Can Ferromagnetic Nanoparticles Help Clean Ocean Oil Spills? The Effect of Ferrofluids & Magnetic Strength on Efficiency of Separating Oil from Water

February 2022

BACKGROUND RESEARCH/PURPOSE:

Oil Spills and Catastrophic Ecological Damage

Crude oil is a fossil fuel that is used to make a range of fuels and products that allow us to heat our homes, operate our cars, produce electricity and power the economy. However, when oil from rigs, pipelines and tankers is accidently spilled in oceans and seas, the ecological damage is devastating and cleanup costs in terms of time, resources and money become a huge burden for government, industry and environmentalists. According to the US Department of Energy, 1.3 million gallons (4.9 million liters) of petroleum are spilled into U.S. waters per year.[1] A major oil spill can lead to double that amount. Furthermore, it is estimated that more than 700 million gallons of waste oil enter worldwide oceans each year, with over half coming from land drainage and improper waste disposal of used motor oil.[2]

Oil spills have drastic effects to marine life. In 2010, an explosion at the BP Deepwater Horizon oil rig led to the largest marine oil spill in history. 206 million gallons of oil and 22,500 tons of methane were spilled into the Gulf of Mexico, 41 miles off the coast of Louisiana.[3] Only 25% of the oil was recovered leaving 154 million gallons of oil at sea.[3] Two million gallons of dispersant were spread to contain the spill causing more toxicity to ocean life. Over 82,000 birds, 6,165 sea turtles, 25,000 marine mammals and a vast number of fish were affected.[3] For example, oiling can coat a bird's wings making it unable to fly or strip away the otter's fur leaving it susceptible to hyperthermia. Oil toxicity caused by dolphins and whales inhaling and ingesting oil can affect heart, lungs, immune function and reproduction and lead to death.[4,5] Oil can make fish and shellfish unsafe for humans to eat.[5] Unfortunately, rescue teams cannot recover and rehabilitate all wildlife impacted as a result of an oil spill. BP spent $15 billion in cleanup costs and another $20 billion in economic damages.[6]

Fortunately, oil density is less than water and, therefore, it floats on the water surface when it leaks or spills. As such, there are multiple historical methods to clean up surface oil spills (Table I) but, unfortunately, these cleanup methods have varying scales and ranges of efficiency and can never remove 100% of spilled oil from the environment.[7] For example, while booms and skimmers are effective in calm seas, they are very inefficient in rough waters like the ocean. Dispersants and burning have environmental consequences for marine life and the atmosphere. Furthermore, scientists need to be very careful that these cleanup methods do not cause additional harm to the environment and ecological health.

Table I. Historical Methods for Oil Spill Cleanup[7]

Method	Description
Oil Booms	Float on water, act as fence to prevent oil spreading or floating away
Skimmers	Machines used to suck up oil from water surface
Sorbents	Materials that soak up oil (hay, peat moss, straw, vermiculite)
In situ burning	Oil floating on surface is burned off
Dispersants	Chemicals sprayed on oil to aid natural breakdown of oil
Hot water/high pressure washing	Dislodges oil from locations inaccessible to machines
Manual labor	Use of hands, rakes, shovels
Bioremediation	Use microorganisms to remove oil
Chemical Stabilization	Elasomizers gelatinize or solidify oil on water surface from spreading
Natural Recovery	Natural means - sun, wind, weather, tides, naturally occurring microbes

Nanotechnology and Magnetism to Clean Oil Spills

A novel methodology to clean oils spills more efficiently while limiting further ecological damage is on the horizon. This technique employs nanotechnology and magnets to magnetically separate oil from water.[8-10] **Nanoparticles** are tiny particles that range in size between 1 to 100 nanometers.[11] Nanoparticles are about 80,000 to 100,000 times smaller than the width of a human hair.[12] Water-repellant nanoparticles that contain iron, **ferromagnetic nanoparticles**, can be created to exhibit magnetic properties.[13] These 10 nM ferromagnetic nanoparticles have the ability to stay suspended in fluids creating a **ferromagnetic fluid or ferrofluid**.[14] Ferrofluids are comprised of ferromagnetic particles, a carrier fluid (usually mineral oil, synthetic oil or water) and a soap-like surfactant to keep the nanoparticles from sticking or clumping together. Ferrofluids behave as normal liquids but in the presence of a strong magnet, the ferrofluid is pulled to the magnet, stiffens and behaves like a solid often creating spike-like structures.[15]

Oil spill cleanup using ferrofluid nanotechnology is hypothesized to work by making the spilled oil magnetic. The ferrofluid spreads and mixes well with the spilled oil. Capillary action will soak up the oil into the pores or cavities of the ferromagnetic particles which magnetizes the oil. Strong magnets are used to separate the magnetized oil from clean water which is sent back to sea. If a method can be devised to then separate the ferromagnetic particles from oil, the clean oil can then be recycled for use in fuels and products.[13] (Figure 1)

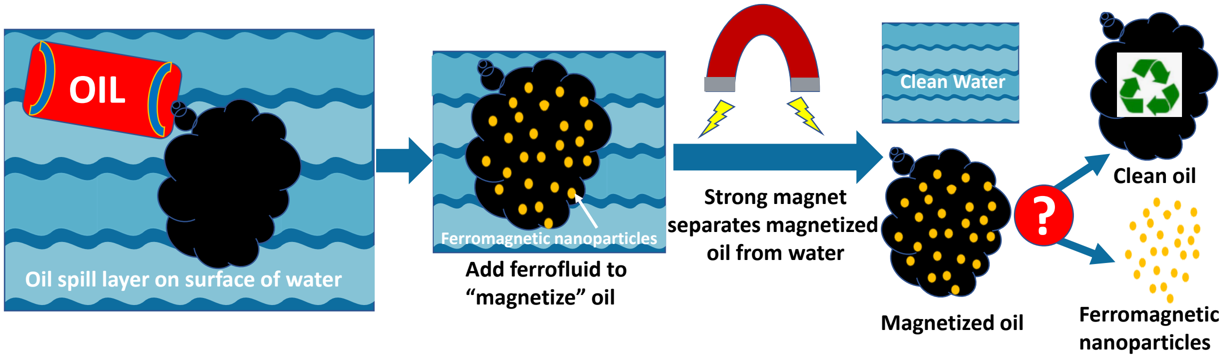


Figure 1. Ferrofluid nanotechnology process for cleanup of oil spills. Ferrofluid in an oil carrier is added to and disperses through the oil on the surface of the water. The ferrofluid "magnetizes" the oil when capillary action draws the oil inside the pores or cavities of the ferromagnetic nanoparticles in the ferrofluid. A strong magnet is applied to separate the oil/ferrofluid mixture from the water. The ferromagnetic nanoparticles containing the oil will attract to the magnet. The clean water can be returned to sea. In the future, one can envision a novel process that could remove the ferromagnetic nanoparticles from the oil to recycle the oil for use in fuels and products. (*Flow chart generated by student but idea derived from http://science buddies.org*[16])

The **objective of this project** is to study the efficiency of separating oil from water using various amounts of ferrofluid and magnets of various strengths. The study will investigate if the ferrofluid will spread and mix through various oils and whether the magnet can remove the oil/ferrofluid mixture from the water. The volume of the oil removed using this ferrofluid cleanup method will be compared to the original volume of the spill and quantified using a variable called **efficiency**. Efficiency is the volume of removed oil divided by the volume of the original oil spill. The efficiency value close to 1 indicates that almost all of the oil has been removed. An efficiency value of zero indicates that little oil has been removed and that the cleanup method is poor.[16] The efficiency of ferrofluid nanotechnology will be tested under a variety of environmental conditions to mimic an oceanic oil spill. Additionally, ferrofluid toxicity to aquatic animal and plant life will also be explored to determine ferrofluid effects on ecological health.

TESTABLE QUESTIONS:

- Do ferrofluids with an oil-based carrier fluid added to spilled oil make it magnetic? How do various amounts of ferrofluids and oil spills affect efficiency of separating oil from water?
- Does this cleanup method have the same efficiency for all oils?
- Does the strength of the magnet affect the efficiency of oil removal?
- Do environmental factors such as currents, water temperature and salt vs. fresh water affect the efficiency of ferromagnetic nanoparticle oil removal?
- Do ferrofluids themselves have a toxic effect on aquatic organisms?

HYPOTHESIS:

If ferrofluids are added to an oil spill, then the oil will mix with water-repellant ferromagnetic nanoparticles and can be magnetically separated from water because magnets attract iron. The higher the concentration of ferrofluid and the stronger the magnet, the more efficient the oil removal.

MATERIALS:

- Fluid Nanotechnology Kit (Home Science Tools: SKU: SB-FERROKT)
  - Ferrofluid, 50 mL
  - Mineral oil, 60 mL
  - Neodymium block magnet, 0.75” X “0.5” X 0.25” (L x W x H)
  - Petri dishes, 90 mm x 15 mm
  - Graduated cylinder, 25 mL
  - Plastic graduated transfer pipettes (1 mL and 3 mL)
  - Nitrile gloves
- Disposable lab coat and lab goggles
- Disposable clear plastic cups, 9 oz (266 mL) and 18 oz (532 mL)
- Plastic zip-loc sandwich bags (16.5 cm X 8.2 cm)
- Food coloring
- Morton’s Salt (1 LB or 737g)
- Spring water
- Thermometer (Celsius)
- Black Sharpie marker
- Bleach
- Paper towels and disposable under pads 23” X 36”

- Oils: Mazola Corn Oil, Bertolli Extra Virgin Olive Oil, Crisco Pure Canola Oil, Crisco Pure Vegetable Oil, Nature's Promise Coconut Oil, Peanut Oil, Johnson's Baby Oil, Prima Kitchen Pure Avocado Oil, Sesame Oil, Briggs & Stratton Engine Oil
- Magnets of different shapes, sizes and materials (neodymium, ceramic, alnico, samarium cobalt)
- *Daphnia Magna* water flea (Carolina Biological Supply, Item #: FAM_142330)
- Brown Planaria Flatworm *Dugesia dorotocephala* (Carolina Biological Supply, Item #: 132955)
- Green Hydra *Chlorohydra viridissima* (Carolina Biological Supply, Item #: 132801)
- Duckweed *Lemna minor* aquatic plant (Carolina Biological Supply, Item #: 161820)

