

Electronic Supplementary Information

Strong base pre-treatment for colorimetric sensor array detection and identification of N-methyl carbamate pesticides

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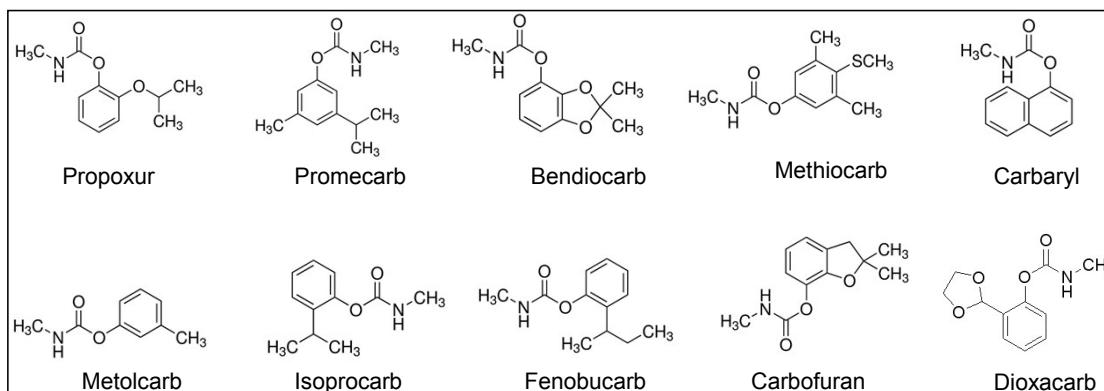
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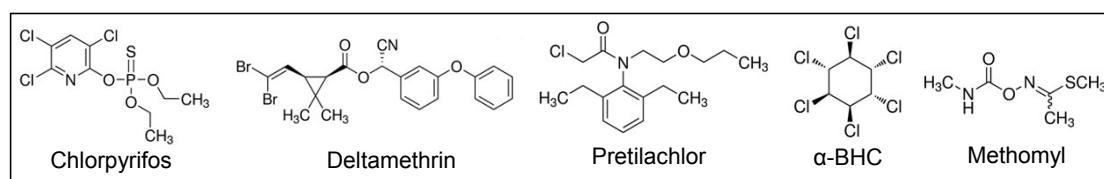
Table S1 Composition of the developed 1×5 phenol responsive array.

Sensor unit	Composition of phenol responsive indicator
1	4-nitrobenzenediazonium tetrafluoroborate (100 μM) in Na_2CO_3 - NaHCO_3 buffer (10 mM, pH 9.5)
2	2,6-dibromoquinone-4-chloroimide (100 μM) in Na_2CO_3 - NaHCO_3 buffer (10 mM, pH 9.5)
3	NaNO_2 (0.15 M)+ H_2SO_4 (0.16 mM)+resorcinol (1.1 mM) in NaOH solution (2.78 M)
4	MBTH (0.4 mM)+ammonium ceric sulfate (0.3 mM) + buffer A (0.04% v/v) in aqueous solution
5	Sodium nitroprusside (0.2 mM)+hydroxylamine hydrochloride (0.8 mM)+buffer B (0.06% v/v) in aqueous solution

Buffer A (pH 14): NaOH (4.8 g), EDTA (2.0 g) and boric acid (0.8 g) were dissolved in 50 mL distilled water, and then mixed with equivalent volume ethanol before use; Buffer B (pH 12): 50 mL of KH_2PO_4 solution (0.1 M) mixed with 1.75 mL of NaOH solution (6.0 M) and then diluted to 100 mL with distilled water.



N-methyl Carbamates



Other Pesticides

Fig. S1 Molecular structures of the investigated pesticides and herbicides.

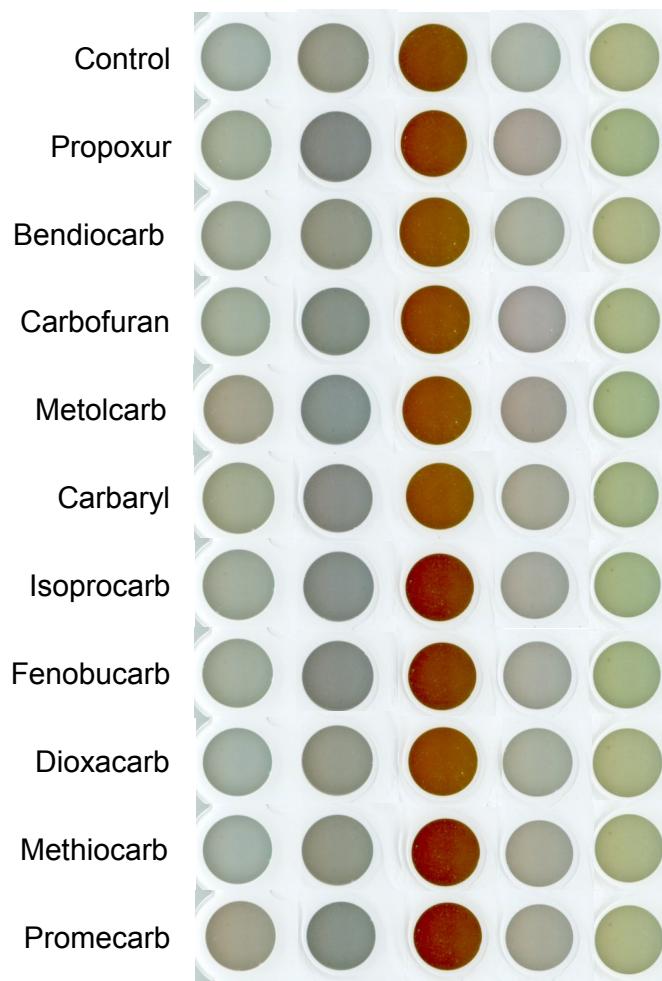


Fig. S2 The colors of the array in the presence and absence of different N-methyl carbamates. The concentrations of N-methyl carbamates were 10^{-4} g/L.

