intervals of 5 to 10 seconds ON, 180 seconds OFF using a solenoid valve that was

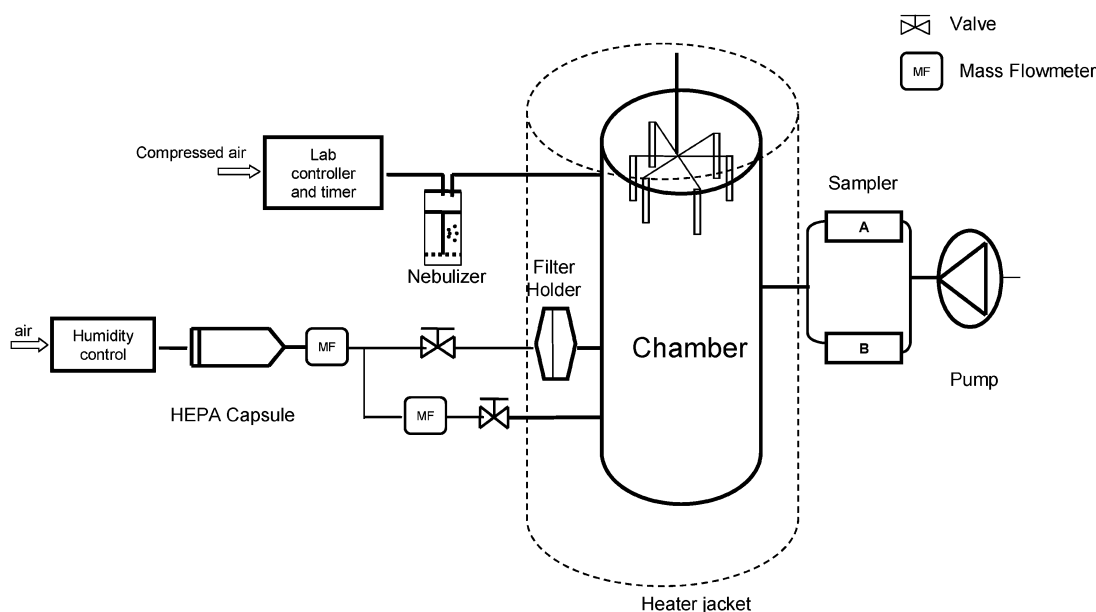


Fig. 2 Schematic of pesticide vapor and aerosol controlled exposure and sampling system.

controlled with a data logging timer (Sciencelab.com, Inc., Houston, TX). Three target concentrations were attempted, and aerosol exposures were conducted at ~ 21 °C and 50% RH with chamber flow rates determined by mass flow meters.

The diazinon flow from one chamber outlet was split into two identical sampling trains and diazinon was collected on quartz fiber/XAD sorbent tubes (OVS-2, 226-30-16, SKC, Eighty Four, PA) attached to a vacuum pump operating at a total flow rate of $4 \text{ L}\cdot\text{min}^{-1}$. Sorbent tubes were analyzed by following procedures outlined in NIOSH method 5600¹⁸ using gas chromatography (GC; Agilent Model HP6850, Foster City, CA) with a 7673 auto sampler, a flame ionization detector and helium as the carrier gas. The filter and front XAD-2 section from the sorbent tubes were transferred to a 7 mL vial, the short polyurethane foam plug with back-up XAD-2 section to a second 7 mL vial and both were extracted with 2 ml of toluene acetone (90/10) desorbing solvent including an internal standard, dibutyl sebacate (DBS) (Sigma Aldrich, St. Louis, MO) using a 1 mL auto pipette. After allowing the sample to stand for 30 minutes to maximize the extraction, 1 to 1.5 mL from each 7 mL vial was transferred to a clean 2 mL GC vial and capped prior to analysis. A $1 \mu\text{L}$ sample extract was injected into the HP-1 ($30.0 \text{ m} \times 320 \mu\text{m} \times 0.25 \mu\text{m}$) methyl siloxane capillary column with an initial oven temperature of 100 °C, then heated to 205 °C at a rate of 3 °C/min until the end of the analysis (35 min). This temperature program achieved adequate separation of all compounds. The diazinon air concentration, c , was calculated as follows:

$$c = \frac{(V/w)(m_f + m_{bk} - m_{bl})}{\eta Q t} \quad (1)$$

where V is the volume of the desorbent solvent used to extract the sample, and w is the volume injected into the GC. The mass of contaminant collected in the front section of the sorbent tube is m_f , the mass collected in the back section is m_{bk} , and the mass of contaminant in the blank is m_{bl} , η is the desorption efficiency, Q is the air sampling flow rate, and t is the sampling time interval.

