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Flourescence-Based Detection of Pesticides via Conjugated Polymer Nanoparticles

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FLOURESCENCE-BASED DETECTION OF PESTICIDES
VIA CONJUGATED POLYMER NANOPARTICLES

BY

WILLIAM J TALBERT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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OF
WILLIAM J TALBERT

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2015

ABSTRACT

The use of synthetic pesticides has played a large role in increasing crop yields throughout the world, but their adverse effects on humans and non-target animals is of major concern due to their toxicity and persistence in the environment. Some of the more persistent examples are organochlorine pesticides, particularly dichlorodiphenyltrichloroethane (DDT) and its metabolites. Reported herein is the development of a detection scheme using organic nanoparticles for the fluorescence detection of a range of pesticides. The nanoparticles were fabricated from a synthetic conjugated fluorescent polymer, and fluorescence experiments were performed using both nanoparticle solution and polymer thin films.

The large extinction coefficients exhibited by conjugated fluorescent polymers (also referred to as conjugated amplifying polymers), such as the one discussed herein, make them useful for chemical detection schemes. In order to maintain this strong fluorescence of the polymer in solution, it must be in an aggregated state, which allows for both intra-polymer and inter-polymer exciton transfer. To achieve this aggregated state in solution, the formation of polymer nanoparticles is used. These nanoparticles allow the polymer to be used for chemical detection of pesticides in solution via fluorescence enhancement.

The 2,1,3-benzooxadiazole-alt-fluorene (PFBO) polymer nanoparticles discussed herein were fabricated using the reprecipitation method, which is the formation of spherical particles as a result of the hydrophobic collapse of the polymer in an aqueous solution, and average particle size was confirmed using dynamic light

scattering. In solution, a limit of detection of 4.5 ppm was achieved for DDT in the presence of the PFBO nanoparticles.

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This work is dedicated to all of the people in my life whose support has made all of this possible. Thank you all for your love and support.

PREFACE

The dissertation of my research has been presented in manuscript format according to guidelines of the graduate school of the University of Rhode Island. The complete dissertation is divided into two manuscripts. The first manuscript (Chapter 1) is being prepared for submission to *Analytica Chimica Acta* with authors W. Talbert, J. Morimoto, and M. Levine. The second manuscript (Chapter 2) was published in *Journal of Chemical Education* in 2015.

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CHAPTER 1

Preparing for Submission to *Analytica Chimica Acta*

Turn-On Detection of Pesticides via Reversible Fluorescence

Enhancement of Conjugated Polymer Nanoparticles and Thin Films

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Manuscript 1

Turn-On Detection of Pesticides via Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin Films

ABSTRACT

Reported herein is the significant fluorescence enhancement of conjugated polymer nanoparticles in the presence of a variety of aromatic organochlorine pesticides. This pesticide-mediated fluorescence enhancement leads to reversible pesticide detection systems with high sensitivity (as low as 5 μ M), as well as significant generality and straightforward reversibility.

INTRODUCTION

The widespread use of pesticides has been highly effective in increasing the harvested yields of many crops worldwide through eliminating the threat of common pests, but their use has also been of concern due to their known and suspected toxicity to humans and other species and long term environmental persistence.¹ One class of pesticides that is of continuing concern is organochlorine pesticides (OCPs), the most common of which is dichlorodiphenyltrichloroethane (DDT), sold commercially as a mixture of the para, para- (compound 1, Chart 1) and ortho, para- (compound 4) isomers.² Dichlorodiphenyldichloroethane (DDD, compound 2) and dichlorodiphenyldichloroethylene (DDE, compound 3) are some of the primary metabolites of DDT, also with known toxicities.³ Other pesticide classes of interest include: (a) aliphatic organochlorines 5 and 6; (b) carbamate pesticides 7 and 8, which are less environmentally persistent but still pose acute health risks;⁴ and (b) synthetic

pyrethroids 9 and 10, which are less acutely toxic and less environmentally persistent, and have been increasing in usage in recent years.⁵

Techniques for the detection of organic pesticides generally rely on chromatography followed by mass spectrometry.⁶ These methods offer good sensitivity and resolving power, but suffer from the high cost of operation and tedious and timeconsuming sample preparations,⁷ which limits the ability to conduct high throughput assays. Newer techniques for pesticide detection include molecularly imprinted polymer systems,⁸ nanoparticle-based immunoassays,⁹ and gold nanoparticle-based Raman spectroscopy.¹⁰ A variety of fluorescence-based methods for pesticide detection have also been reported,¹¹ although in many cases these methods require derivatization steps,¹² chromatographic purification,¹³ and/or are substantially limited in terms of the range of pesticides that can be detected.¹⁴

One method of detection that has shown a lot of promise in the detection of multiple classes of analytes with extremely high sensitivity and selectivity is the use of conjugated fluorescent polymer sensors.¹⁵ Typically, detection efficiencies are optimal in polymer aggregates such as thin films¹⁶ or conjugated nanoparticles,¹⁷ which enable inter-polymer as well as intra-polymer exciton migration.¹⁸ Formation of conjugated polymer-derived nanoparticles can occur through a variety of methods,¹⁹ including reprecipitation,²⁰ in which the hydrophobic polymer collapses upon its introduction into aqueous solution, resulting in the formation of well-defined spherical

nanoparticles.

Figure 1. Pesticides (1-10), polymer 11, and control analytes 12 and 13

Reported herein is the detection of DDT and its metabolites (compounds 1-4) via the fluorescence enhancement of nanoparticles derived from conjugated organic polymers. These particles were fabricated via the reprecipitation of 2,1,3-benzoxadiazole-alt-fluorene (PFBO, polymer 11), synthesized following literature-reported procedures.²¹ This polymer was fully characterized by spectroscopic techniques, with a $M_n = 3.8 \times 10^3$ g/mol and $M_w = 7.3 \times 10^3$ g/mol. The polymer-derived nanoparticles were characterized by dynamic light scattering experiments, with an average particle diameter of 139 nm (see ESI for details on the polymer and nanoparticle characterizations).

The degree of fluorescence changes observed with the introduction of small molecule pesticides to the nanoparticle (or free polymer) solution was calculated according to Equation 1:

$$\% \text{ Change} = \text{PFBO}_{70\mu\text{M}} / \text{PFBO}_{0\mu\text{M}} \quad (\text{Eq. 1})$$

where $\text{PFBO}_{70\mu\text{M}}$ is the integrated polymer fluorescence in the presence of 70 μM analyte, and $\text{PFBO}_{0\mu\text{M}}$ is the integrated polymer fluorescence in the presence of 0 μM analyte. Little to no fluorescence interference from the pesticides themselves is expected due to the fact that these analytes show absorption and emission maxima primarily in the ultraviolet region of the UV-Vis spectra,²² well removed from the absorption and emission of the donor-acceptor polymer (λ_{max} absorption: polymer = 413 nm; nanoparticles = 411 nm; λ_{max} emission: polymer = 507 nm; particles = 534 nm).²³ The concentration of **11** was varied (see ESI for more details), and optimal fluorescence responses were obtained with a 1.25×10^{-3} mg/mL polymer solution.

Results of the fluorescence modification experiments are shown in Table 1, and key trends are discussed in further detail below.

Table 1. Average % change fluorescence of PFBO 11 with added pesticide		
Analyte	% Change Particle^a	% Change Polymer^a
1	224	100
2	117	103
3	346	101
4	308	101
5	92	103
6	89	101
7	100	102
8	101	103
9	210	100
10	333	99
<i>a</i> % Change calculated according to Equation 1: [PFBO particles] = 1.25 E^{-3} mg/ml; [PFBO polymers] = 1.25 E^{-3} mg/mL

Figure 2. Fluorescence changes of PFBO nanoparticles in the presence of pesticides: (A) Compound 1; (B) Compound 2; (C) Compound 3; and (D) Compound 4. The red line represents the fluorescence of PFBO particles in the presence of 70 μM pesticide and the black line represents the fluorescence of PFBO in the presence of 0 μM pesticide. $[\text{PFBO}] = 1.25 \times 10^{-3} \text{ mg/mL}$.