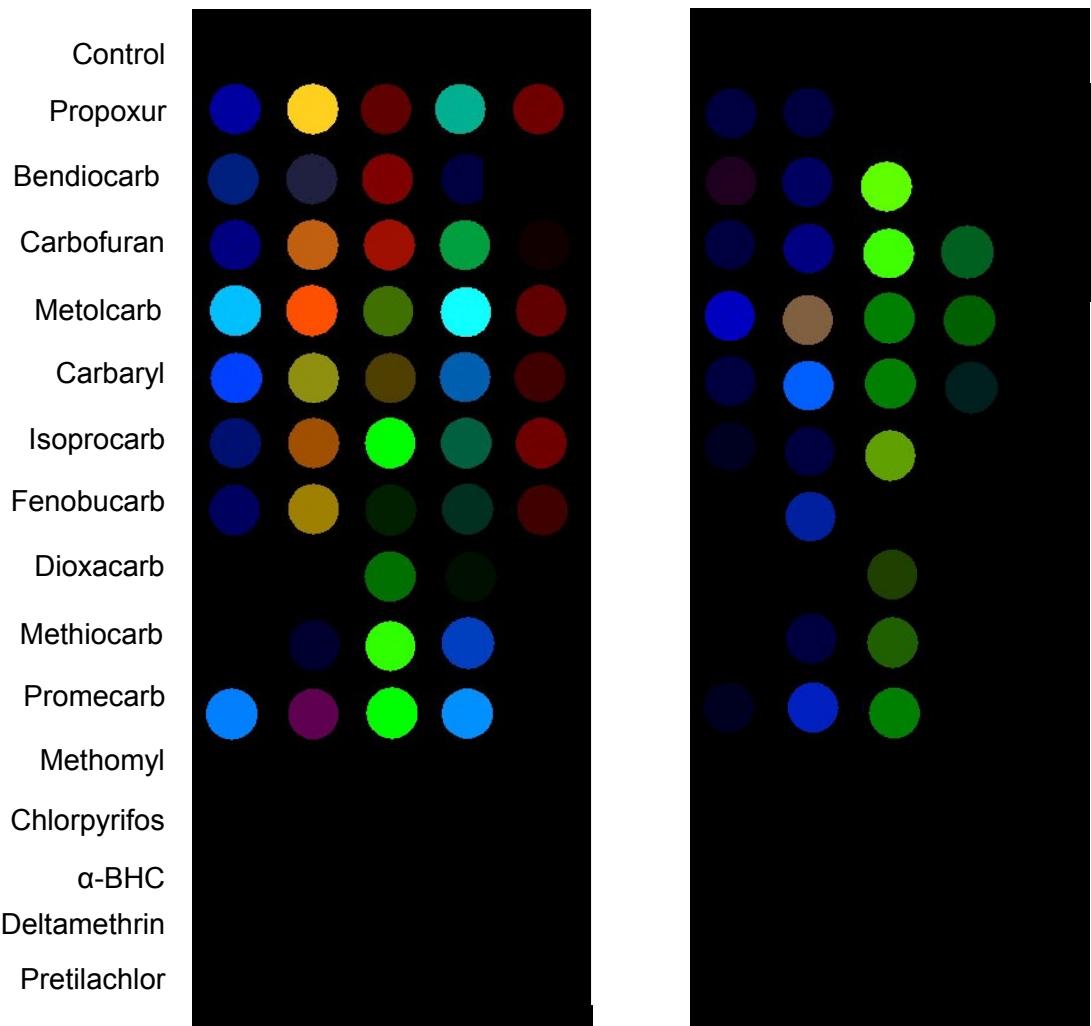


Fig. S3 Color difference maps of the array for all of the investigated pesticides and a control. The concentrations of N-methyl carbamates were 10^{-4} g/L (left) and 10^{-5} g/L (right), respectively; organophosphates (i.e., chlorpyrifos), other kind of carbamates (i.e., methomyl), organochlorines (i.e., α -BHC), pyrethroids (i.e., deltamethrin) and herbicides (i.e., pretilachlor) were at 10^{-3} g/L. For purposes of visualization, the color range of the difference maps for all the pesticides and a control was expanded from 4 to 8 bits per color (RGB range of 4-19 expanded to 0-255, left) and 3 to 8 bits per color (RGB range of 3-10 expanded to 0-255, right). A full database of the color differences are shown in Tables S3 (For each row, the 15 numbers represent the change in R, G, and B values of the 1×5 array, i.e., after exposure – before exposure). All of the experiments were performed in quintuplicate.

