PUBLIC WORKS TECHNICAL BULLETIN 200-1-50
1 SEPTEMBER 2007

COMPARISON OF SOLID SUBSTRATES FOR COLLECTING MILITARY SMOKE AND OBSCURANT CHEMICAL DEPOSITION

Public Works Technical Bulletins are published by the U.S. Army Corps of Engineers, 441 G Street NW, Washington, DC 20314-1000. They are intended to provide information on specific topics in areas of Facilities Engineering and Public Works. They are not intended to establish new DA policy.

DEPARTMENT OF THE ARMY
U.S. Army Corps of Engineers
441 G Street, NW
Washington, DC 20314-1000

CECW-CE

Public Works Technical Bulletin 1 September 2007

No. 200-1-50

Facilities Engineering
Environmental

COMPARISON OF SOLID SUBSTRATES FOR COLLECTING MILITARY SMOKE AND OBSCURANT CHEMICAL DEPOSITION

1. Purpose.

a. This Public Works Technical Bulletin (PWTB) transmits recommendations to enable land managers to assess the level of chemical deposition from smokes and obscurants (S&O) used in military training in an effort to prevent ecological damage to natural habitats.

b. All PWTBs are available electronically (in Adobe® Acrobat® portable document format [PDF]) through the World Wide Web (WWW) at the National Institute of Building Sciences' Whole Building Design Guide web page, which is accessible through URL:

http://www.wbdg.org/ccb/browse_cat.php?o=31&c=215

2. Applicability. This PWTB applies to U.S. Army facilities engineering activities that conduct training exercises using S&O.

3. References.

a. Army Regulation 200-1, "Environmental Protection and Enhancement," 21 February 1997.

b. Endangered Species Act of 1973.

c. Emergency Planning and Community Right-to-Know Act (EPCRA), Title III of the Superfund Amendments and Reauthorization Act of 1986.

d. EPCRA’s Toxic Release Inventory (EPCRA-TRI).

4. Discussion.

a. To provide realistic training conditions in preparation for anticipated and unknown battle conditions, military trainers use smokes and obscurants (S&O) on Army training lands. Many threatened and endangered species (TES) inhabit these same lands and are protected under the Endangered Species Act (ESA). When data on the effects of the use of S&O for training purposes is lacking, training is restricted. Therefore, the use of S&O as it relates to the survivability of TES and their habitats, including aquatic ecosystems, must be ascertained.

b. Any time an S&O is used, an environmental release of an active chemical or compound occurs. The chemicals in the S&O enter the atmosphere, forming a cloud (or fog) that the soldier uses during a training event. These cloud chemicals can adversely affect terrestrial species, and studies have been done relating cloud composition to effects on installation vertebrates. A different fate for this set of cloud chemicals can result if the chemicals deposit onto aquatic surfaces. This set of chemicals has the potential to negatively impact aquatic TES, including fish, mussels, and the associated prey species. It is critical, therefore, to be able to measure and determine the set of chemicals that can deposit from an S&O cloud onto a water surface.

c. Other research has been performed to analyze the chemical content of the S&O cloud by actively collecting the entire S&O cloud from the atmosphere. It is straightforward to understand the relevance of this data since the entire atmospheric S&O cloud is available for inhalation by a terrestrial organism. Only chemicals that settle from the atmosphere onto water will affect aquatic TES. No studies have been done that describes a comparison of substrates that collect and release chemicals that deposit from the atmosphere. This report fills that void by examining the ability of 15 different substrates for the collection of fog oil chemical deposition, 13 different substrates for green smoke grenade chemical deposition, and 14 different substrates for yellow smoke grenade chemical deposition. Installations with training ranges can use this information to design experiments that quantify S&O chemical deposition during realistic training events and thereby mitigate potential effects to aquatic TES.

d. Appendix A to this PWTB investigates various collection media to determine optimal choices for the collection and recovery of the chemical deposition from the most common types of S&O: fog oil, graphite smokes, and colored signaling smokes. Data show that the choice of collection media is critical as there is a large variation in performance.

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APPENDIX A:

Comparison of Solid Substrates for Collecting Military Smoke and Obscurant Chemical Deposition

Introduction

The U.S. Army and other military services must continually maintain a state of high readiness and alertness based on national defense needs. Concurrent with the need for military preparedness and the closely related and necessary maintenance of military training lands is the need and obligation to maintain various natural resources as mandated by the Congress and expected by the public. Preparation for anticipated, unknown, and invariably adverse battlefield conditions requires military training activities using smokes and obscurants (S&O). Many threatened and endangered species (TES) inhabit training areas where S&O are released; therefore, the impact of S&O on the vitality and survivability of TES and their habitats, including aquatic ecosystems, must be an active research area.