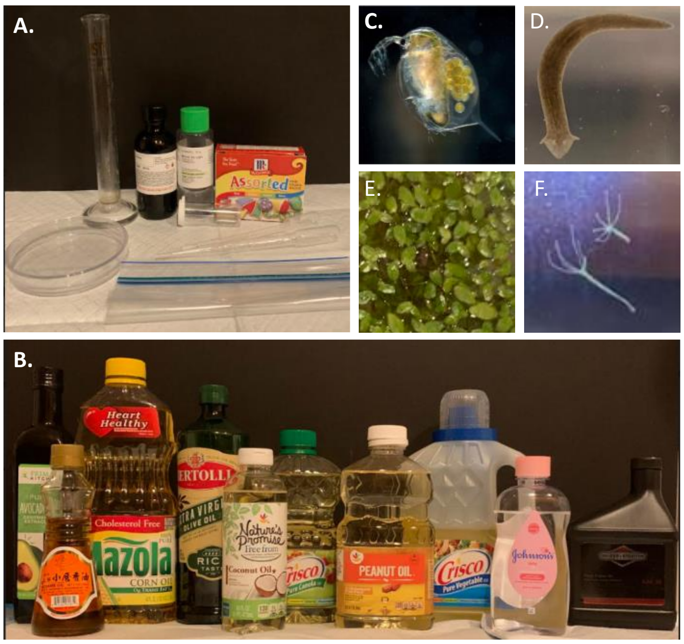


Figure 2. Key Materials and Organisms Used in these Studies

A. Ferrofluid, mineral oil, neodymium magnet, food coloring, petri dishes, plastic sandwich bag, 25 mL graduated cylinder, graduated 1 mL and 3 mL pipettes
B. Different types of oils
C. Female Adult Water Flea *Daphnia magna*
 Image credit: https://www.sciencebuddies.org
D. Planaria Flatworm *Dugesia dorotocephala*
E. Duckweed *Lemna minor* aquatic plant
F. Green Hydra *Chlorohydra viridissima*

PROCEDURES:

I. The Effect of Different Concentrations of Ferrofluid on Oil Spill Cleanup Efficiency[16]

1. **Prepare the colored water to increase visibility**: Add 400 mL of tap water to 18 oz (532 mL) plastic cup, add four drops of green food coloring and mix thoroughly to disperse in the water.

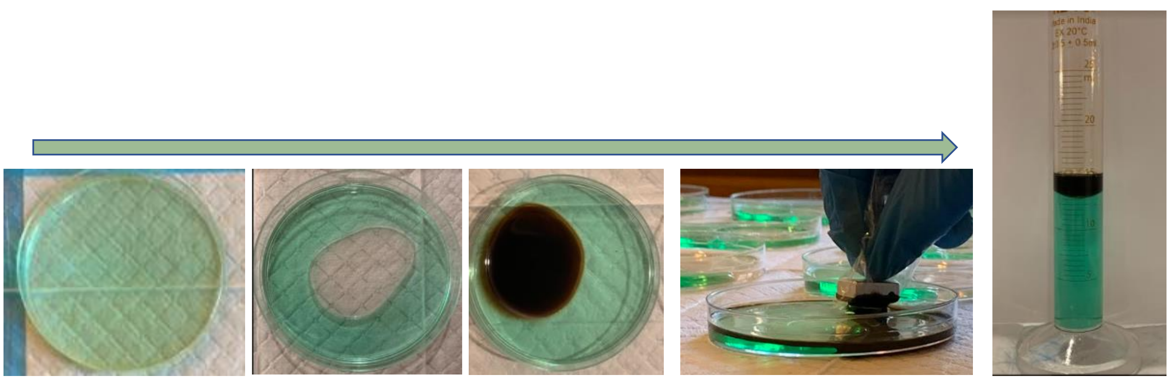
2. **Prepare the "oil spill" in petri dishes**: Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water. Use the 3 mL graduated pipette to add exactly 2.5 mL of mineral oil to each of the petri dishes. It is critical that each petri dish receives the exact same volume of oil in order to compare the results against each other. Aim carefully to release the oil in the middle of the petri dish. (Figure 3)

3. **Make the oil magnetic by adding the ferrofluid**: Invert the bottle of ferrofluid with lid closed several times to mix the bottle before opening. Add 1, 2, 3, 4, 5, 6 or 7 drops of ferrofluid in the oil spill using a 1 mL graduated pipette. For one drop of ferrofluid, place the drop in the middle of the oil spill. For additional drops of ferrofluid, distribute the drops over the oil surface. Make sure that you

have a control dish with no ferrofluid added. Make enough oil spills so that each condition can be tested in triplicate. (Figure 3)

4. **Clean up the oil spill with the neodymium magnet**: Open a clean plastic sandwich bag and put the neodymium magnet (0.75” X 0.5” X 0.75” L x W x H) in one of the corners of the plastic bag. It is now ready to pick up the magnetized oil spill in the oil cleanup procedure. (Figure 3)
   i. Submerge the magnet slightly in the liquid and pass through the total oil spill in one slow movement. It is important to use the same method of moving the magnet through the oil since different methods of moving the magnet through the oil may influence the results.
   ii. Wipe the plastic bag off with a paper towel.
   iii. Place the magnet in the other clean and dry corner of the plastic bag and pass the magnet through the oil a second time. Discard the dirty plastic bag.

5. **Measure how much oil is left on the water.**
   i. Using a 3 mL graduated pipette, transfer all of the leftover liquid (water, oil and ferrofluid) from the petri dish to a 25 mL graduated cylinder. Try to get as much oil out of the petri dish as possible since some will stick to the dish.
   ii. Read the amount of oil left on top of the water (Figure 3). Keep the oil layer level with your eye.
   iii. Discard the fluid in the cylinder in a waste cup. Rinse the cylinder with warm soapy water and dry the inside of the cylinder with a paper towel wrapped around a drinking straw.



Add 14 mL tap water colored with food coloring

Add 2.5 mL mineral oil to simulate “oil spill”

“Magnetize oil” by adding ferrofluid to spill

Use rectangular neodymium magnet to attract magnetized oil to clean spill

Transfer remaining liquids in petri dish to 25 mL graduated cylinder using 3 mL pipette. The amount of remaining magnetized oil (black) is measured at eye level and read at the meniscus or curved part of the fluid.

Figure 3. Methodology for Employing Ferrofluid Nanotechnology to Clean an Oil Spill.

6. **Repeat steps 2-5** two more times for a total of three tests for each cleaning procedure.

7. **Analyze the data** by comparing the volume of oil removed using this cleanup procedure to the volume of the original oil spill and quantifying in a variable called “efficiency”. It is easier to measure the volume of oil left after the cleanup procedure than the amount of oil removed.

   i. Calculate the average volume of leftover mineral oil from the 3 tests.
   ii. Calculate the efficiency of the cleanup procedure using the following equation:

$$\text{Efficiency} = 1 - \frac{\text{Volume of leftover oil (mL)}}{\text{Volume of original oil spill (mL)}}$$

iii. Make a bar graph of the volume left over for the cleanup procedures and the control (no ferrofluid). Make a bar graph of the efficiency of each cleanup procedure and the control.

Safety Precautions:

- **Ferrofluids** are messy and stain skin, clothes and work surfaces. While conducting all experiments with ferrofluids ensure that the ferrofluid is contained. Put the ferrofluid in a secondary containment cup so it does not spill on surfaces. Keep paper towels handy to clean up any spilled ferrofluid quickly. Ensure that you are wearing a disposable lab coat, lab goggles and nitrile exam gloves. Place absorbent pads below work surfaces to protect against staining. Ferrofluid also has a strong smell so be sure to work in a well-ventilated area with windows open.

- **Neodymium magnets** used in these experiments are very strong magnets. Some have the ability to interfere or reset pacemakers. Never put a neodymium magnet in your mouth. It is important to ensure that fingers are not pinched in between magnets. Keep the magnets away from any magnetized materials, computers, cell phones, etc.

II. The Effect of Different Volumes of Oil Spills on Cleanup Efficiency

1. **Prepare the "oil spill" in petri dishes**: Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water. Use the 3 mL graduated pipette to add exactly 2.5 mL, 5 mL, 7.5 mL or 10 mL of mineral oil to three petri dishes so that each condition can be tested in triplicate. Aim carefully to release the oil in the middle of the petri dish.

2. **Make the oil magnetic by adding the ferrofluid**: Invert the bottle of ferrofluid with lid closed several times to mix the bottle before opening. Add 6 drops of ferrofluid in the oil spill using a 1 mL graduated pipette, making sure to distribute the drops over the oil surface. Make sure that you have a control dish with no oil added.

3. Repeat steps 4 through 7 in Section I methods above for oil spill cleanup and data analysis.

III. The Effect of Magnet Strength on Oil Spill Cleanup Efficiency

1. **Prepare the "oil spill" in petri dishes**: Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water. Use the 3 mL graduated pipette to add exactly 2.5 mL of mineral oil to three petri dishes (triplicate test). Aim carefully to release the oil in the middle of the petri dish.

2. **Make the oil magnetic by adding the ferrofluid**: Invert the bottle of ferrofluid with lid closed several times to mix the bottle before opening. Add 6 drops of ferrofluid in the oil spill using a 1 mL graduated pipette, making sure to distribute the drops over the oil surface.

3. Repeat steps 4 through 7 in Section I methods above for oil spill cleanup using the different types of magnets in Table II and data analysis.

Table II. Material, Shape and Dimensions of Magnets Used to Examine Oil Cleanup Efficiency

Picture	Magnet Material & Shape	Magnet Dimensions	Vendor, Catalogue Number
	Neodymium Disc	0.5” diameter, 0.25” thick	Home Science Tools, MG-NEODISC
	Ceramic Disc	0.5” diameter, 0.2” thick	Bunting, DH911
	Alnico Disc	0.5” diameter, 0.25” thick	Bunting, SP-8311
	Neodymium Disc	0.5” diameter, 0.5” thick	Home Science Tools, MG-NEO12X12
	Alnico Disc	0.5” diameter, 0.5” thick	Bunting, SP-8312
	Samarium Cobalt Cuboid	0.75” X 0.75” X 0.32” (LxWxH)	Bunting, SS-805AM
	Neodymium Cube	0.5” X 0.5” X 0.5”	Amazing Magnets, C500D
	Neodymium Cube	0.75” X 0.75” X 0.75”	Amazing Magnets, C750F-M
	Neodymium Rectangular Prism	0.75” X 0.5” X 0.25 ” (LxWxH)	Home Science Tools, MG-NEOBLOK
	Neodymium Rod	0.5” diameter, 0.75” length	Amazing Magnets, R750D-N42
	Neodymium Sphere	0.75’’ diameter	Amazing Magnets, S750F
	Neodymium Ring	0.75” diameter, 0.25” Thick, 0.51’’ hole	Amazing Magnets, H250F-510-DM
	Neodymium Ring	0.75” diameter, 0.375” thick	Amazing Magnets, H375FD-N42
	Neodymium Ring	0.5” diameter, 0.25” thick	Amazing Magnets, DH250D-CB-FN-N42

Magnet photo credits found on the vendor’s websites: amazingmagnets.com, buntingmagnets.com, homesciencetools.com.

<u>Safety Precautions</u>: Neodymium, alnico, ceramic and samarium cobalt magnets vary in their strength and some are quite strong. They may have the ability to interfere and reset pacemakers. Never put these magnets in your mouth and be very cautious not to pinch fingers between magnets. Keep these magnets away from computers, credit cards and other magnetized objects.