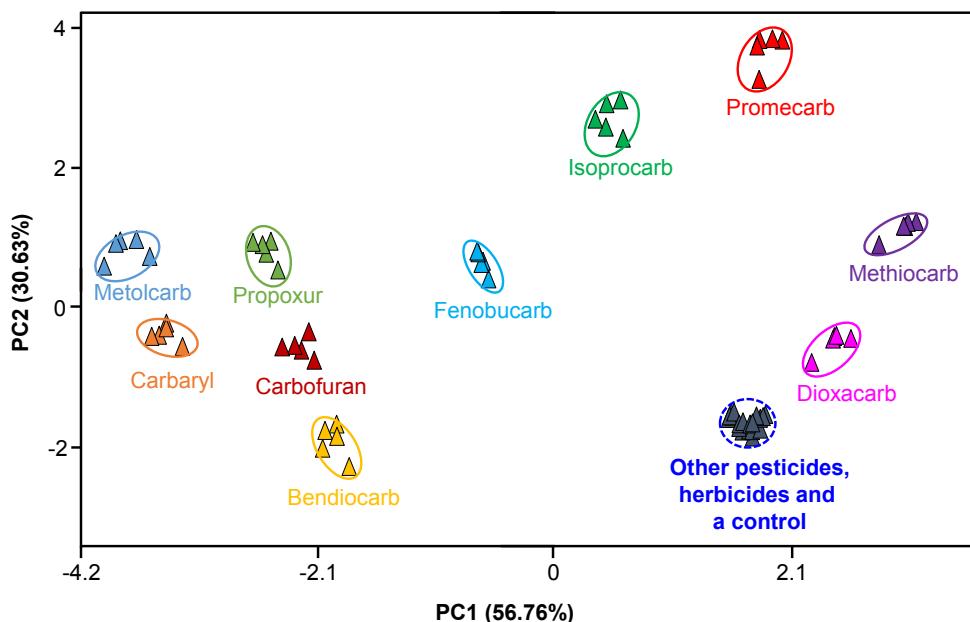


Fig. S4 Two-dimensional principal component analysis plot of the array for N-methyl carbamates, organophosphates (chlorpyrifos), other kind of carbamates (methomyl), organochlorines (α -BHC), pyrethroids (deltamethrin), herbicides (pretilachlor), and a control. All of the experiments were performed in quintuplicate. The concentrations of N-methyl carbamates were 10^{-4} g/L; others were at 10^{-3} g/L.

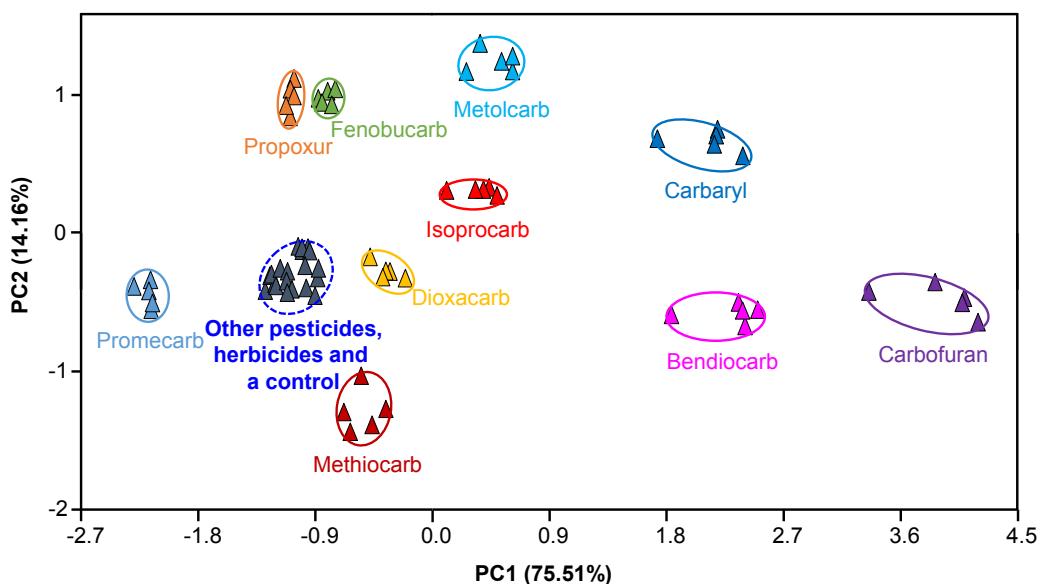


Fig. S5 Two-dimensional principal component analysis plot of the array for N-methyl carbamates, organophosphates (chlorpyrifos), other kind of carbamates (methomyl), organochlorines (α -BHC), pyrethroids (deltamethrin), herbicides (pretilachlor), and a control. All of the experiments were performed in quintuplicate. The concentrations of N-methyl carbamates were 10^{-5} g/L; others were at 10^{-3} g/L.