Fluorescence enhancements of the PFBO nanoparticles were observed in the presence of DDT, o,p-DDT, DDD, and DDE (compounds 1-4, Figure 1). These analytes have similar molecular conformations and electrostatic potential surfaces, as shown through visual inspection of the structures shown in Figure 2, which are different from the other pesticide surfaces shown. Namely, analytes 1-4 all contain localized electron-deficient areas on the electrostatic potential surfaces, whereas other

analytes either contain more diffuse electron-deficient regions or less clearly defined electron deficient potential surfaces available for polymer-analyte interactions.

Figure 3. Electrostatic potential surfaces of analytes **1-10** and a monomeric unit of polymer **11**, calculated using Spartan 10.

Other pesticide classes with significantly different architectures effected markedly different, class-specific fluorescence changes, with the addition of aliphatic organochlorine pesticides **5** and **6** leading to moderate fluorescence quenching; the addition of carbamates **7** and **8** leading to no fluorescence changes; and the addition of pyrethroids **9** and **10** causing overall fluorescence enhancements. However, in the case of pyrethroids **9** and **10**, the increase in the fluorescence emission was not linear with increasing concentration of the analyte, which suggests the existence of more complicated, possibly multiple co-existing analyte-polymer interactions.

Differences in the behaviors of analytes **1-4** compared to **5** and **6** indicates the importance of the aromatic moieties (and not just the electron deficient character) in facilitating the observed fluorescence increases of polymer **11**. The lack of fluorescence enhancement observed in the presence of non-aromatic organochlorine pesticides is likely due to their lack of aromatic character which prevents them from engaging in favorable π - π stacking interactions.²⁴

Overall, the fact that each class of pesticides investigated led to unique fluorescence responses in the nanoparticles highlights the strong relationship between key structural features of the analytes and their interactions with the fluorescent polymer that result in measurable fluorescence changes. Moreover, it indicates the potential of developing class-specific pesticide detection schemes based on these interactions. Interestingly, none of the pesticides led to noticeable changes in the size of the nanoparticles as measured by dynamic light scattering experiments (Figure 3), indicating that the fluorescence changes are due to more subtle mechanisms (*vide infra*).

In contrast to the strong and unique fluorescence responses observed in the case of the conjugated polymer-derived nanoparticles, the conjugated polymer itself displayed a marked insensitivity to the presence of any of the pesticides investigated (Table 1, Figure 4). The strong dependence of the PFBO fluorescence responses on its aggregation state indicates the necessity of inter-chain polymer communication to enable efficient fluorescence enhancement behaviors, a result that has been demonstrated previously in the literature for the detection of other analytes, although not for the detection of pesticides to date.²⁵

Figure 4. Dynamic light scattering experiments of polymer **11**-derived nanoparticles with (A) pesticide **1** and (B) pesticide **2**, indicating no significant changes in particle size in the presence of the pesticides.

Figure 5. Fluorescence changes of PFBO polymer in the presence of pesticides: (A) compound **1**; and (B) compound **2**. The red line represents the fluorescence of PFBO in the presence of 70 μM pesticide and the black line represents the fluorescence of PFBO in the presence of 0 μM pesticide. [PFBO = 1.25×10^{-3} mg/mL].

Literature precedent by Swager and co-workers demonstrated that fluorescent polymer thin films underwent substantial fluorescence enhancements as a result of analyte-mediated reduction of the polymer chain, an effect that was easily reversed by introduction of iodine for re-oxidation.²⁶

Other examples of the susceptibility of conjugated polymer-derived nanoparticles to oxidation and reduction have also been reported.²⁷ Similar reversibility was observed in this nanoparticle system, with the fluorescence increases demonstrated by solutions of polymer **11**-derived nanoparticles in the presence of analyte **1** nearly completely reversed with the addition of iodine (Figure 5A and 5B), pointing to the strong likelihood of an oxidation-reduction mechanism. This fluorescence switching was reversible over several cycles (Figure 5C)

The sensitivity of this detection system was quantified by calculating the limits of detection for analytes **1-4** using literature-reported methods, and the results are summarized in Table 2. These results highlight that the pesticide-induced fluorescence enhancement of conjugated polymer-derived nanoparticles is a sensitive method for pesticide detection, with detection limits approaching the literature-reported levels of concern.²⁸

Figure 6. (A and B) Illustration of redox-dependent fluorescence changes of polymer **11**-derived nanoparticles with alternating additions of I₂ and DDT over 11 cycles.

Table 2. Limits of detection for pesticides 1-4	
Analyte	LOD (μM)
1	5
2	83
3	69
4	58

An extension of this fluorescence-based detection to polymer **11**-derived thin films was conducted by fabricating fluorescent thin films from the spin casting of a polymer **11** solution in chloroform onto glass slides. These films were briefly exposed to the vapor from a solution of DDT **1** in tetrahydrofuran. The measurable response of these films to DDT vapor (Figure 6A) is remarkable considering the low vapor pressure of DDT,²⁹ and indicates high levels of sensitivity in these fluorescent polymer-derived detection systems. Moreover, control experiments indicated that the tetrahydrofuran itself had negligible effects on the photophysical properties of polymer **11** – derived thin films. These fluorescence changes were also reversible with exposure of the thin film to iodine vapor, leading to a nearly complete return to the initial thin film fluorescence state (127% increase followed by 120% decrease, Figure 6).

Figure 7. Fluorescence changes of thin films polymer **11** with exposure to DDT vapors.

Finally, the sensitivity of the nanoparticle fluorescence emission to other aromatic compounds found in food products was measured,³⁰ and neither control analyte was found to effect significant fluorescence changes (102% initial fluorescence with 70 μ M of analyte **12**; 99% initial fluorescence with 70 μ M of analyte **13**). Substantially higher concentrations of the control analytes led to limited fluorescence decreases of the nanoparticle solution (Figure 7), highlighting the selectivity of the system for pesticide analytes.

Figure 8. Fluorescence changes of PFBO nanoparticle solutions in the presence of (A) analyte **12** and (B) analyte **13**. The black line represents emission in the presence of 0 μM analyte, and the blue line represents emission in the presence of 1 mM analyte

In summary, reported herein is the substantial fluorescence enhancement of PFBO-derived nanoparticles and thin films in the presence of aromatic organochlorine pesticides, and marked class-specific fluorescence changes of PFBO-derived nanoparticles in the presence of a variety of other small molecule pesticides. These fluorescence responses have a number of notable features, including: (a) a strong dependence on structural features of the pesticide analytes, with each pesticide class leading to unique and noticeably different fluorescence responses; (b) a requirement for polymer chain aggregation to enable efficient inter-polymer exciton migration; (c) high levels of reversibility through the introduction of iodine vapor for re-oxidation; (d) a ‘turn-on’ rather than ‘turn-off’ fluorescence signal, which has the potential to lead to improved sensitivity in practical detection schemes; and (e) low limits of detection, which approach practical levels of concern in some cases. Efforts towards developing practical turn-on detection systems for aromatic pesticides based on this

research are currently in progress in our research laboratory, and results of these and other investigations will be reported in due course.

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Supporting Information

Turn-On Detection of Pesticides via Reversible Fluorescence Enhancement of Conjugated Polymer Nanoparticles and Thin Films

MATERIALS AND METHODS

All the starting materials, reagents, and solvents were purchased from Sigma Aldrich, Acros Organics, TCI chemicals, Alfa Aesar, or Fisher Scientific and were used as received. All reactions were carried out under an inert atmosphere. Solvents were dried using an MBraun dual solvent purification system prior to use. Reactions were all monitored via analytical thin layer chromatography (TLC) using polyester backed TLC plates. Visualization was accomplished with UV light at 254 nm and/or with a KMnO₄ TLC stain. Product isolation was performed by using preparative TLC plates or silica gel chromatography. Both TLC plates and preparative TLC plates were purchased from Sorbent Technologies, GA. Column chromatography was performed with SiliaFlash F60 (230-400 mesh) silica gel, obtained from Silicycle Inc. Canada.