Diazinon mass readings on the GC were calibrated at least weekly using a 5 point curve of pure diazinon (4-9021, Sigma Aldrich, St. Louis, MO) and DBS at a fixed concentration as the internal standard. Results were plotted as the ratio of the integrated area under the response curve for the diazinon to the area for the DBS on the y-axis and the ratio of the known concentration of the diazinon to the known concentration of DBS on the x-axis. Analytical results were adjusted for a η of 97%, which was calculated by injecting a known mass of pure diazinon into a sorbent tube and extracting it to derive this coefficient. The GC calibration was checked for each analytical run using single point internal standards, and a calculated internal response factor was used to correct measurements during that run. Blank and control samples were prepared with each sample run and used to determine background response and analytical reliability of the total analytical process, respectively. Quality assurance goals were to have results within two standard deviations of the mean of diazinon concentration in the sample and all results fell within two standard deviations ($\pm 5.58 \mu\text{g}$) of the mean ($131.57 \mu\text{g}$ of diazinon/sample).

The LCM response to diazinon vapor and aerosol was characterized by calculating the effective propagation distance of the bright front from the measured area of the optically anisotropic region on the monitor before and after diazinon exposure. A flatbed color image scanner (Epson Expression 1680, Long Beach, CA) operating in transmission mode was used to digitally record the change in the optical appearance of the LCM before and after diazinon exposure. Digital images were recorded by directly scanning LCMs placed between two sheets of crossed polarizing filters. One LCM at a time was placed into a polarizing filter holder, centered under a flatbed scanner, and scanned (24-bit color image) at a resolution of 1200 dots per inch. The raw images were processed and analyzed with Java-based NIH software (Image J, version 1.33u, Bethesda, Maryland, <http://rsb.info.nih.gov/ij>) using the polygon selection tool to outline the optically anisotropic (bright) area. A one cm wide section of the

image was used to calculate area and pixel value statistics for the bright fronts. A typical appearance of a LCM viewed through a crossed polarized filter after diazinon exposure is shown in Fig. 1B. Calculated pre-exposure fronts were subtracted from post-exposure fronts to obtain the change in front area as a result of diazinon exposure. The effective propagation distance of the front into the otherwise dark background was then calculated using this area.

Statistical analysis

Statistical analyses were conducted using SAS version 9.1. The LCMs were fabricated in lots of 36 to 40, and the blocked factorial statistical design for the experiments included a standard exposure condition in each block to adjust for lot-to-lot variability in LCM response. The PROC GLM procedure was used to conduct analysis of variance, with normalized monitor response as the dependent variable, and Duncan's multiple range test ($\alpha = 0.05$) was used to explore differences in mean level of response for various treatment groups. Two models were tested:

$$\text{Model 1: } \text{NMR}_{c*t} = \alpha_{c*t} + \beta_1 c + \beta_2 t + \beta_3 c*t + \varepsilon; \quad (2)$$

$$\text{Model 2: } \text{NMR}_{T*RH} = \alpha_{T*RH} + \beta_0 c*t + \beta_1 T + \beta_2 RH + \beta_3 T*RH + \varepsilon \quad (3)$$

where NMR is normalized monitor response (mm), α is the model intercept, β are model regression coefficients, c is concentration (ppb diazinon), t is time (hrs), T is temperature ($^{\circ}\text{C}$), RH is relative humidity, and ε is the error term. Only statistically significant predictor variables in each model are reported and discussed in subsequent sections. Log_{10} transformed data plots were fitted using the least-squares method.

Results

Table 1 shows results of twelve experiments conducted under varying diazinon concentrations (range: 8 to 108 ppb) and exposure durations (2 to 80 hrs) at fixed temperature and RH levels ($\sim 30^{\circ}\text{C}$, 50% RH). The concentrations ranged between 171 and 769 ppb-hrs, with NMR ranging from 1.06 to 5.44 mm

and percent coefficient of variation, $\% \text{CV} = (\text{SD}/\text{mean}) \times 100$, greater than 20% at high concentrations, but showing better measurement precision ($\% \text{CV}$: 7–23) at lower concentrations (8–20 ppb) over durations longer than 20 hrs. Over the range of measured concentrations, statistical analysis identified both the c and $c*t$ terms as significantly associated with monitor response ($\text{NMR}_{c*t} = 2.97 - 0.087c + 0.0038c*t$; adj. $R^2 = 0.79$, $F = 78$, $p < 0.0001$). The effect of higher concentration on the variability in response over the range of tested diazinon concentrations is shown in Fig. 3. As depicted in Fig. 3, LCMs exposed to higher diazinon concentrations (80–100 ppb) exhibited a reduced response (approximately two-fold lower NMR) compared to those exposed to lower concentrations (~ 20 ppb or lower). Overall, the Log_{10} curve had the best fit, and coefficients of the three experimental blocks were all statistically different ($t = 3.44$, $p = 0.001$).