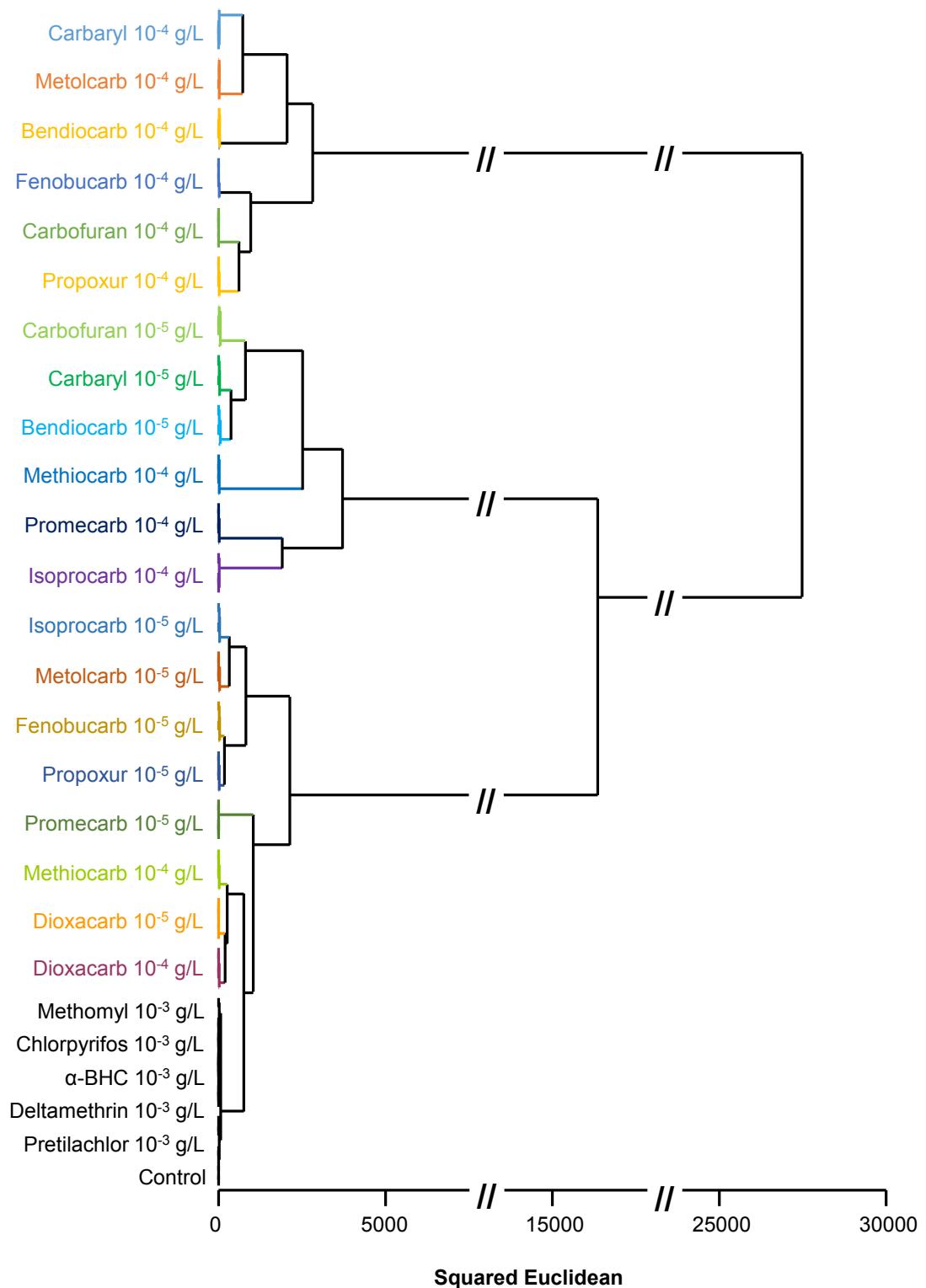


Fig. S6 Hierarchical cluster analysis for N-methyl carbamates, organophosphates, other kinds of carbamates, organochlorines, pyrethroids, herbicides and a control. All of the experiments were performed in quintuplicate.

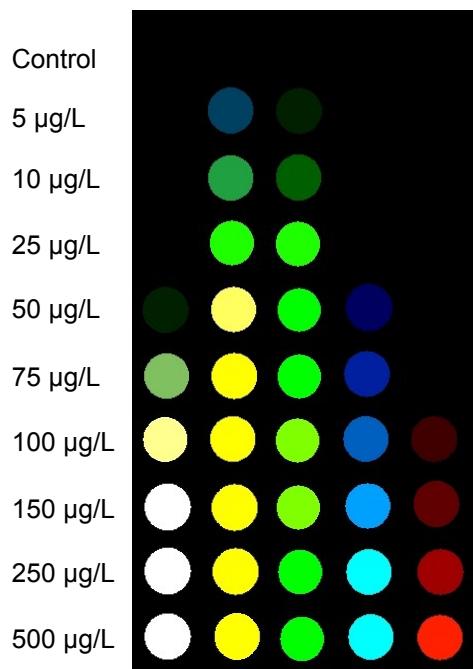


Fig. S7 Color difference maps of the array for carbaryl at different concentrations and a control. For purposes of visualization, the color range of these difference maps of methomyl was expanded from 3 to 8 bits per color (RGB range of 3-10 expanded to 0-255). All of the experiments were performed in triplicate.