¹H NMR and ¹³C NMR spectra were taken on a Bruker 300 MHz spectrometer and were recorded in CDCl₃ at ambient temperature. Fluorescence experiments were recorded on a Shimadzu RF 530 spectrophotometer with 1.5 nm excitation and 3.0 nm emission slit widths for solution measurements and 1.5 nm excitation and 1.5 nm emission slit widths for thin films. Absorbance measurements were recorded on an Agilent 8453 UV-visible spectrophotometer.

Thin films were spin-cast onto 22 x 22 cm glass cover slips using a 1.0 mg/mL PFBO solution in chloroform at 1000 rpm for 20 seconds. For fluorescence experiments,

slides were placed on top of a 20 mL vial containing iodine powder or a 1 mg/mL solution of DDT in THF for 10 seconds.

Dynamic light scattering experiments were run on a Malvern Zetasizer Nano ZS90, measuring particle size at 25°C and a 90° measurement angle, using Mark-Houwink parameters for the calculation of molecular weight.

Gel permeation chromatography (GPC) data were obtained using an Agilent Infinity GPC system equipped with three Agilent PLGel columns 7.5 mm x 300 mm (5 µm, pore sizes: 103, 104 and 105 Å).

Molecular weight and Mw/Mn ratios were determined versus PS standards (500 g/mol – 3150 kg/mol; Polymer Laboratories).

Computational work was performed with Spartan software (Spartan 10, version 1.1.0), obtained from Wavefunction, Inc. CA. All calculations were performed using equilibrium geometry at the ground state, semi-empirical PM3 level. All the conformations shown were energy-minimized.

SYNTHESIS OF FLUORESCENT POLYMER 11 Fluorescent polymer 11 was synthesized following procedures described in the references below. All chemical intermediates and products were fully characterized using ¹H and ¹³C NMR spectroscopy. References: Helgesen, M.; Gevorgyan, S. A.; Krebs, F. C.; Janssen, R. E. J. “Substituted 2,1,3- Benzothiadiazole- and Thiophene –Based Polymers for Solar Cells – Introducing a New Thermocleavable Precursor.” *Chem. Mater.* 2009, 21, 4669-4675; Bouffard, J.; Swager, T. M. “Fluorescent Conjugated Polymers that Incorporate Substituted 2,1,3-Benzooxadiazole and 2,1,3-Benzothiadiazole Units.” *Macromolecules* **2008**, 41, 5559-5562.

Figure S1. Synthesis of Polymer 11

EXPERIMENTAL DETAILS

DETAILS OF NANOPARTICLE FABRICATION

PFBO nanoparticles were formed following a modified literature-reported procedure. 2 mL of polymer solution (2 mg/mL) in THF was added to 8 mL of deionized sonicating water. The solution was allowed to sonicate for 30 minutes, at which point the THF was removed by bubbling nitrogen through the solution for 1 hour. An additional 2 mL of deionized water was added to the solution to make a 0.2 mg/mL stock nanoparticle solution.

DETAILS OF THIN FILM FABRICATION

Thin films were spin-cast onto 22 x 22 cm glass cover slips using a 1 mg/mL PFBO solution in chloroform at 1000 rpm for 20 seconds. For fluorescence experiments, slides were placed on top of a 20 mL vial containing iodine powder or a 1 mg/mL solution of DDT for 10 seconds.

FLUORESCENCE EXPERIMENTAL DETAILS

For fluorescence experiments, two solutions were prepared: one containing dilute PFBO nanoparticles in water (Solution A), and one containing dilute pesticide (**1-10**) in acetonitrile (Solution B). For each run, 2 mL of solution A (1.25×10^{-3} mg/mL or 2.50×10^{-4} mg/mL) was added to the cuvette and mixed with 0.5 mL of solution B (0 – 70 μ M).

DYNAMIC LIGHT SCATTERING DETAILS

To study the size of the nanoparticles, dynamic light scattering (DLS) was used. DLS data were obtained using a Malvern Zetasizer Nano S. A 0.0125 mg/mL solution of PFBO nanoparticles in H₂O was used to determine the Z-average (particle diameter) and polydispersity indices (PDI) of the nanoparticles.

DETAILS OF COMPUTATIONAL INVESTIGATIONS

Computational studies were performed on all of the pesticides under investigation in order to study their molecular geometries and electrostatic potentials. Computational work was performed with Spartan software (Spartan 10, version 1.1.0), obtained from Wavefunction, Inc. CA. All calculations were performed using equilibrium geometry at the ground state, semi-empirical PM3 level.

DETAILS FOR LIMIT OF DETECTION EXPERIMENTS

The limit of detection (LOD) is defined as the lowest concentration of analyte at which a signal can be detected. The limit of quantification is defined at the lowest concentration of analyte that can be accurately quantified. These experiments were conducted following literature-reported procedures:

Saute, B.; Premasiri, R.; Ziegler, L.; Narayanan, R. “Gold Nanorods as Surface Enhanced Raman Spectroscopy Substrates for Sensitive and Selective Detection of Ultra-Low Levels of Dithiocarbamate Pesticides.” *Analyst* **2012**, *137*, 5082-5087.

To determine the limit of detection (LOD) and limit of quantification (LOQ), each fluorophore-analyte combination was examined in the following manner: 2 mL of PFBO nanoparticles in H₂O (1.25 e⁻³ mg/mL) was added to a cuvette, then 100 mL of analyte solution (1 mg/mL) in acetonitrile was added in 20 mL portions. All solutions were excited at 420 nm, and fluorescence emission spectra were recorded 6 times for each addition of analyte.

All fluorescence emission spectra were integrated versus wavenumber. Calibration curves were created with analyte concentration (in mM) on the X-axis and the integrated fluorophore emission of the Y-axis. The curve was fitted with a trend line and a corresponding equation for the line was determined.

For the LOD, the limit of the blank was defined by the following equation:

$$LOB_{LOD} = m_{blank} + 3(SD_{blank})$$

Where m is the mean of the blank integrations and SD is the standard deviation.

The LOB value was then inserted into the line equation as the Y-value, and the X-value was solved for, giving the LOD in mM.

For the LOQ, the limit of the blank was defined by the following equation:

$$LOB_{LOQ} = m_{blank} + 10(SD_{blank})$$

The LOB value was then inserted into the line equation as the Y-value, and the X-value was solved for, giving the LOQ in mM.

SUMMARY TABLES FOR THIN FILM EXPERIMENTS

Ratio of fluorescence in thin films with DDT and I₂ additions:

Ratio is defined as the integrated fluorescence of the film under a given set of experimental conditions to the integrated fluorescence of the film before treatment with any analyte or reagent.

Table S1.

	ratio
Blank	1.00
With DDT	1.27
With I ₂	1.06

Table S2.