IV. The Effect of Different Ways of Moving the Magnet on Oil Spill Cleanup Efficiency

1. **Prepare the “oil spill” in petri dishes**: Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water. Use the 3 mL graduated pipette to add exactly 2.5 mL of mineral oil to three petri dishes (triplicate test). Aim carefully to release the oil in the middle of the petri dish.

2. **Make the oil magnetic by adding the ferrofluid**: Invert the bottle of ferrofluid with lid closed several times to mix the bottle before opening. Add 6 drops of ferrofluid in the oil spill using a 1 mL graduated pipette, making sure to distribute the drops over the oil surface.

3. Repeat steps 4 through 7 in Section I methods above for oil spill cleanup but this time varying the ways the magnet is moved across the oil including:

- Slow movement slightly submerged (few mm below surface of oil) as in Sections I, II, III

- Fast movement slightly submerged (few mm below surface of oil)
- Completely submerge magnet in oil (touch bottom of petri dish)
- Barely skimming surface of oil
- Hovering over the surface of the oil (~1 cm above the surface of the oil)

V. The Effect of Different Kinds of Oils on Oil Spill Cleanup Efficiency

1. **Prepare the "oil spill" in petri dishes**: Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water. Use the 3 mL graduated pipette to add exactly 2.5 mL of the respective oil to three petri dishes (triplicate test). Oils used include: Mazola Corn Oil, Bertolli Extra Virgin Olive Oil, Crisco Pure Canola Oil, Crisco Pure Vegetable Oil, Nature's Promise Coconut Oil, Peanut Oil, Johnson's Baby Oil, Prima Kitchen Pure Avocado Oil, Sesame Oil, Briggs & Stratton Engine Oil. Aim carefully to release the oil in the middle of the petri dish.

2. **Make the oil magnetic by adding the ferrofluid**: Invert the bottle of ferrofluid with lid closed several times to mix the bottle before opening. Add 6 drops of ferrofluid to each different type of oil spill using a 1 mL graduated pipette, making sure to distribute the drops over the oil surface.

3. Repeat steps 4 through 7 in Section I methods above for oil spill cleanup and data analysis.

VI. The Effect of Environmental Factors on Oil Spill Cleanup Efficiency

1. **Prepare water conditions to mimic different environmental conditions:**

   a. Still water (as in Sections I, II, III, IV, V above): Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of room temperature (22°C) green colored water. Conduct in triplicate.

   b. Mimic cold ocean temperatures (7°C or 44.6°F): Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water that was chilled in a refrigerator to 7°C (44.6°F). Conduct in triplicate.

   c. Mimic warm ocean temperatures (29°C or 84.2°F): Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored water that was heated on a stove to 29°C (84.2°F). **Safety Precaution**: Be careful not to spill hot water on the skin to avoid burns. Conduct in triplicate.

   d. Mimic salinity of the ocean: On average, seawater in the world's oceans has a salinity of 3.5% (35g/L salt).[17] Prepare salt water by adding 35 grams of Morton's Salt to 1L of room temperature green colored tap water. Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of the green colored salt water. Conduct in triplicate.

   e. Simulate ocean waves: Using a 25 mL graduated cylinder, fill each petri dish with 14 mL of room temperature (22°C) green colored water. During the cleanup process, rock the petri dish back and forth while moving the magnet through the oil. Be careful not to spill the water while rocking. Conduct in triplicate.

2. **Prepare the "oil spill" in petri dishes**: Use the 3 mL graduated pipette to add exactly 2.5 mL of mineral oil to three petri dishes (triplicate test). Aim carefully to release the oil in the middle of the petri dish.

3. **Make the oil magnetic by adding the ferrofluid**: Invert the bottle of ferrofluid with lid closed several times to mix the bottle before opening. Add 6 drops of ferrofluid in the oil spill using a 1 mL graduated pipette, making sure to distribute the drops over the oil surface.

4. Repeat steps 4 through 7 in Section I methods above for oil spill cleanup and data analysis.

VII. The Effect of Ferrofluids on Aquatic Organisms

Upon receipt of the *Daphnia magna* (water flea), Brown Planaria Flatworm *Dugesia dorotocephala* and Green Hydra *Chlorohydra viridissima* cultures in the mail from Carolina Biological Supply Company, immediately unscrew the cap of the container and put it loosely on the top to let oxygen in, which these organisms need to survive.[18,19] Duckweed *Lemna minor* aquatic plant arrives from Carolina Biological Company wrapped in a wet paper towel. Place the duckweed in an 18 oz plastic cup filled with spring water and they will float on the water. Keep all organisms at room temperature of 22°C.

***Daphnia Magna* Toxicity Assay:**

1. Add 120 mL of room temperature spring water to 9 oz (266 mL) clear plastic cups labelled with the following amounts of ferrofluid to respective cups: 0, 1, 3, 5, 10, 15, and 20 drops. Use 3 cups for each ferrofluid amount.
2. Add 10 living Daphnia to each cup then add the respective drops of ferrofluid to the cup.
3. Wait until 2 hours have passed and then count living and dead Daphnia in each cup. Live Daphnia will move around the cup. Dead Daphnia do not move, lie on the bottom of the cup or float on the surface of the water. Repeat these observations at 4, 6, 8, 10, and 12 hours.
4. Calculate the average number and the percentage of dead and live Daphnia recorded for each ferrofluid concentration and the control over exposure time. Plot a dose-response-curve from the results where the dose (concentration of ferrofluid) is depicted on the x-axis and the response (% dead Daphnia) is represented on the y-axis.

Hydra Toxicity Assay:

1. Green Hydra attach to the walls and bottom of the 4 oz shipping cup, which holds 120 mL of spring water. Using the original packaging containing ~30 Hydra per cup, add the following amounts of ferrofluid to respective cups: 0, 1, 3, 5, 10, 15, and 20 drops.
2. Wait for 2 hours and count living Hydra in each cup. Sick Hydra will disintegrate and lose their structure.
3. Calculate the percentage of live and dead Hydra for each ferrofluid concentration and the control over exposure time (96 hours). Plot a dose-response-curve from the results where the dose (concentration of ferrofluid) is depicted on the x-axis and the response (% dead Hydra) is represented on the y-axis.

Planaria Toxicity Assay:

1. Add 120 mL of room temperature spring water to 9 oz (266 mL) clear plastic cups labelled with the following amounts of ferrofluid to respective cups: 0, 1, 3, 5, 10, 15, and 20 drops. Use 3 cups for each ferrofluid amount.
2. Add 10 living Planaria to each cup then add the respective drops of ferrofluid to the cup.

3. Count living and dead Planaria in each cup every 24 hours for 4 weeks. Live Planaria swim around the cup on the sides, bottom and freely in the middle. Planaria also attach to side and bottom of cup; swirl the cup to awaken.
4. Calculate the average number and the percentage of dead and live Planaria recorded for each ferrofluid concentration and the control over exposure time. Plot a curve from the results where the concentration of ferrofluid is depicted on the x-axis and the % living Planaria is represented on the y-axis.

Duckweed Toxicity Assay:

1. Add 120 mL of spring water to 9 oz (266 mL) clear plastic cups labelled with the following amounts of ferrofluid to respective cups: 0, 1, 3, 5, 10, 15, and 20 drops. Use 3 cups for each ferrofluid amount.
2. Add ~50 living duckweed plants to each cup then add the respective drops of ferrofluid to the cup.
3. Count living and dead duckweed after 7 days. Live duckweed is green and dead duckweed is brown.
4. Calculate the percentage of dead and live duckweed recorded for each ferrofluid concentration and the control. Plot a dose-response-curve from the results where the dose (concentration of ferrofluid) is depicted on the x-axis and the response (% living duckweed) is represented on the y-axis.

Biological Agents and Risk Assessment:
The cultures of *Daphnia magna*, *Hydra viridissima*, *Dugesia dorotocephala* and *Lemna minor* are isolated from local ponds by Carolina Biological Supply Company. These organisms fall in the same line as the classification of all microorganisms within the United States of America being governed by the Public Health Service. Carolina Biological Supply Company under these classification regulations classifies these organisms as Biosafety Level/Shipping Class I. According to the Public Health Service's definition for Biosafety Level/Shipping Class I, these organisms are considered to be non-pathogenic and as such would not be expected to cause harm to healthy people, animals or to the environment.[20] All safety precautions and disposal methods must be strictly followed.

Safety Precautions and Disposal: For maximum safety, maintain proper handling, clean up and disposal of *Daphnia magna*, *Hydra viridissima*, *Dugesia dorotocephala* and *Lemna minor*. Nose and mouth should be kept away from tubes, pipettes or other tools that come in contact with the cultures. Gloves must be worn at all times. For disposal, add 5 mL of bleach to each cup with collected dead/live organisms, mix well and after 20 min pour down the toilet. Do not release in the wild.

DATA:

I. The Effect of Different Concentrations of Ferrofluid on Oil Spill Cleanup Efficiency

The results from this experiment using a 2.5 mL mineral oil spill indicate that increasing concentrations of ferrofluid were able to remove more oil from the petri dish. This is reflected by the smaller volume of oil remaining after the cleanup procedure. There is an inverse relationship between volume of oil left after cleanup and efficiency. Six drops of ferrofluid were sufficient to remove most oil from the petri dish. Increasing to 7 drops of ferrofluid did not result in the removal of remaining residual oil. (Figure 4).

The volume of oil removed using the ferrofluid cleanup procedure was compared to the volume of the original spill and is quantified in a variable called **efficiency** (Methods section I). An efficiency value close to 1 means that almost all the oil has been removed, indicating that the cleanup method works well in removing the spilled oil from the water. An efficiency value close to 0 means that little of the original oil has been removed, indicating that the cleanup method is poor at removing spilled oil from the surface of the water. Using 6 or 7 drops of ferrofluid produced the greatest efficiency value (0.96), indicating that this is the most efficient concentration of ferrofluid to remove the oil.