Table 2 summarizes the results of ten experiments examining monitor response under varying T (25, 30, 35 $^{\circ}\text{C}$) and RH conditions (~ 15 , 50, and 85%) at concentrations ranging between 6 and 9 ppb over 20 hrs. At ($c*t$) ranging between 131 and 198 ppb-hrs, the NMRs were 1.0 to 5.1 mm with $\% \text{CV}$ s of 3 to 25%. Overall model fit was good ($\text{NMR}_{T*RH} = -10.7 + 0.44T + 0.069RH - 0.0027T*RH$; adj. $R^2 = 0.69$, $F = 33.8$, $p < 0.0001$), and the T ($t = 6.77$, $p < 0.001$), RH ($t = 2.43$, $p = 0.018$) and $T*RH$ ($t = -2.87$, $p = 0.006$) coefficients were all highly significant. Better measurement precision was obtained from LCMs exposed at median and high temperatures than from those exposed at low temperatures. Overall, the NMR was significantly lower ($p < 0.05$) for LCMs exposed at 25 $^{\circ}\text{C}$ compared to the NMRs for LCMs exposed at 30 $^{\circ}\text{C}$ and at 35 $^{\circ}\text{C}$. The mean responses of LCMs exposed at the two higher temperature groups, however, were statistically indistinguishable from each other. High humidity reduced NMR at low and high temperature levels, but appeared to have less effect at 30 $^{\circ}\text{C}$ (Table 2). Although the overall NMR was substantially greater in the high temperature (2.5–5.1 mm) as compared to the low temperature (~ 1.0 –2.1 mm) group, both groups displayed significantly lower NMR at high humidity when compared to medium and low humidity groups at the same temperature. This humidity effect was not observed in the medium temperature block, with all experimental groups having NMRs between 4.0 and 4.6 mm.

Table 1 Mean LCM response to pesticide vapor as a function of concentration and time at fixed temperature (30 $^{\circ}\text{C}$) and relative humidity (50%)

Block ^a	Mean Exposure Duration (hr)	Mean Conc. (ppb)	Mean of Conc. \times Time(ppb-hr)	Mean \pm Std. Dev. Normalized Monitor Response (mm) ^b	% CV
1(High Conc.)	2.0	108	216	1.12 \pm 0.20	18%
	4.0	81.3	325	1.06 \pm 0.53	50%
	5.5	90.4	497	2.39 \pm 1.10	46%
	8.0	96.1	769	2.24 \pm 0.62	28%
2(Med. Conc.)	8.0	21.3	171	2.21 \pm 0.51	23%
	16.0	20.5	329	3.07 \pm 0.89	29%
	24.0	21.4	514	4.09 \pm 0.67	16%
	32.0	20.4	653	4.37 \pm 0.57	13%
3(Low Conc.)	20.0	8.96	179	2.41 \pm 0.36	15%
	40.0	8.60	344	4.20 \pm 0.90	21%
	60.0	8.20	492	5.24 \pm 0.43	8%
	80.0	8.03	642	5.44 \pm 0.40	7%

^a A fabrication lot of 38–40 LCM cells were used for experiments for each level of concentration. In each experiment 6 cells were exposed to diazinon, 2 cells were used as lab controls, and the remaining 2 cells used as lot controls. ^b Response represents the mean \pm standard deviation of response from six monitors normalized to response under a standard exposure condition (30 $^{\circ}\text{C}$, 50% RH, and 80 ppb diazinon vapor) repeated for each lot to adjust for lot-to-lot variability.