	Ratio
Blank	1.00
With DDT	0.91
With I ₂	1.04

Table S3. SUMMARY TABLE FOR LOD EXPERIMENTS

Analyte	Equation	R ²	LOD (μM)
1	$y = 210.09x + 38261$	0.9777	4.6
2	$y = 1929.2x + 453988$	0.8212	83.1
3	$y = 1895.3x + 434915$	0.9463	69.3
4	$y = 2454.3x + 292818$	0.9789	58.2

SUMMARY FIGURES OF ALL EXPERIMENTAL DATA

SUMMARY FIGURES FOR LIMIT OF DETECTION EXPERIMENTS

Figure S2. Analyte 1

Figure S3. Analyte 2

Figure S4. Analyte 3

Figure S5. Analyte 4

SUMMARY FIGURES FOR FLUORESCENCE EXPERIMENTS

Figure S6. Analyte 1; [polymer] = 2.5E-4 M

Figure S7. Analyte 1; [polymer] = 1.25E-3 M

Figure S8. Analyte 2; [polymer] = 2.5E-4 M

Figure S9. Analyte **2**; [polymer] = 1.25E-3 M

Figure S10. Analyte **3**; [polymer] = 2.5E-4 M

Figure S11. Analyte 3; [polymer] = 1.25E-3 M

Figure S12. Analyte 4; [polymer] = 2.5E-4 M

Figure S13. Analyte 4; [polymer] = 1.25E-3 M

Figure S14. Analyte **5**; [polymer] = 2.5E-4 M

Figure S15. Analyte **5**; [polymer] = 1.25E-3 M

Figure S16. Analyte **6**; [polymer] = 2.5E-4 M

Figure S17. Analyte **6**; [polymer] = 1.25E-3 M

Figure S18. Analyte 7; [polymer] = 2.5E-4 M

Figure S19. Analyte 7; [polymer] = 1.25E-3 M

Figure S20. Analyte **8**; [polymer] = 2.5 E-4 M

Figure S21. Analyte **8**; [polymer] = 1.25E-3 M

Figure S22. Analyte **9**; [polymer] = 2.5E-4 M

Figure S23. Analyte **9**; [polymer] = 1.25E-3 M

Figure S24. Analyte **10**; [polymer] = 2.5E-4 M

Figure S25. Analyte **10**; [polymer] = 1.25E-3 M

FREE POLYMER (NOT IN PARTICLE FORM):

Figure S26. Analyte 1; [polymer] = 2.5E-4 M

Figure S27. Analyte 1; [polymer] = 1.25E-3 M

Figure S28. Analyte 2; [polymer] = 1.25E-3 M

Figure S29. Analyte 3; [polymer] = 1.25E-3 M

Figure S30. Analyte 4; [polymer] = 1.25E-3 M

Figure S31. Analyte **5**; [polymer] = 1.25E-3 M

Figure S32. Analyte **6**; [polymer] = 1.25E-3 M

Figure S33. Analyte **7**; [polymer] = 1.25E-3 M

Figure S34. Analyte **8**; [polymer] = 1.25E-3 M

Figure S35. Analyte **9**; [polymer] = 1.25E-3 M

Figure S36. Analyte **10**; [polymer] = 1.25E-3 M

CHAPTER 2

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Addressing the STEM Gender Gap by Designing and Implementing an Educational Outreach Chemistry Camp for Middle School Girls

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Manuscript 2

Addressing the STEM Gender Gap by Designing and Implementing an Educational Outreach Chemistry Camp for Middle School Girls

ABSTRACT

There continues to be a persistent, widespread gender gap in multiple STEM disciplines at all educational and professional levels: from the self-reported interest of pre-school aged students in scientific exploration, to the percentages of tenured faculty in these disciplines, more men than women express an interest in science, a confidence in their scientific abilities, and ultimately more men than women decide to pursue scientific careers. Reported herein is an intensive outreach effort focused on addressing this gender gap: a full-time, week-long chemistry camp that was designed and implemented for middle school girls in the state of Rhode Island. The camp schedule included multiple hands-on experiments, field trips, and significant interactions with female scientists, all of which were designed to increase the participants' interest in and enthusiasm for science. The success of the program in changing the participants' attitudes towards science was measured through administration of a pre-camp and post-camp survey, and the survey results demonstrated a strong success in changing the participants' attitudes towards the widespread applicability of science, their perceived level of support for scientific study, and their interest in pursuing STEM-related careers.

INTRODUCTION

There is a significant dearth of female chemists at the highest levels of academia: at the top 50 schools (measured by research funding), only 18% of tenured and tenure-track positions were held by females in 2012-2013.¹ The numbers are slightly more encouraging across all STEM disciplines at all academic institutions, with approximately 25% of full-time, full professor positions held by females in 2015.² Research indicates that this gender gap may start as early as elementary school, with female students having a more negative attitude towards science than males starting as early as 4th grade.^{3,4} This gender gap is likely reinforced by the fact that high school science teachers spend significantly more time addressing the boys in the classroom, a fact that has been well-documented in the literature as recently as 2013.^{5,6}

This gender gap has a multitude of potential causes that have been investigated in the literature, including: (a) a lack of female scientist role models,^{7,8} which contributes to childrens' perceptions that scientists are overwhelmingly white males;^{9,10} (b) girls' self-perception that they lack aptitude and ability to succeed in STEM disciplines;¹¹ and (c) teachers', parents', and other authority figures' reinforcement of these stereotypical notions.^{12,13} These phenomena affect children as young as 4 years old,¹⁴ and continue to affect students' attitudes, perceptions, and experiences throughout their K-12 education, ultimately culminating in significant gender gaps in college students' choices of majors and careers.¹⁵⁻¹⁷ Educators have attempted to address this gender gap through increasing girls' access to female role models,¹⁸⁻²⁰ and through conducting outreach activities specifically targeted towards female students.^{21,22}

A concurrent problem in STEM education is the lack of hands-on laboratory time in the formal middle school and high school curricula, which is attributable to a

general decrease in funding for STEM education,^{23,24} as well as an increased prevalence of standardized testing that de-emphasizes hands-on experimental training.²⁵ To address this issue, educators have conducted hands-on outreach workshops,²⁶⁻²⁸ developed creative methods to increase the time devoted to hands-on learning,^{29,30} and implemented innovative uses of technology to conduct virtual field trips³¹ and virtual science experiments.^{32,33}

To simultaneously address both of these issues: the persistent gender gap in STEM disciplines and the lack of hands-on science education, we developed a full-time, week-long chemistry camp for middle school girls in Rhode Island. Hands-on full-time outreach programs for girls have previously been reported by this³⁴ and other journals;³⁵⁻³⁷ review articles on this topic have also been published.³⁸ Only one of the previously reported full time programs was focused on chemistry, and in that case focused particularly on analytical chemistry experiments. Key novel elements of our reported program are the inclusion of multiple field trips, discussions with female scientist role models, and a broader range of hands-on scientific activities, including investigation of material properties through relay races on Non-Newtonian fluids.

The camp schedule included 11 hands-on scientific activities, significant interactions with female scientists, and two field trips to explore scientific issues. The main goals of the camp were to ensure that the participants understood (1) the direct relevance and applicability of science in their everyday lives, and (2) that scientists comprise a diverse demographic group. Reported herein is the development, implementation, and evaluation of this chemistry camp, as well as implications for future outreach efforts.

CAMP OVERVIEW

The chemistry camp was run from April 21-25, 2014, at the University of Rhode Island Kingston campus. Participants were recruited from middle schools throughout the state of Rhode Island, and 40 girls (out of a total application pool of 87 girls) were selected to participate. The camp capacity was set at 40 due to space and budgetary constraints. Of the 40 accepted girls, 36 actually attended the camp, with the other 4 girls declining to participate at the last minute. The application procedure required the girls to briefly state why they were interested in attending the chemistry camp, and what they hoped to gain from their participation. The girls were not required to have any pre-requisite knowledge; all necessary content was delivered in a short, interactive lecture prior to the start of each activity. At the conclusion of each activity, the questions in the camp booklet were answered in interactive group sessions. All funding for the camp was provided by the Dreyfus Foundation Special Grant Program in the Chemical Sciences. The supporting information to this article includes the full booklet that was provided to all camp participants, which includes a detailed background for each experiment, instructions for how to execute the experiment successfully, and post-experiment questions and points for further discussion.

Participants were responsible for arranging their own transportation to and from camp each day. In addition to the 11 major activities discussed below, students also participated in multiple swimming breaks throughout the week, watched selected science videos, and engaged in extensive interactions with invited speakers, camp volunteers, and the PI, Dr. Levine.

PARTICIPANT DEMOGRAPHICS

The 36 participants came from communities throughout the state of Rhode Island, with the largest contingent from Pawtucket (9/36 of the girls). The participants came from public schools (17), private schools (14), charter schools (1), and home schools (4). 25% of the girls were from non-white minority groups (9/36).