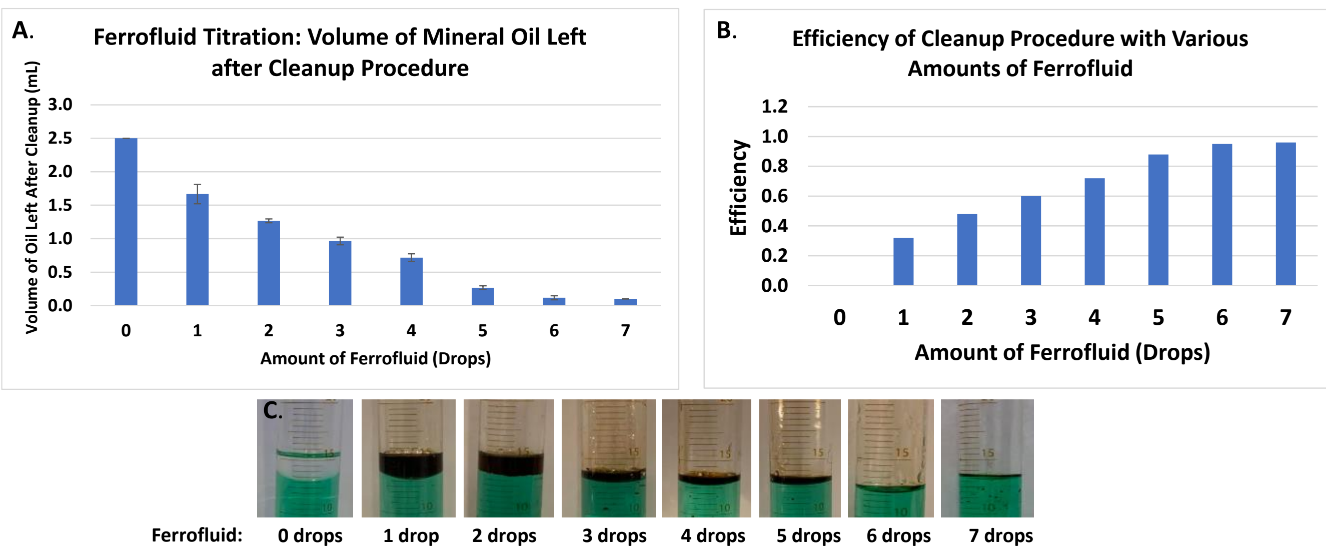


Figure 4. The Effect of Different Concentrations of Ferrofluid on Oil Spill Cleanup Efficiency. 2.5 mL of mineral oil were placed in the center of a petri dish containing 14 mL of green colored tap water. The oil was made magnetic by distributing the indicated amount of ferrofluid across the oil surface. A rectangular neodymium block magnet inside a plastic sandwich bag was used to clean the oil spill by slightly submerging it and slowly passing it through the total oil spill in one movement. A second pass with the magnet in a clean plastic bag was then carried out. The entire contents of the petri dish were transferred using a 3 mL graduated pipette to a 25 mL graduated cylinder and the volume of oil (black liquid) left after cleanup was determined. **Plot 4A** is the average volume of oil leftover from 3 independent experiments and error bars represent standard deviation. **Plot 4B** is the efficiency of the cleanup procedure calculated from the averages of 3 separate experiments in Plot A as described in

Methods. **Figure 4C** is a picture of the oil (black liquid) remaining in the petri dish and measured by a graduated cylinder.

Observations: The ferrofluid mixed well with the oil spill. The black magnetic ferrofluid floated towards the neodymium magnet dragging the oil with it. For all 3 replicates, there was a residual amount of oil remaining at 6 drops and 7 drops of ferrofluid. When ferrofluid is added to a petri dish containing only the colored water, ferrofluid droplets sat at the bottom of the dish.

II. The Effect of Different Volumes of Oil Spills on Cleanup Efficiency

This experiment examined how various amounts of oil spills affect the efficiency of separating oil from water using ferrofluid. The data indicate that as the volume of the oil spill increases, the ability of 6 drops of ferrofluid to remove the spill becomes significantly less efficient (Figure 5). There is an inverse relationship between volume of oil left after cleanup and efficiency. Six drops of ferrofluid are very efficient at removing the 2.5 mL spill (efficiency = 0.93) but were much less efficient at removing a 10 mL oil spill (efficiency = 0.26).

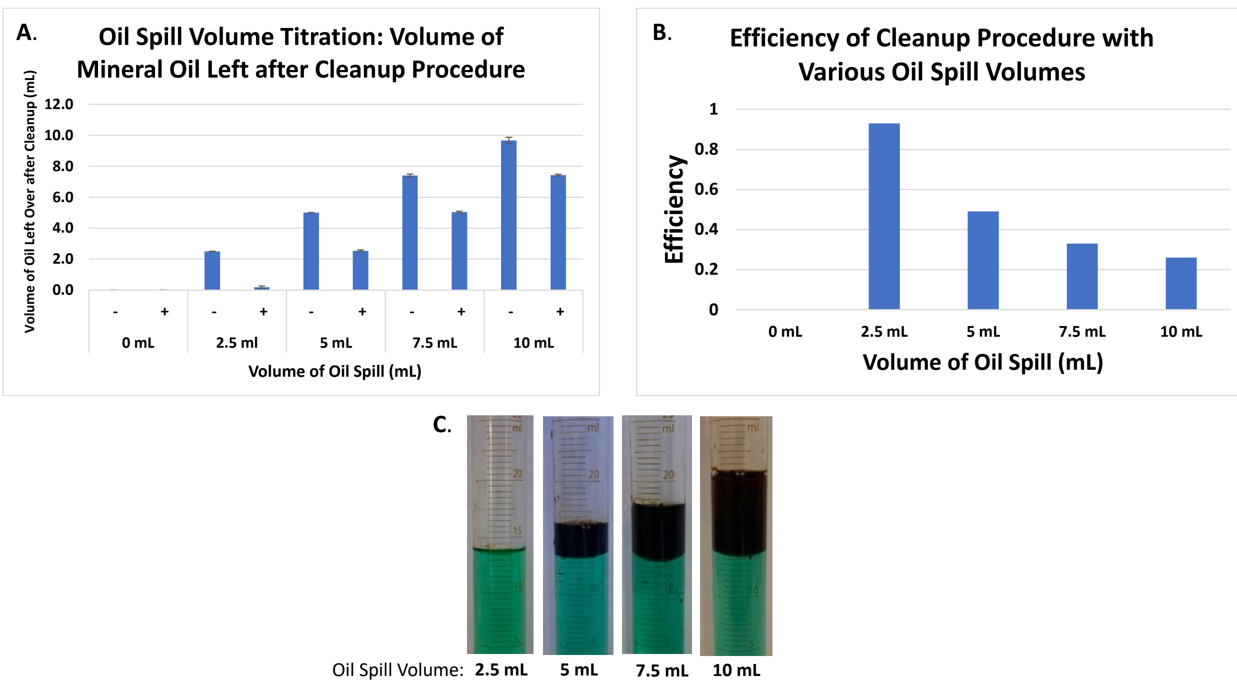


Figure 5. The Effect of Different Volumes of Oil Spills on Cleanup Efficiency. The indicated volume of mineral oil was placed in the center of a petri dish containing 14 mL green colored tap water. The oil was made magnetic by distributing 6 drops of ferrofluid across the oil surface. A rectangular neodymium block magnet inside a plastic sandwich bag was used to clean the oil spill by slightly submerging it and slowly passing it through the total oil spill in one movement. A second pass with the magnet in a clean plastic bag was then carried out. The entire contents of the petri dish were transferred using a 3 mL graduated pipette to a 25 mL graduated cylinder and the volume of oil left after cleanup was determined. **Plot A** is the average volume of oil leftover from 3 independent experiments -/+ 6 drops of ferrofluid at each volume of oil spill. Error bars represent standard deviation. **Plot B** is the efficiency of

the cleanup procedure calculated from the averages of 3 separate experiments with 6 drops ferrofluid in Plot A as described in Methods. **Figure 5C** is a picture of the oil (black liquid) remaining in the petri dish and measured by a graduated cylinder.

Observation: Six drops of ferrofluid did not have enough power to completely cleanup oil spills greater than 2.5 mL.

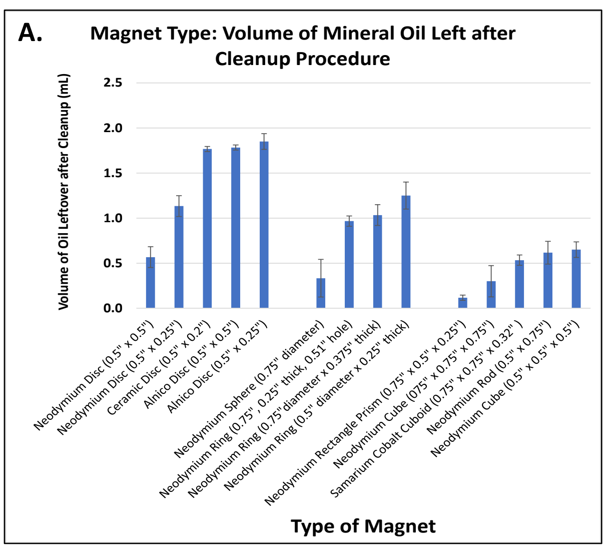
III. The Effect of Magnet Strength on Oil Spill Cleanup Efficiency

Several factors determine the strength of a magnet, including material type, shape and size. This experiment examines how magnet material type, size and shape affect the efficiency of oil removal with ferrofluid (Figure 6). There is an inverse relationship between volume of oil left over after cleanup and efficiency. The data indicate the following trends:

1. **Material Type**: Neodymium magnets are more efficient at cleaning the oil spill than samarium cobalt, ceramic or alnico magnets of relatively the same size and shape. Ceramic magnets were slightly more efficient at cleaning the oil spill than alnico magnets of the same size and shape.

2. **Shape:** Rectangular prism, cube, and rod-shaped magnets are more efficient in cleaning the oil spill than ring-shaped magnets. Ring-shaped magnets are more efficient than disc-shaped magnets of similar size.

3. **Size:** The larger neodymium cube is more efficient at oil removal than the smaller sized neodymium cube. Larger neodymium rings are more efficient than smaller sized neodymium rings. Larger neodymium discs are more efficient than smaller neodymium discs.



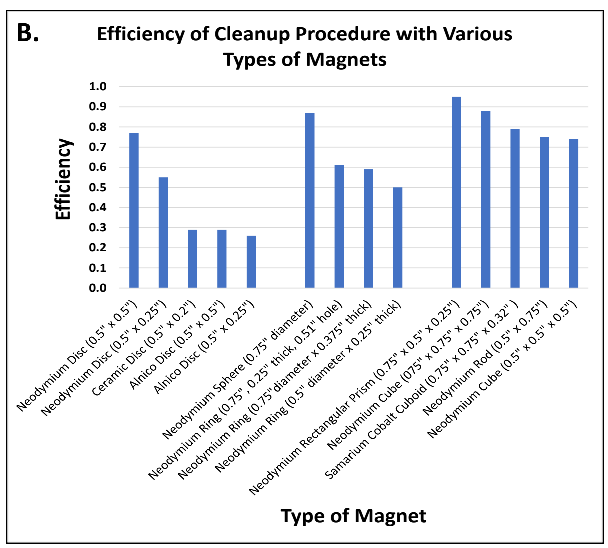


Figure 6. The Effect of Magnet Strength on Oil Spill Cleanup Efficiency. 2.5 mL of mineral oil were placed in the center of a petri dish containing 14 mL green colored tap water. The oil was made

magnetic by distributing 6 drops of ferrofluid across the oil surface. Magnets listed in Table I were respectively placed inside a plastic sandwich bag and used to clean the oil spill by slightly submerging it and slowly passing it through the total oil spill in one movement. A second pass with the magnet in a clean plastic bag was then carried out. The entire contents of the petri dish were transferred using a 3 mL graduated pipette to a 25 mL graduated cylinder and the volume of oil left after cleanup was determined. **Plot A** is the average volume of oil leftover from 3 independent experiments and error bars represent standard deviation. Photo Inset: Examples of magnetized oil covering surface of a neodymium ring and neodymium rectangular magnet. **Plot B** is the efficiency of the cleanup procedure calculated from the averages of 3 separate experiments in Plot A as described in Methods.