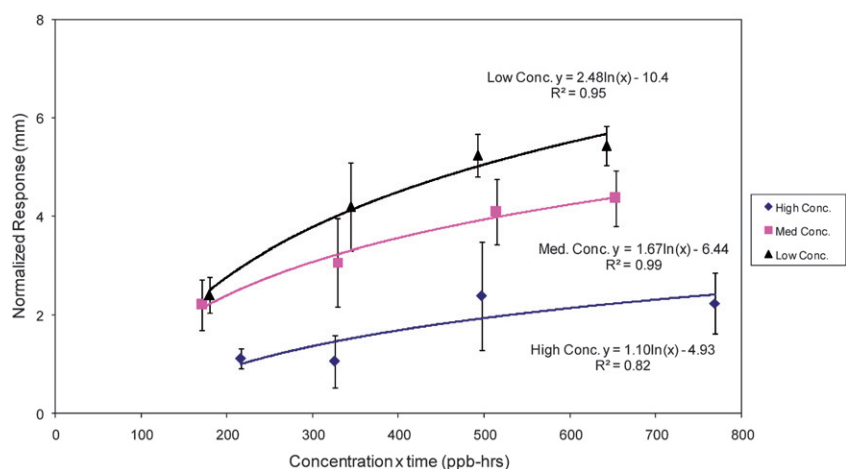


Fig. 3 Log least squares plots of the variation in LCM response to varying levels of diazinon concentration. Each data point represents an average of six measurements normalized to the standard exposure condition to account for lot-to-lot variation. The error bars represent the standard deviation of the mean response.

Table 2 Mean LCM response to pesticide vapor as a function of varied temperature and relative humidity at a fixed exposure duration (20 hrs) and consistent concentration (~8 ppb)

Block	Mean Conc (ppb)	Mean Temp. (°C)	Mean RH(%)	Conc. Time (ppb-hr)	Mean ± Std. Dev. Normalized Monitor Response (mm) ^a	%CV
1(High Temp.)	8.81	34.7	16.3	176	5.08 ± 0.16	3%
	8.40	34.7	49.5	168	5.10 ± 0.15	3%
	8.06	35.2	89.1	161	2.48 ± 0.15	6%
2(Med Temp.)	7.62	30.4	17.4	152	3.98 ± 0.50	13%
	7.41	30.2	48.2	148	3.96 ± 0.40	10%
	7.96	30.3	87.1	159	4.58 ± 0.66	14%
3(Low Temp.)	6.56	25.3	14.8	131	1.23 ± 0.27	22%
	9.92	24.9	51.6	198	2.06 ± 0.42	20%
	6.89	23.9	86.9	137	0.98 ± 0.19	19%
	7.85	25.1	87.5	157	1.06 ± 0.26	25%

^a Response represents the mean ± standard deviation of response from six monitors normalized to response under a standard exposure condition (30 °C, 50% RH, and 80 ppb diazinon vapor) repeated for each lot to adjust for lot-to-lot variability.

Table 3 Mean LCM response to pesticide aerosol as a function of varied concentration at a fixed exposure duration (4 hrs) and consistent RH (~ 50%)

Mean Conc. (ppb)	Mean Temp. (°C)	Mean RH (%)	Conc. Time(ppb-hr)	Mean ± Std. Dev. Normalized Monitor Response (mm) ^a	%CV
7.3	21.5	54.0	29.2	0.27 ± 0.08	31%
25.3	20.6	50.3	101.0	0.94 ± 0.30	33%
33.5	20.5	43.9	134.0	0.92 ± 0.34	37%
298	20.8	47.1	1190	1.24 ± 0.23	18%

^a Response represents the mean ± standard deviation of response from six monitors normalized to response under a standard exposure condition (30 °C, 50% RH, and 80 ppb diazinon vapor) repeated for each lot to adjust for lot-to-lot variability.

Range finding experiments conducted to explore LCM response to aerosol exposure used experimental concentrations ranging between 7 and 298 ppb over 4 hours, at 50% RH and ~21 °C (Table 3). The magnitude of NMR after aerosol exposure was less than that observed in vapor-only experiments, with mean NMRs ranging from 0.3 to 1.2 mm where $c \cdot t$ exposures ranged from 29 to 1190 ppb-hrs. The lowest ppb-hr exposure was below the lowest exposure in vapor-only experiments, and the LCM response following a 4 hour exposure was not significantly

different from zero. Across the range of integrated exposures NMR was relatively small compared to earlier experiments at similar ppb-hrs of exposure, and overall measurement precision was lower than observed for vapor-only exposures.

Discussion

The experiments performed to detect vapor phase diazinon show that this prototype liquid crystal monitor had varied but

consistent response within experimental blocks and relatively good precision when compared to a standard reference method. Higher NMR as a function of integrated exposure at low vapor concentrations suggests saturation of the liquid crystal sensing system at some of the higher concentrations tested here, a finding that is supported by aerosol exposure results. Although the LC-based monitor appears to sense the presence of combined vapor and aerosol exposures, NMR to vapor-only exposures showed greater measurement precision than to aerosol exposures. High RH levels reduced NMR, while increased temperature appears to improve overall monitor performance.