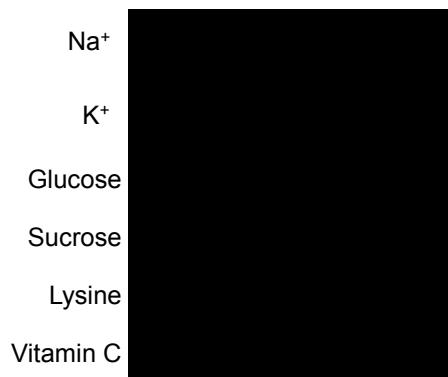


Fig. S8 Color difference maps of the array for a variety of possible interferants in food samples; the color range of these difference maps was expanded from 3 to 8 bits per color (RGB range of 3-10 expanded to 0-255). All of the experiments were performed in triplicate. The concentrations of Na⁺, K⁺, glucose, sucrose, lysine and vitamin C were 10⁻³ g/L.

Table S2 The RSDs for the quintuplicate tests.

N-methyl carbamates	RSDs	
	10^{-5} g/L	10^{-4} g/L
Carbaryl	6.8%	2.0%
Metolcarb	4.8%	2.5%
Isoprocarb	6.9%	4.7%
Carbofuran	6.4%	2.7%
Propoxur	7.0%	3.3%
Promecarb	4.7%	4.6%
Methiocarb	1.3%	5.2%
Bendiocarb	6.6%	2.8%
Dioxacarb	1.1%	13.5%
Fenobucarb	6.0%	5.1%

Table S3 Database for pesticides at different concentrations and a control (R1 to R5, G1 to G5, and B1 to B5 refer to the differences of the red, green, and blue (RGB) values from the center of every indicator solution (in 96-well plates) from the “before” and “after” images, respectively).