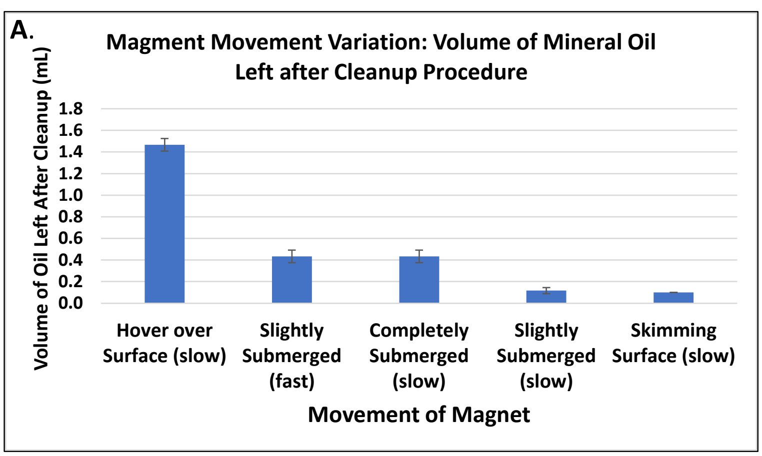
Observations: The oil adhered to the bottom of the magnet and "crawled" up the sides of the magnet. Magnets with larger surface areas attracted more of the magnetized oil. The clear plastic bag covering ring-shaped magnets prevented the magnetized oil from ascending into the interior of ring.

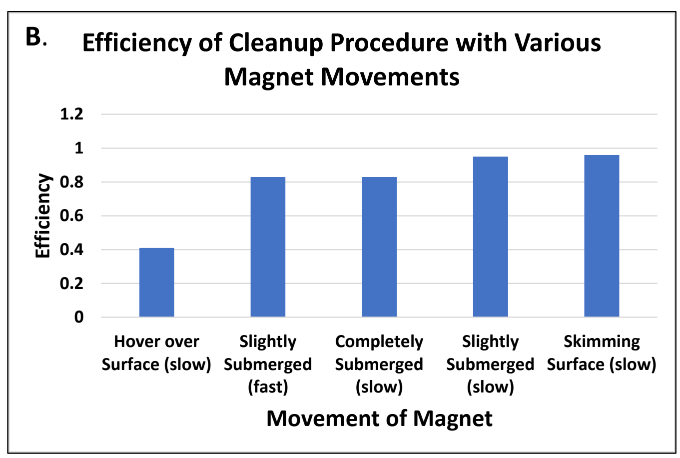
IV. The Effect of Different Ways of Moving the Magnet on Oil Spill Cleanup Efficiency

This experiment tests the cleanup efficiency with different ways of moving the magnet (Figure 7). The following conditions were tested:

- Hover the magnet over the surface of the oil spill (~ 1 cm from the surface).
- Slightly submerge magnet in the oil spill (few mm below surface) with **slow** movement – this is the method that was used in all other experiments in this project
- Slightly submerge magnet in the oil spill (few mm below surface) with very **fast** motion
- Completely submerge magnet in the oil with magnet touching the bottom of the petri dish
- Skimming the surface – barely touching the oil

There was an inverse relationship between the volume of oil left after the cleanup procedure and the efficiency. Hovering over the surface was the least efficient method (efficiency = 0.4). Fast/slightly submerged and completely submerged movement had an efficiency of 0.8. Slow/slightly submerged and skimming the surface were the most efficient ways to remove the oil (efficiency = 0.96).





C.

Hover Over **Slightly Submerged** **Completely Submerged** **Skim Surface**

Figure 7. The Effect of Different Ways of Moving the Magnet on Oil Spill Cleanup Efficiency. 2.5 mL of mineral oil were placed in the center of a petri dish containing 14 mL green colored tap water. The oil was made magnetic by distributing 6 drops of ferrofluid across the oil surface. A rectangular neodymium block magnet was placed inside a plastic sandwich bag using various types of movement: hovering over the surface, fast/slightly submerged, completely submerged, slow/slightly submerged, and skimming the surface slowly. A second pass with the magnet in a clean plastic bag was then carried out. The entire contents of the petri dish were transferred using a 3 mL graduated pipette to a 25 mL graduated cylinder and the volume of oil left after cleanup was determined. **Plot A** is the average volume of oil leftover from 3 independent experiments and error bars represent standard deviation. **Plot B** is the efficiency of the cleanup procedure calculated from the averages of 3 separate experiments in Plot A as described in Methods. **C**. Illustration of techniques for movement of the magnet.

Observations: When the magnet was hovered over the surface of the spill, the magnetized oil “jumped” from the surface toward the magnet. When slightly submerged or skimming the surface of the oil, the oil adhered to the bottom of the magnet and “crawled” up the sides of the magnet. When the magnet was fully submerged, it tended to smash the ferrofluid into tracks at the bottom of the petri dish.

V. The Effect of Different Kinds of Oils on Oil Spill Cleanup Efficiency

This experiment examines if the ferrofluid cleanup method has the same efficiency for other types of oils (Figure 8). Ferrofluid was most efficient at cleaning up mineral oil, baby oil and motor oil with efficiencies of 0.95, 0.95 and 0.81 respectively. Avocado and corn oil had efficiencies of 0.5 and extra virgin olive oil, sesame oil, canola oil and peanut oil had efficiencies ranging from 0.40 - 0.47. Ferrofluid was least efficient at cleaning up vegetable oil (efficiency = 0.39) and coconut oil (0.32).

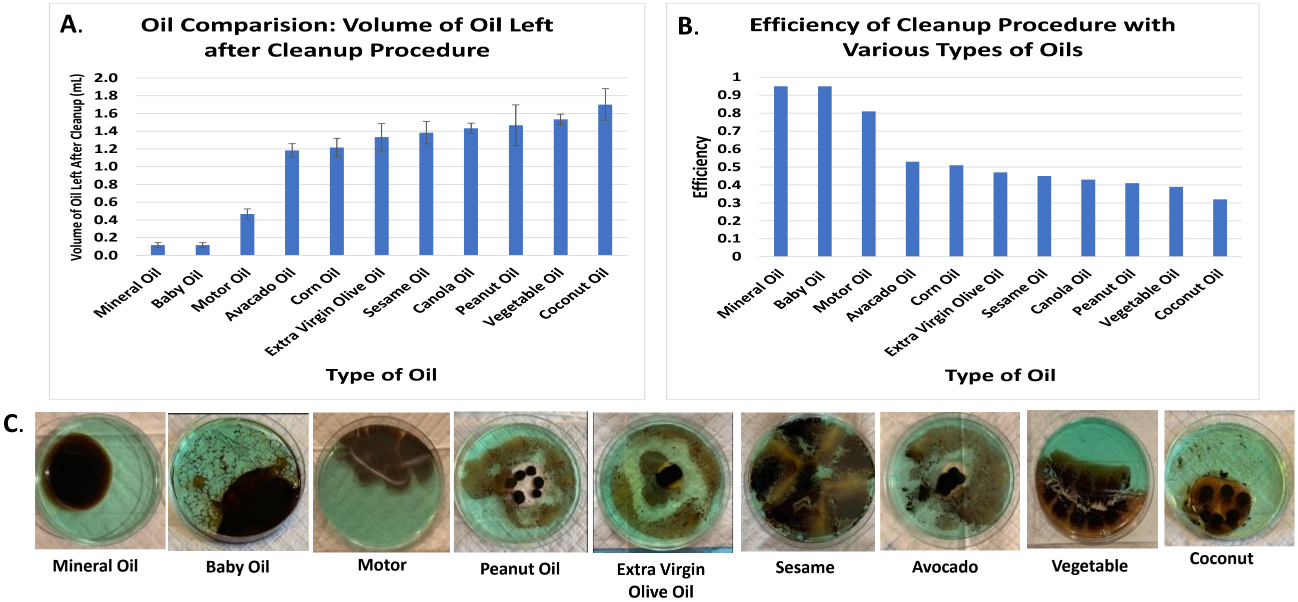


Figure 8. The Effect of Different Kinds of Oils on Oil Spill Cleanup Efficiency. 2.5 mL of the respective oil were placed in the center of a petri dish containing 14 mL green colored tap water. The oil was made magnetic by distributing 6 drops of ferrofluid across the oil surface. A rectangular neodymium block magnet was placed inside a plastic sandwich bag and used to clean the oil spill by slightly submerging it and slowly passing it through the total oil spill in one movement. A second pass with the magnet in a clean plastic bag was then carried out. The entire contents of the petri dish were transferred using a 3 mL graduated pipette to a 25 mL graduated cylinder and the volume of oil left after cleanup was determined. **Plot A** is the average volume of oil leftover from 3 independent experiments and error bars represent standard deviation. **Plot B** is the efficiency of the cleanup procedure calculated from the averages of 3 separate experiments in Plot A as described in Methods. **C.** Ferrofluid patterns in different oils.

Observations: Oils used in this study have different viscosities. Ferrofluid dispersed throughout the mineral oil, baby oil and motor oil. For peanut oil, extra virgin olive oil, avocado oil, vegetable oil and coconut oil, ferrofluid sunk to the bottom of the petri dishes in distinct droplets. Ferrofluid in sesame oil spread somewhat before sinking to bottom.

VI. The Effect of Environmental Factors on Oil Spill Cleanup Efficiency

This experiment examines environmental factors, such as wave currents, water temperature, salt vs. fresh water, effect on the efficiency of ferromagnetic nanoparticle oil removal (Figure 9). Ferrofluid oil removal had very consistent oil removal properties for still tap water, cold water, warm water and salt water (efficiency = 0.95). Ferrofluid cleanup in wavy conditions resulted in an efficiency of 0.86.