HANDS ON EXPERIMENTATION

As mentioned in the introduction, one goal of the camp was to educate the participants about the applicability of science in their everyday lives through hands-on experimentation. This hands-on experimentation has been shown to be crucial to encouraging general interest in and enthusiasm about STEM disciplines.³⁹ To that end, the camp schedule included 11 hands-on activities (Table 1). For each activity, the participants learned about the key scientific background, conducted the experiments, and discussed the results. Selected photographs of these activities are shown in Figure 1.

Figure 1. Photographs of hands-on scientific activities (clockwise from top left): running on corn starch in water; making a pH indicator from red cabbage; exploring

explosions of Diet Coke and Mentos; tie-dying T-shirts; and making red-colored slime.

Table 1. Overview of Hands-on Activities

Activity Number	Title	Activity Synopsis	Scientific Discussion	References
1	Polymers of Everyday Objects	Isolation of the super-absorbent polymer from diapers: Study of hair gels through the addition of salts to collapse the hydrogel	Definition of a polymer, how polymers are used	40,41,42,43
2	Forensic Science Investigation with Lipstick	Mock forensic investigation using chromatography to separate lipstick pigments, to identify which fictional character left a lipstick stain on a wine glass	Theory and applications of chromatography	
3	Lava Lamp Construction	Construction of home-made lava lamps using oil, water, salt, and food coloring	Densities of liquids, and the ability of ionic compounds to perturb those densities	44
4	Square Bubbles	Construction of “square bubbles” using pipe cleaner boxes to frame the bubbles, and a water-glycerin-dish soap mixture to construct long-lasting bubbles	Surface tension of water and how that tension is related to the molecular structure of water and its fundamental properties	45,46
5	Oil Spill Cleanup	Clean-up of a mock oil spill in a fish tank using a variety of materials, including absorbent pads, feathers, cotton balls, and super-absorbent polymer	The effects of anthropogenic oil spills such as the Deepwater Horizon spill of 2010, and currently used state-of-the-art methods for oil	47,48

			spill cleanup and environmental remediation	
6	Jelly Fish In A Bottle	Construction of a mock jelly fish with a plastic bag filled with air	Density of gases and fluids, and how the mock jelly fish can float to the top of the water mixture	
7	Walking on Corn Starch	Relay races across containers filled with corn starch and water mixtures	Non-Newtonian fluids and the effect of pressure on those fluids' properties	49
8	Make Your Own pH Paper	Use of red cabbage to make a pH indicator, and testing of the pH of common household objects, including bleach, vinegar, antacids, and Coca-Cola	Acidity and basicity	50
9	Diet Coke and Mentos Explosions	Adding Mentos to Diet Coke and observing the explosion	Nucleation of bubbles and the chemical basis of explosions	51
10	Non-Newtonian Fluids	Making Oobleck, Gak and slime	Non-Newtonian fluids and the effect of pressure on those fluids' properties	52
11	Tie-Dying T-Shirts	Tie dying t-shirts using multiple colors and patterns	Color pigments; science of dyeing clothing	53

CAMP FIELD TRIPS

Field trips are a crucial educational tool in encouraging students' interest in STEM disciplines,^{54,55} unfortunately, budgetary and time constraints have made field trips in formal educational settings a fairly rare phenomenon.⁵⁶ We directly addressed the shortage of field trips in the girls' formal education by traveling on two field trips

during the week: to the Narragansett Bay Commission in Providence, Rhode Island, and to Mystic Aquarium in Mystic, Connecticut. The Narragansett Bay Commission trip provided the girls with the opportunity to conduct hands-on water testing, tour the water treatment facility, and watch an educational video detailing the water treatment process. The Mystic Aquarium trip provided the girls with the opportunity to learn about the science of marine ecosystems and marine life, as well as to conduct a hands-on squid dissection.

FEMALE ROLE MODELS

Literature has shown that one reason that girls and women at all educational levels lose interest in the STEM fields is the lack of female role models.⁵⁷⁻⁵⁹ To address this issue, the camp schedule provided ample interactions with female scientists, including: Dr. Stefanie Sydlik, a post-doctoral research fellow at Massachusetts Institute of Technology; Professor Mindy Levine, an assistant chemistry professor at the University of Rhode Island, and female graduate students and undergraduate students in the chemistry department at the University of Rhode Island. The interactions with female scientists included a brief presentation by Dr. Sydlik about her career, her goals, and what her daily work entails, followed by an extensive, participant-directed question and answer session. The participants also had ample informal question and answer time with Dr. Levine and the other graduate students throughout the week.

EVALUATION

As mentioned in the introduction, a key goal of the chemistry camp was to demonstrate the applicability of science in the girls' daily lives, and to educate them

about possibilities for females to pursue STEM careers. Our success in achieving this goal was evaluated through administering pre-camp and post-camp surveys to all camp participants. The survey questions were selected from published surveys that measured students' attitudes about science relevance,⁶⁰ and in particular asked the participants to rate their responses to the questions shown in Table 2 on a scale of 1-5 (1 = strongly agree; 5 = strongly disagree). Asterisks next to the question numbers indicate those questions that had the most significant differences in responses pre- and post-camp.

The results of this survey are summarized in Table 2. A paired t-test conducted on this data gave a two-tailed P value less than 0.0001 for the cumulative survey scores, considered to be extremely statistically significant. Several of these results merit further discussion: (1) For all questions, the average responses were higher at the start of the week than at the end of the week, meaning that more of the girls agreed with these statements after participating in the chemistry camp. This trend reflects the desired outcome for most of the survey questions; for example, more girls agreed that, "Science will help me to understand the effect I have on the environment," (1.89 pre-camp; 1.32 post-camp), and that, "Science can help me to make better choices about various things in my life" (2.14 pre-camp; 1.71 post-camp). However, more girls also agreed with the statement that, 'I do not expect to use science much when I get out of school,' although that difference was among the smallest of the questions asked (difference = 0.32), and it also had the highest absolute value both pre- and post-camp (3.86 and 3.54, respectively), indicating most of the participants disagreed or strongly disagreed with that statement.

Table 2. Survey responses pre- and post-camp participation

Item number	Survey Statements for Response ^a	Average survey Response Scores, ^b <i>N</i> =28 ^c		Difference
		Pre-Camp	Post-Camp	
1	Science will help me to understand the effect I have on the environment.	1.89	1.32	0.57
2	Science helps me to ask others for help with my work.	2.71	2.25	0.46
3	Using scientific methods helps me think things through.	1.89	1.54	0.36
4	Science can help me decide how to treat my cold or illness.	2.36	1.71	0.64
5	Usually, it is bad to have any feelings about the scientific issues I am considering.	3.75	3.04	0.71
6	Science should be required in school.	1.61	1.36	0.25
7	Science could help me figure out how to spin/shoot/throw/hit a ball.	2.71	1.96	0.75
8	Science class helps me evaluate my own work.	2.32	1.71	0.61
9	I do not expect to use science much when I get out of school.	3.86	3.54	0.32
10	I am interested in a career as a scientist or engineer.	2.68	2.18	0.50
11	Making decisions can be difficult when I don't understand the choices.	1.82	1.39	0.43
12	My intuition helps me make decisions in science.	2.61	1.89	0.71
13	I have support from others to excel at science.	2.18	1.71	0.46
14	Using scientific methods helps me decide what to buy in the store.	3.25	2.50	0.75
15	Science will help me	2.04	1.46	0.57

	understand the importance of recycling.			
16	Learning science can help me understand about things that affect people's health.	1.89	1.43	0.46
17	Science can help me to make better choices about various things in my life (e.g., food to eat, car to buy).	2.14	1.71	0.43
^a See ref 60 ^b The scale for the survey item response scores is 1–5, with 1 indicating “strongly agree” and 5 indicating “strongly disagree”. ^c 28 of the 36 participants consented to participate in this study; the results reported herein are based only on the surveys of the 28 consenting participants.				