It is clear from these results that the LCM sensing system has a varied response to the wide range of concentrations employed in these experiments. The LCM response at standard conditions (30 °C, 50% RH) was fairly consistent within the low and medium concentration regime blocks, with similar intercepts and relatively consistent slopes. The highest absolute vapor concentration exposures (81 to 108 ppb), however, showed greater variability and an apparent plateau of response at cumulative exposures exceeding 500 ppb-hrs. In contrast, NMR values from the low and medium vapor concentration exposures (8 to 21 ppb) are higher and more comparable to one another. Although there was some lot-to-lot variability in response of the LCM to diazinon vapor, the overall effect of lot was relatively small when compared to the effect of absolute concentration.

These results suggest that using the LCM configuration tested here, the minimum measurable response is less than ~175 ppb-hrs, and saturation of the liquid crystal occurs at the higher vapor and aerosol concentrations employed. While high-end saturation is a potential limitation, we note that human exposures are typically at the low end of the concentrations tested in this study. In field work using a backpack sprayer and the NIOSH reference sampler we have observed air concentrations in and around diazinon sprayed plants in the range of 0.1–1 ppb (1.2 to 12.5 µg/m³) and applicator personal air concentrations of approximately 0.6 ppb (~7.5 µg/m³) with cumulative exposures to a pesticide applicator of 1.6 to 2.1 ppb-hrs. Field LCM results indicated that both of these exposures were below the lower limit of LCM sensitivity, which is consistent with results observed in the laboratory. This suggests that to measure exposures at typical levels some increase in sensitivity is needed, either by modifying monitor material properties or configuration, or by coupling this passive sampler with a pump to increase mass flow of pesticides to be monitored. As presently configured, the LCM is perhaps better suited to low level measurements over longer time scales than were tested in our field trials or laboratory experiments.

Although there was no clear effect of RH on LCM response at 30 °C, these results show that there was a clear reduction in response at high humidity levels in both the low and high temperature groups. It is notable that the medium and high temperature exposures appear to improve measurement precision, perhaps assisting the diffusion of the pesticide into the liquid crystal. Given that overall measurement precision was between 3 and 25% in these experiments, it is plausible that the effects of temperature and RH on the LCM can be used to adjust the NMR value at the time of readout if these data are collected. The high temperature/high RH conditions used in these experiments were included to bound monitor performance and are conditions not likely to be encountered or exceeded in diazinon spray

applications (at least in the US). During the growing season it is more conventional to apply the pesticide early in the day when lower temperatures and comparatively high RH prevail. Given that the LCM performance appears to be relatively consistent over the range of tested RH levels at 30 °C, it appears to have reasonable measurement precision, and to be less sensitive to the effect of RH at lower temperature than at high temperatures. The monitor has potential for field use if coupled with algorithms that adjust for these factors or with additional technology (*e.g.* selective membranes) that can minimize these observed effects.

The LCM has several strengths as a potential exposure dosimeter: small size, low weight, and relatively consistent and precise response to diazinon vapors near the range of environmental conditions that are relevant for assessing human and ecological exposure. Its major limitations are sensitivity, and effects of ambient temperature and RH. These shortcomings are relatively minor and may be addressed in part by refinement of the LCM design, such as outfitting the liquid crystal monitor with active sampling equipment to increase sensitivity, or changing the chemistry and/or configuration of the LCM. The sensitivity of the liquid crystal-based detection depends on the relative strength of interaction (*i.e.*, competition) between the functional group of target analyte and liquid crystals for binding to the chemically functionalized surface. A possible refinement that incorporates filters/membranes in the monitor to remove moisture from the air sampling train prior to interaction with the sensor surface may reduce the effect of humidity on monitor response. These simple modifications may lead to a small prototype LCM with improved sensitivity, precision, and accuracy under varied environmental conditions.

A final limitation of the present work is that the surface chemistry used in this monitor was optimized for sensing diazinon, and these experiments did not test the LCM response to other OP pesticides. Using the LCMs described here, the ability of the targeted analyte to displace the LC is dependent upon the relative binding strengths of the LC and the targeted analyte for a given metal ion. The comparative binding strengths of different classes of compounds containing various functional groups can likely be fine-tuned by choice of metal ion on gold coated surfaces, self assembled monolayer functionalization, and LC overlay. Thus, by applying different surface chemistries to the sensor surfaces in the LCMs, the monitor may be able to discriminate between two organophosphate pesticides with similar active functional groups.

Abbreviations

%CV Percent	Coefficient of Variation
DBS	Dibutyl Sebacate
GC	Gas chromatography
LC	Liquid Crystal
LCM	Liquid Crystal Monitor
NIOSH	National Institute of Occupational Safety and Health
NMR	Normalized Monitor Response
OP	Organophosphate
ppb	parts per billion
RH	Relative Humidity
T	Temperature
t	Time
c	Concentration

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