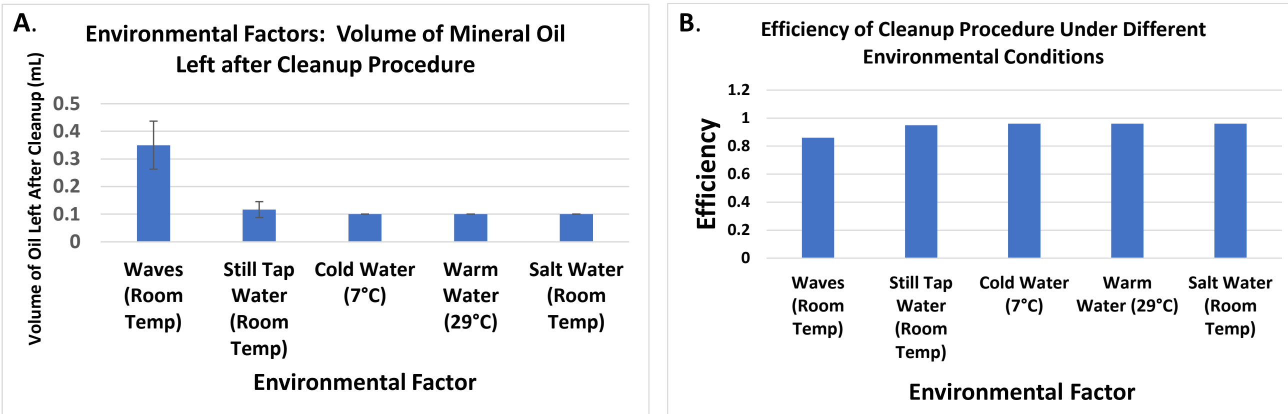
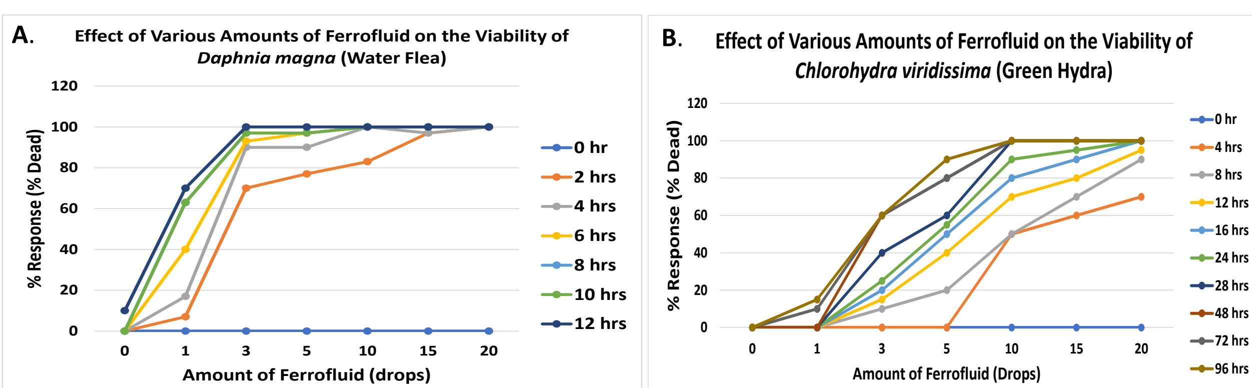


Figure 9. The Effect of Different Environmental Factors on Oil Spill Cleanup Efficiency. 2.5 mL of mineral oil were placed in the center of a petri dish containing 14 mL green colored tap water under conditions mimicking ocean environments including waves, cold/warm temperature and salt water. The oil was made magnetic by distributing 6 drops of ferrofluid across the oil surface. A rectangular neodymium block magnet was placed inside a plastic sandwich bag and used to clean the oil spill by slightly submerging it and slowly passing it through the total oil spill in one movement. A second pass with the magnet in a clean plastic bag was then carried out. The entire contents of the petri dish were transferred using a 3 mL graduated pipette to a 25 mL graduated cylinder and the volume of oil left after cleanup was determined. **Plot A** is the average volume of oil leftover from 3 independent experiments and error bars represent standard deviation. **Plot B** is the efficiency of the cleanup procedure calculated from the averages of 3 separate experiments in Plot A as described in Methods.

VII. The Effect of Ferrofluids on Aquatic Organisms

This experiment seeks to determine if ferrofluid nanoparticles themselves harm aquatic organisms. A series of dose response experiments were carried out to determine if ferrofluids have a toxic effect on aquatic organisms. Figure 10 (A-E) demonstrates cytotoxicity in *Daphnia magna* (water fleas) and *Chlorohydra viridissima* (hydra). Most Daphnia are dead at 4 hours after treatment with 3 drops ferrofluid (Figure 10A). More Hydra died at higher ferrofluid concentrations and more death occurred after longer incubation times. The IC_{50} or cytotoxic dose that causes 50% Hydra death was 5 drops ferrofluid at 16 hours.



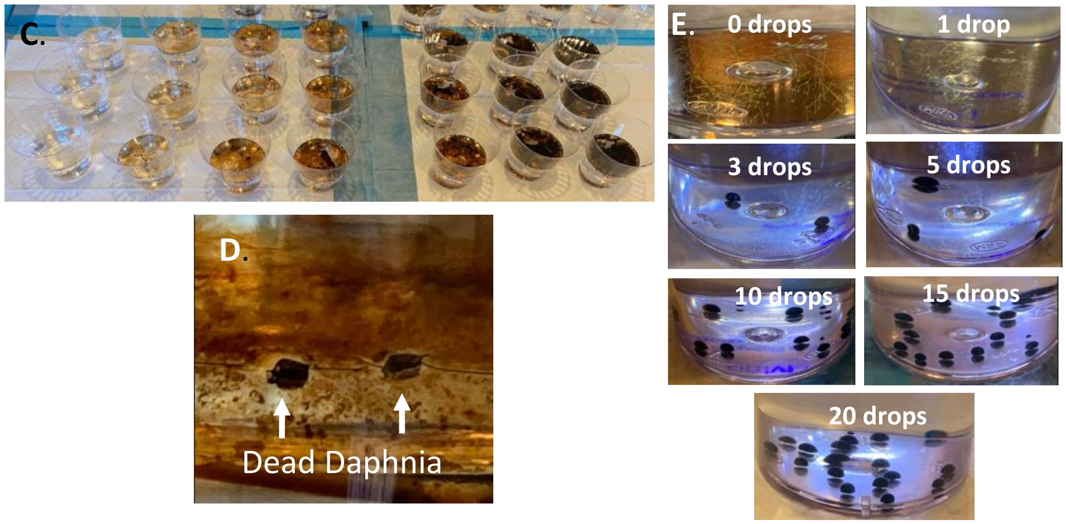


Figure 10. The Effect of Ferrofluids *on Daphnia magna* and *Chlorohydra viridissima*. Plot A. Ten Daphnia were added to a 9 oz (266 mL) clear plastic cup filled with 120 mL spring water followed by addition of the respective number of drops of ferrofluid. Living and dead Daphnia in each cup were counted at the indicated time point. The graph represents the percentage of dead Daphnia from an average of 3 tests per ferrofluid concentration. **Plot B.** Thirty Hydra in 120 mL spring water were treated with the indicated amount of ferrofluid. The percentage of living and dead Hydra were determined at various time points up to 96 hours and percentage of dead Hydra is represented on the graph. **C.** Daphnia cups with different concentrations ferrofluid. **D.** Dead Daphnia that were caught in the oil film/residue on the side of the cup**. E.** Cytotoxicity of Hydra at different concentrations.

Observations: For both Daphnia and Hydra cups, ferrofluid remained as distinct drops at bottom of the cup. A layer of oil floated on the surface of the water which is most likely the carrier fluid. The greater the amount of ferrofluid, the thicker the oil residue on the surface of the water. Live Daphnia moved around the cup. Dead Daphnia did not move, laid on the bottom of the cup or floated on the top. There were more dead Daphnia at higher ferrofluid concentrations and more death occurred after longer incubation times. Some Daphnia got stuck in the oily residue at the side of the cups which led to their demise. Hydra attached to the sides and bottom of the plastic cup and did not contact the oil residue. Dead Hydra disintegrated.

A series of dose response experiments were carried out to determine if ferrofluids have a toxic effect on the aquatic organism *Dugesia dorotocephala* (Planaria flatworm) and aquatic plant *Lemna minor* (Duckweed). Figure 11 (A-F) demonstrates cytotoxicity in Planaria and duckweed. The majority of the Planaria were still alive after 28 days. Less than 20% duckweed had died after 7 days of exposure to ferrofluid.

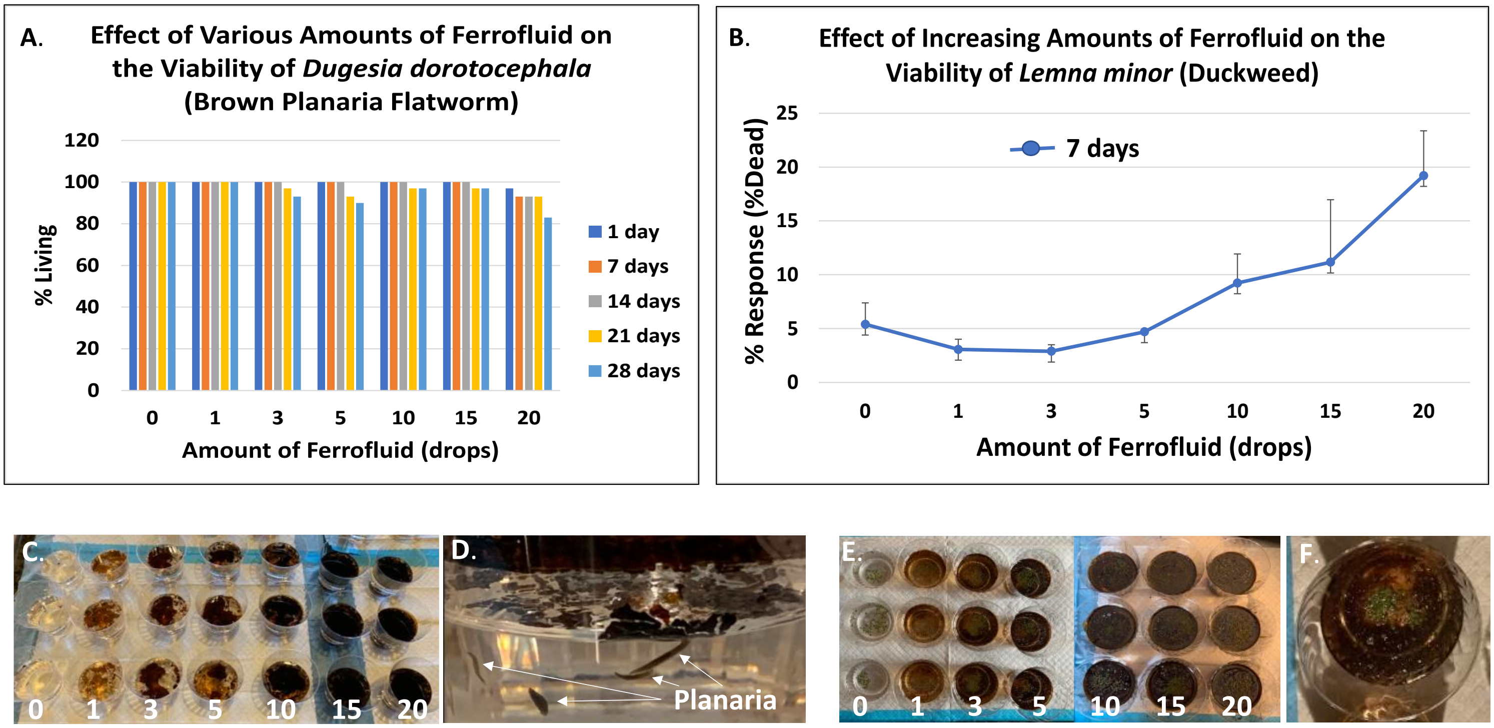


Figure 11. The Effect of Ferrofluids *on Dugesia dorotocephala* (brown Planaria flatworm) (A) and *Lemna minor* (duckweed aquatic plant) (B). Plot A. Ten Planaria were added to a 9 oz (266 mL) clear plastic cup filled with 120 mL spring water followed by addition of the respective number of drops of ferrofluid. Living and dead Planaria in each cup were counted at the indicated time point over the course of one month. The graph represents the percentage of living Planaria from an average of 3 tests per ferrofluid concentration. **Plot B.** Approximately 50 duckweed plants were placed in 120 mL spring water and treated with the indicated amount of ferrofluid. The average percentage of living and dead duckweed plants from 3 trials were determined after one week of exposure to the ferrofluid. Error bars represent standard deviation. **C.** Treatment of Planaria at different ferrofluid concentrations. **D.** Planaria swimming around the ferrofluid. **E.** Treatment of duckweed at different ferrofluid concentrations. **F.** Duckweed floating on surface of water among oily film/residue on surface.