	R1	G1	B1	R2	G2	B2	R3	G3	B3	R4	G4	B4	R5	G5	B5
Control-1	-0.626083	0.350723	0.040573	0.770233	1.130081	1.21373	-0.30011	-0.504951	-0.000683	-0.012634	-0.07341	0.13623	-0.09491	-0.448959	-1.042343
Control-2	-0.292755	0.7536	0.142029	0.659271	1.268005	0.907135	-0.189484	-0.174126	-0.000683	0.07341	-0.116776	0.106522	-0.372131	-0.284393	-1.091171
Control-3	-0.623184	0.365219	0.269562	0.905777	1.158752	1.162506	-0.455109	0.1847	0.000683	0.025604	-0.031403	0.184708	-0.095596	-0.419937	-0.855576
Control-4	-0.573914	0.260864	0.104355	0.854904	1.162521	1.067261	-0.331177	-0.209969	0.002048	0.015717	-0.052933	0.18779	0.05394	-0.319901	-1.253326
Control-5	-0.544922	0.281158	0.379715	0.55719	1.250946	0.956985	-0.397736	0.346535	0.002731	-0.01948	-0.106522	0.167969	-0.009216	-0.445451	-1.305908
propoxur 10-4 g/L-1	2.7173	4.993515	14.997955	19.599182	17.662003	6.707397	-6.467041	0	0.456802	15.60704	13.268005	11.086029	12.38647	0.659271	
propoxur 10-4 g/L-2	3.444519	5.824509	16.22908	21.084671	18.690338	8.09935	-5.320923	-0.309322	0.002048	1.156021	16.627869	14.166946	10.711853	1.613174	0.127686
propoxur 10-4 g/L-3	2.27211	4.681122	14.916687	21.581085	19.171738	8.132126	-5.407654	-1.513485	-0.004438	1.251282	16.825882	14.34552	10.780136	1.432528	0.226349
propoxur 10-4 g/L-4	2.711166	5.171387	15.325714	21.703659	19.32605	8.739151	-5.381363	-0.572552	-0.000341	1.365311	17.32811	14.78627	10.760315	1.231812	-0.047104
propoxur 10-4 g/L-5	3.743256	5.942993	15.772263	21.764084	18.899612	8.673264	-5.25708	-0.989758	-0.002048	1.554108	17.528503	14.872314	11.392288	2.110275	1.079208
bendiocarb 10-4 g/L-1	1.950836	6.034194	12.585526	6.862411	6.830307	8.747345	-8.81221	-20.44519	0	0.192178	4.91362	8.059738	0.530534	0.532608	0.204163
bendiocarb 10-4 g/L-2	2.540115	9.948105	16.918747	7.794128	7.130768	9.518428	-6.602249	-17.309666	0.004438	1.41925	5.182663	8.218842	0.252655	-0.081589	-0.299298
bendiocarb 10-4 g/L-3	2.011612	10.379303	17.03653	7.627853	6.862076	9.486176	-7.249237	-18.577328	-0.001707	1.55275	5.117447	8.232849	0.930359	0.569489	0.570847
bendiocarb 10-4 g/L-4	1.996597	8.699203	15.87027	8.7265	6.833389	9.539764	-7.45134	-18.309662	0.010925	1.437012	5.036545	8.361206	0.240356	-0.034836	-0.358139
bendiocarb 10-4 g/L-5	2.817688	8.874023	15.825776	7.606689	5.929321	8.427444	-8.430176	-20.552067	0.004097	1.495728	5.053604	8.400818	0.952194	0.694778	0.91806
Carbofuran 10-4 g/L-1	2.336288	3.690338	12.251282	16.961075	10.206894	5.596786	-8.994537	0	1.035507	14.836472	8.385452	4.876404	-0.504608	-0.664734	
Carbofuran 10-4 g/L-2	3.048141	6.424451	13.631271	18.12223	10.643234	4.985978	-7.436325	-8.621029	0.004438	1.748383	15.857971	9.150988	5.200409	-0.318192	-0.287125
Carbofuran 10-4 g/L-3	1.914642	3.527481	12.368713	18.124619	10.862762	6.48378	-8.072723	-10.546604	-0.004097	1.898254	16.127686	9.127014	5.091507	-0.445877	-0.3479
Carbofuran 10-4 g/L-4	2.506317	3.89621	12.452042	18.28064	11.019791	6.561966	-8.502213	-10.329803	0.001707	1.949463	16.377609	9.472855	5.556152	0.14476	0.167984
Carbofuran 10-4 g/L-5	2.978836	4.472183	13.44075	18.024582	10.859665	6.312729	-8.588593	-11.238651	0.001707	2.219528	16.680435	9.690985	5.115738	0.104813	0.317856
Metolcarb 10-4 g/L-1	1.688965	16.077499	27.658585	19.545242	9.938202	-0.563339	-9.858679	-11.229774	0	5.311707	20.756309	19.130081	10.891083	1.680485	0.272095
Metolcarb 10-4 g/L-2	2.946411	14.41243	25.452713	19.806427	9.681808	-1.061798	-8.517242	-10.035847	0.003756	5.99147	21.683517	19.79924	11.005127	1.309662	0.172073
Metolcarb 10-4 g/L-3	2.120514	11.538406	22.761353	20.188797	9.987171	-1.441101	-8.893143	-10.835438	-0.005804	5.609085	21.542257	19.509735	11.565384	1.72551	0.683167
Metolcarb 10-4 g/L-4	2.472519	13.836792	24.938202	20.511444	10.26561	-1.089462	-9.634689	-11.019798	0.009901	6.011597	22.564697	12.219119	11.056335	1.157043	0.176178
Metolcarb 10-4 g/L-5	3.595764	12.897919	23.697845	20.181625	9.832703	-1.43428	-10.634689	-13.70229	0.004097	6.336624	22.739502	21.055313	11.050522	1.206894	0.560593