(2) The questions with the greatest pre-camp to post-camp differential were, “Science can help me figure out how to spin/shoot/throw/hit the ball” (Question 7), and “Using scientific methods helps me decide what to buy in the store” (Question 14), with an 0.75 differential pre-camp to post-camp measured for both of these questions. Interestingly, both of these questions directly address the applicability of science in daily life, and particularly in areas that are not traditionally considered to fall in the scientific realm. The dramatic change in the girls’ responses in a one-week time period indicate the success of the program in teaching the participants that science is relevant to a wide range of topics.

(3) One key goal of the camp was to encourage the girls’ interest in STEM disciplines and STEM careers. The successful realization of that goal was evident in the response to Question 13, which asked about the girls’ perceived support for excelling at science (pre-camp: 2.18; post-camp: 1.71). Moreover, the girls’ interest in pursuing a career in STEM disciplines also increased (pre-camp: 2.68; post-camp 2.18).

Overall, the survey results demonstrate measurable changes in the attitudes of the camp participants towards science, and in particular demonstrate their increased appreciation for the applicability of science in several diverse areas of life. These changes are even more noteworthy given the short time frame (only 5 days) that elapsed between the two administered surveys, and are a positive indication that analogous outreach efforts can have measurable beneficial effects.

CONCLUSIONS AND FUTURE DIRECTIONS

Reported herein is the design, implementation, and evaluation of a full-time, week-long outreach program targeting middle school girls in the state of Rhode Island. This program consisted of multiple components, including hands-on experiments, field trips, and interactions with female scientists, each of which was designed to increase the girls' excitement for and appreciation of science. Survey results demonstrate that participation in the program did in fact have the desired effect in enhancing such excitement and appreciation, as well as the girls' interests in pursuing STEM-related careers. Moreover, each component of the program (each experiment, trip, or female scientist discussion) can be run as an independent event, and is also likely to increase the participants' excitement for and exposure to science.

One unanswered question is whether the positive effects observed in the survey responses will persist long-term, with girls who have participated in this program maintaining their scientific enthusiasm over subsequent months and years. Future efforts will focus on conducting follow-up surveys of the program participants, to track their long-term interest in science, as well as their choice of college, college major, and future career. In future years, we will also administer more detailed

surveys to elucidate the effects of each aspect of this program (experiments, field trips, and scientist interactions) on impacting girls' attitudes about science. This ongoing outreach activity at the University of Rhode Island is currently being funded by private and corporate donations.

ACKNOWLEDGEMENTS

Funding is acknowledged from the Dreyfus Foundation Special Grant Program in the Chemical Sciences.

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Supporting Information

Addressing the STEM Gender Gap by Designing and Implementing an Educational Outreach Chemistry Camp for Middle School Girls

LIST OF EXPERIMENTS:

POLYMERS

- I. The Incredible Melting Hair Gel:** Hair gels are a type of hydrogel that already has water in it. In this experiment, we will break the polymer/water network by adding salt. The salt will displace the water and disrupt the hydrogel.
 1. Put some hair gel in the center of a plate. What is the consistency of your hair gel? Is it thick, runny, firm, or soupy?
 2. Add a spoonful of salt and sprinkle generously over the hair gel.
 3. Watch the polymer break apart. What are your observations?
 4. After a set period of time, pour the water off of the plate and into a graduated cylinder. Record how much water your gel released.
 5. Compare your results to those of others who had different hair gels. Which gel had the most/least amount of water? How does this relate to how “strong” the hair gel is?
- II. Diaper Polymers:** One of the most common uses of sodium polyacrylate is in baby diapers. Sodium polyacrylate can hold 300-500 times its weight in water, so they are ideal to help keep a baby dry. This experiment is in two parts.

Part 1 Steps:

1. Take a diaper and carefully remove the excess bands (this will be demonstrated to you).
2. With the bottom section remaining, add some water to the section.
3. Once you notice the water has been absorbed, CAREFULLY cut the bottom section into two pieces. What are your observations about the two sections?
4. Remove the material inside the diaper sections. What do you see? Is there a gel-like substance inside?
5. Cleanup.

Part 2 Steps:

1. Take 1 spoonful of sodium polyacrylate and add it to a cup.
2. Add water to the cup and mix the polymer and water together. Record the amount of water you added to the polymer.
3. You should see the water turn gel-like and grow in size. Record any and all observations here. You can take some of the gel out of the cup to gather more information about the gel-like material.
4. Destroy the hydrogel. Using a spoon, punch a hole in the bottom of the cup. Add salt to the gel, and mix it up. You should start seeing water coming out of the bottom of the cup. What did we do to the polymer/water mixture when we added the salt??
5. Cleanup.

III. You Clean that Oil Spill, Diaper Polymer: Sodium polyacrylate is also used to clean oil spills. We will recreate a small oil spill and see how well the technique works.

1. Fill a small plastic fishbowl about halfway with water.
2. Add some oil to the fishbowl. You should have a layer of oil on top of your water
3. Add sodium polyacrylate to the oil and do not mix. Record your observations as you watch this happen.
4. After some time, try to remove some of the oil and polymer from the water. What do you see? Is this easy to do? Discuss with your partner how well this works.
5. Cleanup.

FORENSICS:

IV. Lipstick Chromatography: Lipsticks are made a mixture of colored pigments that give rise to the specific lipstick color. We can separate the different pigments out to see what colors a lipstick is made from using paper chromatography. Chromatography is a technique used in laboratories to separate a complex mixture into its individual components. Paper chromatography has two phases: a stationary phase (the paper) and a mobile phase (the solvent). Depending on the characteristics of each pigment, they will either have a high affinity for the stationary phase (so they will not move as much up the paper) or they will have a high affinity for the mobile phase (they will move far up the paper). Because of this, we can manipulate the

mobile phase as needed to ensure that each of the spots on the chromatogram (the chromatography paper after the pigments have been separated) are far enough apart so we can clearly differentiate between components. By comparing the chromatogram from an unknown sample to a series of known samples, we can identify what the unknown sample is.

1. Obtain 2-4 strips of chromatography paper (depending on how thick it is, you may be able to do 1-2 spots on each paper). Your instructors will tell you how many to use.
2. Using a ruler, draw using a pencil (not pen: ink is made of different compounds, so it too will be separated if used on chromatography paper) a line ~2 cm from the bottom of the strips of filter paper.
3. Label each piece of paper with the sample(s) of lipstick that will be on the paper.
4. In the beaker, place ~10 mL of solvent into the beaker and cover it with the beaker cover
5. Take the samples of lipstick and dissolve them in some of the solvent system. Try to minimize how many solids pieces there are.
6. Dip a toothpick into each sample and “spot” your chromatography paper. Be sure that the spot is on the line you drew in the bottom
7. Place the chromatography paper into the chamber you made (the beaker with solvent in it). Be careful when doing this!
8. Watch the compounds separate out. What do you see?

9. When the solvent is near the top of the paper, take the paper out and mark the solvent line with the pencil. Allow the paper to dry fully.
10. Find the darkest place of each spot and make a dot.
11. Measure the distance between the line you drew at the bottom and the solvent line you marked. Record this number.
12. Measure the distance between the bottom line and each spot you drew.
13. Calculate the retention factor using the equation below:

$$R_f = \frac{\text{Distance traveled by one lipstick component from the spotted pencil line}}{\text{Distance the solvent moved from the spotted pencil line}}$$

14. Complete the table.

Table S1. Data table for Lipstick Chromatography

Lipstick Sample	Colors Seen (Components)	Distance Between the Bottom Line and the Top Line (cm)	Distance Lipstick Components Moved (cm)	R _f Value
Crime Science (C)	1.			
	2.			
	3.			
	4.			
Mrs. Sternman (W)	1.			
	2.			
	3.			
	4.			
Ms. Sternman (D)	1.			
	2.			
	3.			
	4.			
Ms. Justice (A)	1.			
	2.			
	3.			
	4.			