Observations: Live Planaria moved around the cup. They were not affected by swimming over the ferrofluid drops at the bottom of the cups nor swimming through the oil residues floating on the surface of the water. As weeks went by, some Planaria (~30%) looked smaller in size. Duckweed floated on the surface of the cup and were not affected by thick oil residues at the higher concentrations of ferrofluid.

ANALYSIS:

I. The Effect of Different Concentrations of Ferrofluid on Oil Spill Cleanup Efficiency and II. The Effect of Different Volumes of Oil Spills on Cleanup Efficiency

The purpose of these experiments was to determine if ferrofluids with an oil carrier could make an oil spill magnetic. The goal was to have the ferromagnetic particles from the ferrofluid spread and mix with the spilled oil, making it magnetic. The carrier fluid used in the ferrofluid is a light hydrocarbon oil.[21] Likewise, the mineral oil used to create the oil spill is a refined petroleum-based hydrocarbon oil.[22]

Therefore, the carrier fluid mixed well with the spilled mineral oil and the ferrofluid naturally spread and mixed with the oil spill to magnetize the oil. In essence, the ferrofluid transformed the oil slick into a more dilute ferrofluid magnetizable mass. Through capillary action, the oil is absorbed in the pores/cavities of the ferromagnetic particles. Since the ferrofluid is attracted to magnets, the application of a strong magnetic force separated the oil/ferrofluid mixture from the water. A ferrofluid with a non-oil-based carrier, such as water, would not be effective in cleaning the oil spill. The water carrier, which suspends the ferromagnetic particles, would not mix with the oil spill. When the oil-based ferrofluid was added to a petri dish containing only the colored water (no oil spill), ferrofluid droplets sat at the bottom of the dish and did not disperse in the water since the oil-based carrier does not mix with water.

Figure 4 showed that an optimal amount of ferrofluid needs to be added to the oil spill of a fixed volume to most efficiently clean up the spill. The higher the concentration of ferrofluid, the more efficient the oil spill cleanup. In this case, 6 drops of ferrofluid were optimal to efficiently clean a 2.5 mL oil spill. The data in **Figure 5** using 6 drops of ferrofluid indicates that as the volume of the oil spill increases, the ability of 6 drops of ferrofluid to remove the spill becomes much less efficient. Therefore, as the volume of oil spill increases, more ferrofluid will be needed to achieve a saturating amount to clean the spill. Applied at a much larger scale, great amounts of ferrofluid would be needed to clean up large oil spills on the ocean since the relationship of ferrofluid and oil spill volume is linear.

Potential sources of error: A very small amount of residual oil remains in the petri dish after transfer to the graduated cylinder for measurement. This may bias the results toward a more efficient cleanup. However, this was consistent and systemic with all petri dishes and, therefore, should not have significant effects on the calculation of the efficiency across samples. Bubbles in the graduated cylinder can also influence the accuracy of measuring how much oil volume remained. It is also very important in creating the oil spill that all drops of ferrofluid be placed directly on the oil. If ferrofluid accidentally drops on the water instead of the oil spill, it will sink to the bottom as droplets and not fully magnetize the oil.

III. The Effect of Magnet Strength on Oil Spill Cleanup Efficiency

Several factors determine the strength of a magnet, including size, shape and material. This experiment examines how magnet material type, size and shape affect the efficiency of oil removal with ferrofluid (Figure 6).

- **<u>Material Type</u>**: Every substance in made of atoms with electrons in motion. Electron movement generates an electric current, which causes the electron to act like a mini-magnet. [23] Most substances have equal number of electrons spinning in opposite directions, which cancels their magnetism. [23] Strongly magnetic substances, however, have electrons spinning in the same direction and these substances make the strongest magnets. [23] There are 4 categories of permanent magnets (listed according to decreasing strength): neodymium > samarium cobalt > alnico > ceramic.[24] Neodymium and samarium cobalt magnets are both rare earth types and are the strongest of the permanent magnets. Alnico magnets (made of **<u>al</u>**uminum, **<u>ni</u>**ckel, and **<u>co</u>**balt) are less strong than the rare earth magnets but stronger than ceramic magnets, which are the most commonly used in daily living. Data from this project supports that the neodymium magnets are more efficient at removing oil vs. ceramic and alnico magnets of the same size and shape (disc). With all other conditions remaining the same, this implies that the increased efficiency is due to the greater strength of the neodymium magnet. The neodymium rectangular prism magnet was more efficient (0.96) than samarium cobalt magnet (0.79) given similar shape, which reflects that neodymium magnets are stronger than samarium magnets.

- **<u>Size</u>:** In most cases, typically the bigger the magnet, the stronger.[25] For example, when a piece of iron is magnetized, the north-seeking poles of the atoms align.[23] The force generated by the aligned atoms creates the magnetic field.[23] Therefore, a larger piece of iron would have more atoms to align, resulting in a stronger magnetic field then a small piece of iron.[23] This was shown to be the case comparing the better efficiency (0.88) of the larger neodymium cube (0.75"x 0.75" x 0.75") vs. the efficiency (0.74) of the smaller neodymium cube (0.5"x 0.5" x 0.5"). Additionally, the larger neodymium disc (0.5" x 0.5") displayed higher efficiency vs. the smaller neodymium disc (0.5" X 0.25), with respective efficiencies of 0.77 and 0.55. Lastly, the larger diameter neodymium ring (0.75") was more efficient than the smaller diameter neodymium ring (0.5"), with respective efficiencies of 0.61 and 0.50.

- **<u>Shape:</u>** The shape of a magnet can affect its strength. For example, the pointed end of a magnet will be stronger than the rest of the magnet because the shape effects the distribution of the magnetic energy in the space it occupies.[26] Generally, the more surface area that a magnet's pole has in direct contact with a target, the "stronger" the magnet will be.[27] As an example, a 1" cube has twice the magnet material as a rectangular plate that is 2" long x 1" wide x 0.250" thick, but the rectangle has 2x the contact surface area, and will have a stronger attachment force to a target.[27] In another example, a 1.5" sphere has a very small contact area and much less strength when attached to a target even though it has 75% more magnet material when compared to a 1" cube with a greater contact area.[27] This study found that neodymium rectangular prism and cube shaped magnets (surface areas between 1.4 and 3.4 in^2) had greater cleanup efficiency compared to neodymium disc and ring-shaped magnets (surface areas between 0.69 – 1.7 in^2) due to the larger surface areas and the more contact with the ferromagnetic particles.

In summary, the 'strength' of a magnet is not just the magnet itself, but the entire magnetic circuit, the magnet (shape, size, material), target material, shape of the target, and any gaps between the magnet and target.[27]

One **potential source of error** was the manner in which the clear plastic sandwich bag covered the magnet. For square or rectangular magnets, the plastic bag sat flat against the surface of the magnet. However, with the disc, sphere, and ring-shaped magnets, the plastic bag was somewhat bunched around the magnet. This may influence the strength of the magnet to attract the ferrofluid due to the gaps between the magnet and the target.

IV. The Effect of Different Ways of Moving the Magnet on Oil Spill Cleanup Efficiency

For consistency across all experiments in this project, the rectangular neodymium magnet was slightly submerged in the oil spill (few mm below surface of oil) and moved with a slow, gliding motion to enable oil spill cleanup. This experiment tested different ways of moving the magnet to enhance the cleanup efficiency. The results showed that slow movements were more efficient than fast movements. A slightly submerged magnet or skimming the surface with the magnet was most efficient since more surface area of the magnet came in contact with the magnetized oil. Hovering over the surface (~1 cm) was the least efficient method as the magnetized oil did not come in contact with the entire surface of the magnet. In the case of hovering over the surface, the strength of the magnet was reduced due to the gap between the magnet and the target, hence a reduced oil spill cleanup efficiency. The next test that could be performed to improve efficiency is increasing the number of passes with the magnet through the oil/ferrofluid mixture.

One **source of error** could be the reproducibility of the exact height of the magnet for each test conducted in triplicate. Also, when the magnet was fully submerged, it tended to smash the ferrofluid into tracks at the bottom of the petri dish which may have affected the cleanup efficiency since less ferrofluid stuck to the magnet.

V. The Effect of Different Kinds of Oils on Oil Spill Cleanup Efficiency

The success of the ferrofluid method to remove oil spills is largely dependent on its ability to mix well and disperse through the oil. Ferrofluids must be miscible (forming a homogenous mixture when added together) with a wide range of petroleum oils and with the tarlike heavy hydrocarbons of a typical oil spill.[28] In addition to high magnetic susceptibility, it is desirable that the ferrofluids be less dense than fresh or ocean water and have low spreading on water.[28] Many of the desirable characteristics of ferrofluids involve the properties of the carrier fluid which must be hydrocarbon oil soluble but water insoluble.[24] Therefore, the selection of the carrier fluid is critical to enable the ferrofluid to spread wide through the oil spill and to form a stable suspension with the oil in order to "absorb" the oil in the pores of the ferromagnetic particles.