Carbaryl 10-4 g/L-1	2.756561	8.132477	23.359512	13.855591	13.789337	5.051544	-11.095596	-16.735748	0	1.554108	19.105129	15.308975	7.906448	0.603622	-0.560257
Carbaryl 10-4 g/L-2	4.349274	11.058044	22.412237	15.106522	14.328111	5.893478	-10.513824	-15.120174	0.004438	1.855927	11.573242	15.736084	8.471161	0.827927	-0.649033
Carbaryl 10-4 g/L-3	2.870605	9.565369	23.770218	15.182999	14.456131	6.009641	-10.794815	-16.475246	-0.001024	2.193924	11.826904	15.812912	8.750427	1.117447	0.115402
Carbaryl 10-4 g/L-4	2.359177	7.971649	24.927277	15.359512	16.432162	-11.274155	-16.86412	-0.11949	1.759644	11.838653	15.819046	8.89006	1.814357	0.021515	
Carbaryl 10-4 g/L-5	2.579376	7.476959	24.575254	15.281326	14.302429	5.76886	-9.917374	-15.491978	0.00478	2.257058	12.231812	16.038643	9.108566	1.617966	0.976089
Isoprocarb 10-4 g/L-1	2.067596	5.334595	11.225342	14.182663	9.048477	-0.884613	-1.96312	-22.608055	-0.003073	2.262878	10.185394	8.441101	11.378281	1.401169	-0.01059
Isoprocarb 10-4 g/L-2	3.641861	7.105148	13.18573	15.318542	9.833054	-0.696823	-0.517242	-26.24159	0	1.547108	19.105129	15.308975	7.906448	0.603622	-0.616943
Isoprocarb 10-4 g/L-3	2.730286	6.212692	12.254684	14.328781	9.650742	-1.014343	-1.296692	-22.941959	0.0015364	3.050522	11.497101	12.206162	11.447601	1.249573	-0.057022
Isoprocarb 10-4 g/L-4	3.214752	6.788666	12.732681	15.06282	9.962969	-1.428818	-1.500854	-23.119495	0.003414	3.139633	11.912949	9.652435	11.417542	1.131104	-0.036865
Isoprocarb 10-4 g/L-5	3.627182	7.365997	13.200058	14.842941	9.265243	-1.924746	-2.066574	-24.972343	-0.003756	3.403214	12.072372	9.680786	11.76442	1.578018	0.944687
Fenobucar 10-4 g/L-1	2.04541	4.125305	10.493347	14.615906	12.229767	4.541138	-0.69101	3.574257	0.000683	1.060425	7.980914	6.518424	8.693405	1.644952	0.657211
Fenobucar 10-4 g/L-2	2.037216	4.380676	10.863777	16.409363	13.307617	6.078857	0.165588	5.593037	0.00239	1.594055	8.663712	6.89621	7.992493	0.876755	-0.091156
Fenobucar 10-4 g/L-3	1.571518	3.90065	10.348923	16.520309	13.531921	6.306931	0.527145	5.346878	0.001366	1.717651	6.753494	6.750427	9.233762	1.774005	0.968582
Fenobucar 10-4 g/L-4	1.92012	4.353699	10.910217	16.727554	6.494019	4.949536	6.379993	0.000341	1.728912	9.100723	7.227371	8.834747	1.300781	1.764002	
Fenobucar 10-4 g/L-5	2.555085	4.791748	10.955948	16.640152	13.693405	6.489929	0.035955	6.455788	0.001707	1.800278	9.174118	7.181976	9.095932	1.68692	1.286438
Dioxacarb 10-4 g/L-1	-0.221237	0.057358	0.283707	0.427094	-0.346199	0.508369	3.512466	3.4000216	0.02316	1.279266	-0.815292	-0.174454	1.273182	-0.174454	-0.174454
Dioxacarb 10-4 g/L-2	-0.016037	0.556503	1.210312	-0.112671	-1.198021	-0.806001	4.229095	11.405251	-0.00239	1.9935	-0.273132	-0.16217	1.9935	-0.16217	-0.16217
Dioxacarb 10-4 g/L-3	-0.147842	0.190842	0.39502	-0.691136	-1.789001	-0.504265	4.404572	12.156029	-0.005463	1.857635	-0.312042	-0.340057	1.857635	-0.312042	-0.340057
Dioxacarb 10-4 g/L-4	-0.182132	0.282349	0.772614	-0.365646	-1.723457	-0.997269	3.575958	11.147491	0	2.376236	0.260834	-0.006149	2.376236	0.260834	-0.006149
Dioxacarb 10-4 g/L-5	0.027664	0.27449	0.598696	-0.802031	-1.44384	-0.028273	4.164215	11.994194	0	2.354058	0.191193	0.090914	2.355408	0.191193	0.090914
Methiocarb 10-4 g/L-1	-1.326721	-0.590988	-0.617279	3.272446	0.08091	-7.807098	-7.202454	22.726207	0.021168	1.148849	2.186401	2.691017	1.148849	2.186401	2.691017
Methiocarb 10-4 g/L-2	-1.393982	-0.613861	-0.237976	3.398773	0.593719	-9.897232	-8.027649	24.664391	0	0.832352	1.273132	0.832352	1.273132	0.832352	1.273132
Methiocarb 10-4 g/L-3	-0.988052	-0.423355	-0.159439	2.810516	-0.774323	-7.193374	-7.333477	25.666779	-0.005463	1.773651	0.26282	0.752823	1.773651	0.26282	1.773651
Methiocarb 10-4 g/L-4	-1.096968	-0.309033	-0.200776	2.703659	-1.238647	-10.250938	-8.053604	25.141685	0	1.240625	2.362579	2.811195	1.242065	2.362579	2.811195
Methiocarb 10-4 g/L-5	-0.601227	0.000687	0.206223	2.68692	-1.075798	-2.3									