LAVA LAMP IN A CUP

V. Buiding the Lava Lamp: To investigate the effect that salt has on oil by making a lava lamp... in a cup! Lava lamps are decorative novelty lights that were invented by Edward Craven-Walker in 1963 in England. The lamp contains water and a colored wax in the top chamber and a light at the base.

The wax that is used is paraffin wax, which is also used in candles. Wax has similar properties to oil, and as such the wax normally sits on top of the water because it is less dense (lighter in weight) to water, which is more dense (heavier weight). However, in Figure 1 (2), we see that the wax actually rests on the bottom when the lamp is off. This is due to an additive that the manufacturers mix with the wax that make it more dense (heavier) than water, so the wax sits at the bottom, near the lamp that is in the base. When the lamp is turned on, the wax (being right on top of it) becomes heated and expands, making it less dense than water. As a result, it rises above the water (Figure 1, red line, (3)). Once the wax reaches the top of the lamp, the wax cools just enough (because it is not near the lamp anymore) to increase its density and it falls to the bottom of the lamp (Figure 1, blue line, (3)). This process repeats until the lamp is turned off.

Salts are formed when ions (one positively charged and the other negatively charged) come together to make a neutral compound. Table salt is sodium chloride, NaCl, with sodium being positively charged (Na^+) and chloride being negatively charged (Cl^-). When you buy salt, it is a solid (NaCl). However, when you add salt to water, it dissolves. The reason for this is

because water can “pull apart” the solid salt into its individual components (Na^+ and Cl^-) which are water soluble. Water contains a positive end and a negative end. Because opposites attract, the positive sodium associates with the negative end of the water, while the negative chloride associates with the positive end of water. These different associates make it water soluble. This association arises from ionic bonds, in which opposite charges attract one another.

Figure S1. Dissolved Salt in Water.

1. Fill the cup with water until it is about 2/3 full. Be sure there is enough room for oil at the top.
2. Add several drops of food coloring.
3. Slowly pour the oil into the glass. Where is the oil?
4. Sprinkle the salt into the glass. What do you see?

SQUARE BUBBLES

VI. Making Square Bubbles: To investigate surface tension by making square bubbles. Bubbles are extremely thin films of soapy water to form a hollow

sphere. They only last a few seconds before they pop because the water evaporates (although this can be delayed with glycerin), or they make contact with an object. The bubbles tend to change color and/or show a rainbow pattern, and this occurs when light is reflecting off the front and back surface of the bubble, causing interference with one another (this is why the colors appear to “swirl” around the bubble surface). Bubbles are hollow spheres because this shape is best to enclose as much air as possible with as little bubble solution as possible. This is also due to the attractive forces between the molecules in the bubble; think of it like a bunch of friends holding hands and running around. It’s easier to move in a circle instead of a square or rectangle or triangle, and in molecules this all relates to surface area.

Bubble Solution

1. In a large container, add 2 gallons of distilled water.
2. Add $\frac{1}{4}$ cup of liquid dish soap.
3. Add ~4 tablespoons of glycerin.
4. Mix together.

Square Bubble Maker (This will act as a support for the bubbles)

1. Cut all of the pipe cleaners and straws in half.
2. Divide the pipe cleaners into four groups of three.
3. Taking one of the groups of three pipe cleaners, twist the ends together to form a pyramid with no base (see figure 1). Repeat for the remaining pipe cleaner groups.

4. Slide a straw over each pipe cleaner. We do this because the bubbles would soak the pipe cleaner, and we would not be able to create bubbles with it.
5. Start joining the four pyramids together by twisting the ends together, and continue until you form a cube.

Figure S2. Diagram of pipe cleaner pyramid for step 3.

Square Bubbles!

1. Dip the bubble maker into the bubble solution, ensuring it is fully submerged in the bucket.
2. Take your bubble maker out.
3. Gently shake the cube until you have an hourglass shaped bubble in the bubble maker.
4. Dip the pipette into the bubble solution and blow a bubble into the center of the bubble maker.

TIE DYE

VII. Make your own Tie Dye Shirt: Learn the science behind how tie dyeing a shirt works. To tie dye a shirt, the shirt is first soaked in a solution of sodium carbonate. Sodium carbonate is a common chemical that you can find in your home as it is the main chemical found in laundry detergent and bubble bath solutions (although this is much more concentrated!). Cotton t-shirts contain mostly cellulose. When sodium carbonate, a weak base, is added, the pH is raised. As a result, the hydrogen that was bonded to the oxygen (seen in blue with green square) “leaves” and what results is a negatively charged oxygen (seen in blue with red square) and sodium bicarbonate (baking soda!).

Figure S3. Formation of the negatively charged oxygen on cellulose

This negatively-charged oxygen is now an open bonding site for our dye. As we add different dyes to the shirt, these bonding sites “capture” the dye and thus the shirt goes from white (when it was regular cellulose) to whatever color you’ve chosen (Figure S4).

Figure S4. Dye attaching to the negatively charged oxygen of cellulose.

Part A

1. Soak the shirt in the sodium carbonate solution for ~10 minutes or so.
2. After the time is over, put on gloves. Take the shirt out of the water and wring it out, removing as much of the solution as possible.

Part B

1. Using the rubber band, tie the shirt however you want. Be creative!
2. STRIPES: Lay the shirt flat on the table. Roll the shirt from the bottom to the top so that you have a long tube. Use the rubber bands to space the stripes apart from one another. If you only want a few stripes, use a few rubber bands; for more, add more.
3. SPIRAL: Lay the shirt flat on the table. Put your thumb and index finger in the center of the shirt, and move them in a circle to create a spiral around the center point where your fingers are. Once it is spiraled, use three rubber bands to make six sections. You need at least six sections for

this to work well, but you can of course add more rubber bands if you want more sections.

4. POLKA DOTS: Lay the shirt flat on the table. Pinch the shirt in random locations and secure with a rubber band. Then, add another rubber band below it to create a “pyramid” on the shirt. You should have at least three per pyramid. You can make the dots bigger if you would like by making your “pinches” bigger.

Part C: Dyeing the Fabric

Use the bottles of dye provided to add colors to your shirt. Be creative! Make sure you’re wearing gloves for this part. If you touch the shirt with your hands, you can contaminate the undyed portion of the shirt and the dye may not affix to the shirt as well.

Part D: When You’re Done Adding Color

Wrap the shirt in newspaper and place it inside a plastic bag. Seal the bag.

Part E: Washing the Shirt

1. This is very important: the first wash affixes the color. Be sure to do these steps exactly.
2. After 24 hours, unwrap the shirt and remove the rubber bands. Rinse the shirt in equal parts cold water and white vinegar until the shirt no longer feels soapy. When this happens, the pH of the shirt is neutral (pH=7).
3. The dye will not stain drains but will stain other fabric, so be careful when washing the shirt. Also be sure you’re wearing gloves!

4. Place the shirt in a washing machine and use two tablespoons of dish soap; wash with the normal cycle. DO NOT USE LAUNDRY SOAP OR DISHWASHER SOAP: This will reverse the dye!
5. Air-dry the shirt.
6. In the future, wash the shirt with colored clothes only. Use regular laundry detergent and color safe bleach only.

OIL SPILLS

VIII. Oil Spill Clean Up: Oil spills are an example of an anthropogenic (man-made) event. They are accidental releases of hydrocarbons (molecules containing only hydrogen and carbon) into the environment and can be very difficult to cleanup. Two of the most well-known examples of oil spills are the Exxon Valdez (1989) and Deepwater Horizon (2010) spills. They are two prominent examples of two types of oil spills. The Valdez spill was a surface spill, where the oil was released from a ship (also known as “buoyant oil”). The Deepwater Horizon spill was unique because it occurred at depth in the Gulf of Mexico. However, both spills left devastation in the areas they affected and left oil that needed to be cleaned up. Not only are some of the hydrocarbons in oil toxic and carcinogenic (cancer-causing) to wildlife and humans, but oil is also very “goopy” so wildlife that get caught in oil die if they are not cleaned fast enough.