The goal of this experiment is to determine if this cleanup method has the same efficiency for different oils. The results in Figure 8 indicate that the ferrofluid cleanup of mineral oil (used for all other experiments in this project) and baby oil were most efficient (efficiency = 0.95.) This is logical since baby oil is essentially mineral oil with fragrance added. Mineral oil is petroleum-based hydrocarbon that is a by-product of refining crude oil, so it is miscible with the hydrocarbon-based carrier fluid in the ferrofluid mixture.[29]

The ferrofluid removed motor oil at an efficiency of 0.81 while the other vegetable oils/cooking oils had poorer efficiencies (0.32-0.53). Like the carrier fluid in the ferrofluid mixture, motor oil is 90% hydrocarbon-based stock distilled from crude oil with the remainder constituting the additives.[30] Therefore, it is expected to be miscible with the carrier in the ferrofluid. Although crude oil and vegetable oils are both natural oils, they share very different properties. Crude oil is extracted from the earth and are made up of hydrocarbons, whereas vegetable cooking oils are derived from the seeds, nuts and fruits of plants and consist of fatty acids (linoleic, palmitic, oleic) and complex mixtures of triacylglycerols and diacylglycerols.[31, 32] This study showed that the ferrofluid mixture and vegetable oils did not mix as effectively (Figure 8C). This is demonstrated by the fact that the ferrofluid formed droplets at the bottom of the petri dish vs. spreading in the vegetable oils. Therefore, it is rational that ferrofluid cleaned up the motor oil spill more efficiently than the vegetable oils due to the properties of the ferrofluid's carrier fluid and its miscibility with the spilled oils.

Source of Error: The viscosity of the various cooking oils was of different consistency and, therefore, more or less oil can be transferred from the petri dish to the graduated cylinder. Due to the viscosity, the transfer may not have been systemic and there could be variations of how much residual oil is left over in the petri dish. Also, because the ferrofluid did not disperse as well in some oils and sank to the bottom of this dish, the inability to mix well with the oil would make the oil cleanup process less efficient.

VI. The Effect of Environmental Factors on Oil Spill Cleanup Efficiency

Many traditional oil spill cleanup methods have drastically reduced efficiency under various environmental and atmospheric conditions. For example, the oil recovery efficiency of oil skimmers to remove oil spills is 50% in choppy ocean waters.[33] Environmental factors including water temperature and salinity and ocean conditions influence the effectiveness of dispersants. For instance, the efficiency of oil spill cleanup with dispersants drops to 51-74% over time due to oil weathering and emulsification depending on type of oil spilled.[34]

The purpose of this set of experiments was to examine the efficiency of ferrofluid nanotechnology in conditions that mimic the ocean. Conditions such as salt water vs. spring water, and warm and cold temperatures did not affect the efficiency of oil recovery by ferrofluids (Figure 9, efficiency = 0.96). The efficiency was only slightly reduced by 9.5% when waves were simulated by rocking the petri dish. This data suggests that the ferrofluid methods for oil removal is robust and efficient even under unfavorable conditions.

One **potential source of error** is that the petri dish was shallow and only contained 14 mL of water. A deeper container would allow more rigor in creation of "ocean-like" waves. Ideally, at a larger scale, the agitation which occurs through wind and wave action should enhance the dispersion of ferrofluid in the oil slick improving efficiency compared to other methods.[28] While conducting this experiment with waves, it is important that the ferrofluid drops are added directly to the oil spill. If the ferrofluid drops hit the water, then they will sink to the bottom resulting in less cleanup efficiency.

VII. The Effect of Ferrofluids on Aquatic Organisms

The use of nanoparticles has been controversial due to the concerns that nanoparticles could have the ability to enter cells and damage marine life and cause still unknown environmental effects.[10] Therefore, the purpose of these experiments was to examine the effects of ferrofluids on aquatic life. Daphnia magna (water flea) is a commonly used model for toxicity assessment of chemicals and pharmaceuticals.[35] Therefore, Daphnia was used to examine the cytotoxic (or toxic to cells) effects of ferrofluid. This study showed that Daphnia were quite sensitive to ferrofluids and died within 4 hours of exposure to 3 drops of ferrofluid (Figure 10A).

Potential Source of Error: Without an oil spill in the water, the ferrofluids in an oil-based carrier fluid sink as droplets at the bottom of the cup and did not disperse. Since the ferrofluid did not disperse efficiently, it might not come in contact with the aquatic organisms as effectively. The ferrofluids also leave an oily film floating on the surface of the water and sides of the cup, which increased with increasing amounts of ferrofluid. Some Daphnia got stuck in the oil on the side of the cup and it prevented them from swimming leading to their demise (Figures 10C and 10D). To definitively determine if Daphnia are cytotoxic to ferrofluid, a ferrofluid with a water-based carrier should be used to better disperse the ferrofluid throughout the cup. This would rule out the variable that Daphnia were killed due to getting stuck in the oil residue vs. cytotoxicity due to the ferrofluid itself.

Green Hydra *Chlorohydra viridissima* were also sensitive to death after exposure to increasing amounts of ferrofluid with an IC_{50} value of 5 drops of ferrofluid after 16 hours of treatment (Figures 10B and 10E). Hydra adhere to the bottom of the cup, are stationary and did not come in contact with the oily residue/film floating on the surface of the cup. Hydra were less severely affected by ferrofluid requiring longer treatment times and higher concentrations to produce the cytotoxic effect compared to Daphnia. It is important to note that these experiments daphnia, hydra and planaria could not be conducted in the 14-mL petri dish since these organisms can easily deplete the oxygen in the smaller volume of water and lead to the death of the culture.[18,19] Therefore, these experiments were carried out at a larger volume (120 mL).

Under the same treatment conditions, planaria were unaffected by the presence of large doses of ferrofluids in their environment (Figures 11A, 11C, 11D). Most planaria were living after 4 weeks of exposure to ferrofluids. An interesting observation was that about 30% of planaria looked smaller as the weeks went by. Planaria can go without food for 90-days and are able to withstand long-time fasting periods by shrinking and degrowing.[36] Likewise, duckweed was very sturdy on exposure to ferrofluids even while floating in the oily residue/film on the surface of the water. At the highest ferrofluid concentration, <20% of the duckweed died after 7 days (Figures 11B, 11E, 11F).

Potential Source of Error: A number of journal publications demonstrate that waterborne iron inhibited Daphnia, Hydra, Planaria and *Lemna minor* growth, reproduction and survival.[37-41] In future studies, it would be important to differentiate between the ferrofluid/ferromagnetic nanoparticle toxicity and general sensitivity to iron for these organisms.

In summary, these results suggests that different aquatic organisms have different sensitivity for cytotoxicity to ferrofluids. If the cleanup procedure is swift with less exposure to aquatic life, the environmental impacts will be substantially minimized.

CONCLUSIONS:

These experiments supported the hypothesis that if ferrofluids are added to an oil spill, then the oil will mix with water-repellant ferromagnetic nanoparticles and can be magnetically separated from water because magnets attract iron.

1. The higher the concentration of the ferrofluid added to the oil spill, the more efficient the cleanup until saturation occurred.

2. As the volume of the oil spill increases, more ferrofluid is needed to efficiently clean up the spill.

3. Magnet material, size and shape determine the strength of the magnet and effect the efficiency of oil spill cleanup.
    - The stronger the magnetic material, the more efficient the oil spill removal (neodymium > samarium cobalt > alnico > ceramic). Neodymium magnets are the strongest type of magnet and most efficiently cleaned the oil spill compared to samarium cobalt, alnico and ceramic magnets of the same size and shape.
    - The bigger the magnet, the stronger and more efficient for ferrofluid oil spill cleanup.
    - Rectangular prism and cube-shaped magnets demonstrated greater cleanup efficiency vs. ring- and disc-shaped magnets due to greater surface area coming in contact with the ferrofluid.

4. Slow movements of the magnet were more efficient at oil spill cleanup versus fast movements. Slightly submerging the magnet or skimming the surface with the magnet was more efficient than hovering over the surface since more surface area of the magnet came in contact with the magnetized oil.

5. Ferrofluids are not equally miscible in all types of oil. Ferrofluid miscibility is dependent on its carrier fluid. The hydrocarbon-based ferrofluid mixed well with petroleum/hydrocarbon-based mineral oil, baby oil and motor oil for efficient oil spill cleanup. However, ferrofluid and a variety of fatty acid-based vegetable oils did not mix as effectively and, therefore, had much less oil spill cleanup efficiency.

6. Environmental factors such as heat, cold, and salinity had no negative effects on ferrofluid cleanup efficiency. Wave-like perturbation only reduced oil spill cleanup efficiency by < 10%.

7. Different aquatic organisms displayed different sensitivities to ferrofluid cytotoxicity. *Daphnia magna* were very sensitive to cytotoxicity after ferrofluid treatment (100% death at 4 hours with 3 drops of ferrofluid) whereas green Hydra were less severely affected, requiring longer treatment time and higher ferrofluid concentrations to produce cytotoxic effects. Under the same conditions, Planaria and duckweed were significantly more resistant to cytotoxicity after ferrofluid treatment.

In summary, the data from these collective experiments proved that a ferrofluid can be used in conjunction with a strong magnet to efficiently remove an oil spill from water on a small scale. If the cleanup procedure is swift with minimal exposure to aquatic life, the environmental impacts will be substantially minimized using this unique technique.

FUTURE STUDIES:

- The big question remaining is if this method of using ferrofluid nanotechnology to clean oil spills is scalable to oceanic levels. In this experiment, 6 drops of ferrofluid were used to clean up a 2.5 mL oil spill in 14 mL of water. The efficiency could be further investigated by double or tripling the quantities. For example, comparing the efficiency of using six drops ferrofluid to clean up 2.5 mL of oil, twelve drops for 5.0 mL, etc. These studies could also be scaled to a larger volume in a baby pool or tub and then into sea water depending on whether a magnet large enough could be acquired and ferrofluid quantities obtained.

- This project could be expanded to look at ferrofluids with different carrier fluids and how they act across different environments and oil types. For toxicity tests, it would be important that the carrier fluid be miscible with water. One could research how people make up their own ferrofluid with jet-printer ink and optimize it to clean up a specific oil spill.

- To more extensively test the effects of ferrofluid toxicity on marine life and ecological health, this project can be expanded to include a larger variety of aquatic plants (i.e., algae or Elodea, etc.) and marine animals (i.e., snails, fish, shellfish etc.). Since microorganisms play a large part in ecosystems and the food chain, it would also be good to include bacteria and plankton.

- One can also inquire if different life stages of Daphnia or other aquatic organisms (baby, juvenile or adult) react the same way to ferrofluids.

- It would also be very interesting to test the effects of ferrofluids on human-derived cell lines in culture to assess the safety risk posed to environmentalists and scientists involved in large scale oil spill cleanups.

- It would also be interesting to study how different sizes, shapes, surface areas, and coatings of the ferromagnetic nanoparticles affect their properties to “magnetize” oil and the subsequent cleanup efficiency.

- The present studies showed that a strong magnet can separate the oil/ferrofluid mixture from the water. The clean water can then be returned to sea. One can elucidate the best processes to “demagnetize” the oil (i.e., remove the ferromagnetic nanoparticles from the oil) in order recycle the oil for use in fuels and products.

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Photos, Diagrams and Figures:

All photos, diagrams and figures are by the student except the photo of the *Daphnia* magna (Figure 2C) which is credited to Science Buddies and the magnets on Table II which are credited to the respective vendor websites: amazingmagnets.com, buntingmagnets.com, homesciencetools.com.