	R1	G1	B1	R2	G2	B2	R3	G3	B3	R4	G4	B4	R5	G5	B5
Dioxacarb 10-5 g/L-1	-0.208252	0.139969	0.534302	2.349258	1.822815	0.814613	3.767838	3.04541	0.023216	-0.061111	0.988388	2.089447	-0.60498	-0.398422	-0.847382
Dioxacarb 10-5 g/L-2	-0.170364	0.095245	0.322296	2.238647	1.688293	0.232849	4.936508	5.340042	0	0.092514	1.453384	2.742584	-0.67157	-0.420624	-0.906792
Dioxacarb 10-5 g/L-3	-0.027664	0.265961	0.400131	2.25708	1.519974	0.321953	4.528503	4.363266	-0.001366	-0.115402	1.343796	2.477982	-0.590988	-0.493347	-0.875725
Dioxacarb 10-5 g/L-4	-0.027649	0.293945	0.447922	2.223282	1.496414	0.173439	4.088425	4.213722	0	0.095245	1.297028	2.659958	-0.694427	-0.39946	-0.911575
Dioxacarb 10-5 g/L-5	-0.044373	0.317505	0.621719	2.097641	1.456467	-0.302155	3.829971	4.273125	0	-0.049164	1.004776	1.934448	-0.632629	-0.337311	-0.672585
Methiocarb 10-5 g/L-1	-0.513824	-0.288162	-0.621719	-1.228409	-2.911232	-3.653122	3.623764	4.978149	0.021168	-0.890411	-0.007858	1.158417	0.655853	1.023209	1.26664
Methiocarb 10-5 g/L-2	-0.005112	0.290878	0.199722	-2.018433	-3.946396	-5.52475	4.128036	7.094566	0	-0.931717	0.055298	1.160126	0.426758	0.623077	0.595428
Methiocarb 10-5 g/L-3	-0.054977	0.005127	-0.464661	-2.664047	-4.727898	-6.041649	4.231476	6.488564	-0.003414	-0.656891	0.220551	1.191193	0.320938	0.615921	0.694435
Methiocarb 10-5 g/L-4	0.171738	0.378616	0.015015	-3.089447	-5.537727	-7.172073	3.538742	5.441444	0	-0.637421	0.187439	1.225677	0.502563	0.799927	1.037552
Methiocarb 10-5 g/L-5	0.283371	0.41243	0.049515	-3.006836	-5.255043	-6.110275	2.801636	4.77774	0	-0.589615	0.506317	1.639465	0.545578	0.784576	1.03653
Promecarb 10-5 g/L-1	-0.506653	1.192551	4.290192	-1.223969	-3.153633	-6.850113	-1.28952	-8.289856	0.018778	0.207916	1.695114	2.507339	0.674973	0.742905	0.753159
Promecarb 10-5 g/L-2	-0.492645	1.613861	5.28508	-1.936493	-4.510071	-9.072716	-1.329453	-7.589287	0	0.314102	1.794464	2.530212	0.213379	0.25264	0.335953
Promecarb 10-5 g/L-3	-0.404587	1.244446	4.635376	-1.56163	-4.001709	-7.422325	-1.75351	-9.068962	0.001024	0.264923	1.586884	2.272797	0.193924	0.320938	0.470467
Promecarb 10-5 g/L-4	-0.607361	1.317856	4.900986	-1.446564	-3.927277	-7.665413	-1.38443	-8.117111	0	0.428131	1.644592	2.216461	0.375565	0.352341	0.354042
Promecarb 10-5 g/L-5	-0.312393	1.520645	5.138275	-1.991119	-4.538063	-8.094574	-1.537735	-7.621033	0	0.194611	1.509735	2.09082	0.403549	0.419266	0.770569
Pretilachlor 10-3 g/L-1	-1.337997	-1.570831	-2.833725	0.538071	0.751114	-0.197327	-1.184708	-1.288147	-3.016037	-0.669861	-0.698196	-0.088074	-0.25264	0.059052	-0.245132
Pretilachlor 10-3 g/L-2	-0.223969	-0.44281	-1.479691	0.377945	0.908173	-0.19426	-1.073395	-1.346527	-2.684189	-0.772629	-0.566406	-0.386826	-0.199722	-0.076813	-0.118469
Pretilachlor 10-3 g/L-3	-0.361893	-0.657898	-1.813934	0.484467	0.649017	-0.246506	-0.744293	-0.955276	-3.456474	-0.736084	-0.568787	-0.426773	-0.097305	-0.074417	-0.338684
α -BHC 10-3 g/L-1	-0.86377	-0.725845	-0.449631	0.519974	0.779785	-0.48822	-0.697159	-1.356094	-3.387497	-0.875046	-0.564362	-0.338013	0.023895	-0.238312	-0.088089
α -BHC 10-3 g/L-2	-0.49881	-0.246841	0.078186	0.411407	0.746338	-0.131775	-0.488907	-1.006836	-2.792755	-0.654144	-0.771255	-0.556503	-0.048477	-0.110626	-0.296356
α -BHC 10-3 g/L-3	-0.476273	-0.320236	-0.136566	0.352005	0.863083	-0.106186	-0.24855	-0.557175	-2.52681	-0.680435	-0.559921	-0.446915	-0.122574	-0.109589	-0.336975
Methomyl 10-3 g/L-1	-1.544205	-1.414474	-1.173096	0.486511	0.629562	-0.281998	-0.374878	-0.921478	-2.761688	-0.808807	-0.641525	-0.460907	-0.778427	-0.753494	-0.079895
Methomyl 10-3 g/L-2	-1.007858	-0.898254	-0.505981	0.589951	0.588943	-0.222595	0.001709	-0.474213	-2.70195	-0.779785	-0.441788	-0.536026	-0.803345	-0.874023	0.321609
Methomyl 10-3 g/L-3	-1.019455	-0.759308	-0.643219	-0.161819	0.42746	-0.515884	0.394333	-0.132462	-2.3974	-0.314102	-0.16217	-0.059402	-0.735062	-0.688965	-0.121872
Deltafemethrin 10-3 g/L-1	-1.625473	-1.503586	-1.832016	0.349945	0.630249	-0.024918	0.234879	-0.275528	-2.52919	-0.541809	-0.404922	-0.315125	-0.859009	-0.923172	-0.077148
Deltafemethrin 10-3 g/L-2	-0.582108	-0.374191	-0.746338	0.181641	0.495392	-0.097977	1.037552	0.569473	-2.145096	-0.612503	-0.320587	-0.381012	-0.78833	-0.925232	-0.318207
Deltafemethrin 10-3 g/L-3	-0.705017	-0.562988	-1.040283	0.222946	0.517242	-0.403214	1.593384	1.109589	-1.068283	-0.44725	-0.133499	-0.117096	-0.675323	-0.943665	-0.136566
Chlorpyrifos 10-3 g/L-1	-0.254364	-0.313065	-1.33049	0.259811	0.909531	1.089096	0.261871	1.240021	1.523041	-0.471832	-0.426758	-0.951859	-0.886658	-0.651077	-0.207932
Chlorpyrifos 10-3 g/L-2	-0.86377	-0.725845	-0.449631	0.368042	1.092178	1.36293	0.435638	1.042343	1.569122	-0.575958	-0.339706	-0.845337	-0.915329	-0.683853	-0.232849
Chlorpyrifos 10-3 g/L-3	-0.934799	-0.694443	-1.111984	0.533966	1.135193	1.580734	0.274155	0.225677	0.008881	-0.553085	-0.359177	-1.257431	-0.278946	-0.355408	0.15535