The cleanup methods used in oil spill cleanup include:

A. SKIMMERS. Boats are equipped with “vacuums” which suck up water into the ship. Special equipment on the ship separate the oil and water

from one another and the excess water is pumped out and the oil is stored on board. However, they only work well in calm waters where the oil-water interface is at a constant level in the boat, so they are not useful at all times.

B. BOOMS. Booms are like the foam tubes you see at swimming pools, but they are made with special materials which can physically block off oil. As a result, they can help prevent an oil mass from spreading too far. However, if the water is very turbulent the oil can easily wash over it.

C. CHEMICAL DISPERSANTS. Dispersants are used to break up a large oil mass into smaller oil droplets on the ocean surface. Because the oil droplets are so small, the oil is more easily accessed by oil-eating bacteria, which can break the oil down naturally. However, there is still a lot of debate about the effects of dispersants to ocean life.

D. ABSORBENT PADS: These pads are used to clean oil off of rocks on beaches.

E. BACTERIA: Oil seeps are a natural occurrence, and so are oil-eating bacteria. Because bacteria naturally break down the oil, a lot of effort is put into making the oil easier for the bacteria to access (such as dispersants).

F. DETERGENT: To clean oil from wildlife, detergent (dish-washing liquid) is quite effective.

Part A

1. Add water to the pie pan. This is your ocean.
2. Add a rock to one side of the pie pan. This is your shore.
3. Add a small amount of oil to one side of the pie pan, opposite the rock.
4. Dip the feather into the oil.
5. Record all observation.

Part B: Skimmers

1. Use the spoons to try to pick up the water and move it to a waster container. Try to get as much oil as possible and not as much water.
2. Records observations.

Part C: Booms

1. Add more oil to the pan if needed.
2. Take a length of nylon and add some cotton balls. Wrap the nylon around the cotton balls and tie off each end to make a boom.
3. Put the boom in the water.
4. After the boom has been in contact with the oil for a few moments, take the boom out and feel how heavy it is.
5. Record how well it worked to prevent the oil from moving around and whether or not you think the boom also removed water.

Part D: Absorbents

1. Add more oil to the pan if needed.
2. Take a length of absorbent pad and try to clean up the oil this way.
3. Repeat for all pad samples.
4. Record how heavy the pads are after absorption.

5. Record how effective the pads were at absorbing the oil.

Part E: Dispersants

1. Add more oil to the pan if needed.
2. Add a dropper full of detergent to the oil spill. What do you see?
3. Stir the pan with the spoon to simulate waves, tides and wind. What happens to the spill?

Part F: Dispersants and Feathers

1. Take the oiled feather and try to clean it with some detergent. Does it work well?
2. Finally, rank each method (1=best) to compare the different methods

DIET COKE AND MENTOS

IX. Making Diet Coke explode using Mentos: What happens when you combine Diet Coke with Mentos? You probably have seen this done before, and you know that when you combine them you get an explosion of soda! So, why does this happen?

To be honest, there is no clear definite reason for this behavior, but there is a popular theory. Have you ever felt the surface of Mentos? It's not completely smooth, but instead, is rather bumpy. This gives the candy a large surface area, since the ridges add to the total surface of the candy. Soda is carbonated, and the fizz is caused by carbon dioxide. These two features – the rough surface of the Mentos and the bubbles from the soda – come together to form the soda explosion. As the candy is dropped into the soda,

the rough surface causes nucleation of the carbon dioxide. In other words, the gas bubbles are able to collect in the ridges of the candy, so the many small bubbles we usually see quickly multiply until the pressure caused is released, and that's when we see the explosion of soda!

So, the last question is why does this work better with Diet Coke than other sodas? It is believed that the reason is that Diet Coke uses different ingredients and is less sticky compared to other soda formulations, so it is much more effective at producing the carbon dioxide gas needed to get a larger soda explosion.

FUN WITH FLUIDS

X. Classifying Fluids:

A **fluid** is a substance with no definite shape, and is easily deformed by outside pressure. Any liquid or gas is a fluid.

Viscosity is the property of a fluid that describes how easily it can flow. If a substance doesn't flow easily, it's said to be viscous. So we could call molasses viscous, when compared with water.

A **Newtonian fluid** is a fluid that has a constant viscosity. Water is a Newtonian fluid. These fluids behave as you'd expect them to. They're called Newtonian, because Isaac Newton found equations to correctly describe their behavior.

A **Non-Newtonian fluid** has a viscosity that changes under different conditions. These can get either more viscous or less viscous when pressure is applied.

A **Dilatant**, or **shear-thickening** fluid gets more viscous when more pressure is applied. Oobleck is a good example.

A **pseudoplastic** fluid, or a **shear-thinning fluid** gets less viscous when you apply pressure. Ketchup is a good example of this.

Part A: Classifying Fluids: You will receive a variety of fluids. Experiment with them, and determine if they're **Newtonian** or **non-Newtonian**. If they're non-Newtonian, find out if they're **shear-thickening** or **shear-thinning**. Record your observations as you go.

Part B: Optimizing the Oobleck Recipe: You will get cornstarch and water. Mix them in different ratios, to try and find the best mixture. What ratio worked best?

Part C: Optimizing the Gak Recipe

1. Empty the 4 oz bottle of glue into a bowl.
2. Fill the empty bottle with warm water and shake. Pour the glue-water mixture into the mixing bowl and use the spoon to mix well.
3. Add some food coloring to the bowl.
4. Measure 1/4 cup of warm water into the plastic cup and add a 1/2 teaspoon of Borax powder to the water. Stir the solution – don't worry if all of the powder dissolves. This Borax solution is the secret linking agent that causes the Elmer's Glue molecules to turn into slime.
5. While stirring the glue in the mixing bowl, slowly add a little of the Borax solution. Immediately you'll feel the long strands of molecules starting to connect. It's time to abandon the spoon and use your hands

to do the serious mixing. Keep adding the Borax solution to the glue mixture (don't stop mixing) until you get a perfect batch of Elmer's slime.

6. When you're finished playing with your Elmer's slime, seal it up in a zipper-lock bag for safekeeping.

pH PAPER

XI. Make Your Own pH Paper: Red cabbage contains a pigment molecule called flavin (an anthocyanin). This water-soluble pigment is also found in apple skin, plums, poppies, cornflowers, and grapes. Very acidic solutions will turn anthocyanin a red color. Neutral solutions will result in a purple color. Basic solutions appear in greenish-yellow. Therefore it is possible to determine the pH of a solution based on the color it turns the anthocyanin pigments in red cabbage

Table S2. pH Scale for Anthocyanin Pigments in Red Cabbage

pH	2	4	6	8	10	12
Color	Red	Purple/Pink	Violet	Blue	Blue-Green	Yellow-Green

1. Your instructor will be coming around to distribute the Red Cabbage Pigment Solution. Help them filter it by holding your coffee filter above your 250mL beaker. Fill each of your test tubes about halfway with the red cabbage solution.

2. Place your 5 (or 6) pieces of filter paper on the bottom of your beaker.
Then ask your instructor to pour more solution into the beaker to cover the filter paper.
3. Notice that each of your test tubes is labeled with the name of a household chemical, and that one of these chemicals is on your table.
Add some of this chemical to the correct test tube until you see a color change.
 - a. For liquids (coke, vinegar, and dish soap) use your pipet and pipet bulb to transfer some to your test tube
 - b. For solids (baking soda, sodium hydroxide, and Tums) use your spatula to transfer some to your test tube.
4. When you see your solution change color, use the table provided in the introduction to estimate the pH of the solution. Record the color change and the estimated pH in your lab notebook.
5. When you are done with your household chemical, let your instructor know and he/she will bring you a new one. Continue testing chemicals until you have tested all 6. Make sure to record each one in the table below.

Table S3. Table for recording pH of various household chemicals.

Household Object	Color	pH
Vinegar		
Sodium Hydroxide		

Baking Soda		
Dish Soap		
Tums		
Soda		