The Endangered Species Act (ESA) prohibits any action that adversely affects TES and their habitats. When data on the effects of military actions and training on TES are lacking, performance is restricted so that liberal protection of TES is provided. The U.S. Army, as the Conservation Pillar lead for the U.S. military services, has identified investigation of the impacts of military training and operations on TES as an area of high importance (U.S. Army 1999; 2000). The U.S. Army Threatened and Endangered Species Advisory Group, which is composed of Headquarters Department of the Army, Major Army commands, and installation program experts, has further identified military S&O as areas of priority focused research investigation.

Use of S&O on training lands results in a release of a cloud of chemicals that drifts over the environment. If the cloud chemicals deposit onto aquatic systems, they can enter the water column and thereby induce acute or chronic toxic effects on aquatic TES. The research described here tests the ability of various solid filtration media to collect chemicals that deposit from the atmosphere, to retain these compounds and, finally, to release these chemicals during analysis. Ranking these filter substrates provides researchers, installations, and environmental assessors with a valuable tool for finding the best filters to use during training events to measure the chemical deposition onto aquatic ecosystems.

Smokes and Obscurants

The U.S. military uses S&O for many purposes including training, signaling, and reconnaissance. The three most common S&O in use today are: (1) fog oil (FO), a visual obscurant, (2) graphite smoke, an electromagnetic obscurant, and (3) colored signaling smokes (red, green, and yellow). Any type of S&O use necessitates an environmental release of the active chemical or compound. These chemical releases have the potential to adversely affect indigenous flora and fauna.

The FO obscurant is used to create visually limiting conditions for field training and maneuvering. It is a middle distillate petroleum oil containing hundreds of thousands of different organic constituents (Getz et al. 1996; Katz et al. 1980). FO is an example of a complex organic compound mixture that will have a combined effect from these many constituents.

Graphite smoke is used as an infrared obscurant, dispersing fine particles of graphite into the air (National Research Council [NRC] 1999a). Little is known regarding the environmental impact of graphite; however, it is nonvolatile and will be persistent.

Colored smokes are used for screening troops from view, signaling, and marking field positions. These smokes are known to contain, generate, and disperse toxic and carcinogenic chemicals into the environment (NRC 1999b). Colored smokes are examples of specific and identified organic chemicals released into the environment.

Environmental Purpose

Since training for adverse and unknown battlefield conditions requires military training activities using S&O, quantifying the emissions resulting from S&O use and assessing the potential health and environmental impact of these emissions has become a critical issue for the U.S. Army. The need for such data has been identified as a result of problems occurring at military installations. For instance, over the course of many years (1955 to 1972), spills, leaks, and standard practices of hazardous waste disposal at the Massachusetts Military Reservation in Cape Cod, MA, created groundwater plumes that migrated off base to impact drinking water supplies. This high profile case has heightened public awareness of the environmental effects of military training. Since that time, requirements such as reporting under the Emergency Planning and

Community Right to Know Act - Toxic Release Inventory (EPCRA-TRI) have also been identified.

Because of the balance that must be maintained between military preparedness and conservation of biodiversity, a great deal of research has been committed to conservation of terrestrial TES on military installations, and specific studies have been conducted to examine the inhalation impacts of FO upon terrestrial vertebrates such as the red-cockaded woodpecker and the house sparrow (e.g., Driver et al. 2002a; 2002b). However, very little work has been published quantifying the effects of S&O on aquatic life (Poston et al. 1988).

While it is important to study the S&O in the atmosphere to understand inhalation effects on terrestrial species, aquatic species will be affected only by the fraction of the S&O cloud that settles and deposits on the water surface. For instance, FO will form a hydrophobic layer at the aquatic surface. The oil can then (1) affect oxygen transport into the water causing species stress, (2) contribute to the water soluble fraction of hydrocarbons in the water column, which has a direct toxic effect on fish, mussels, other benthic organisms, and the aquatic stages of insects, and (3) impact organisms that must pass the air/water interface during its lifecycle thereby necessitating also passing through the oil layer. Graphite particles can also settle onto the water surface and slowly settle through the water column to ultimately rest in the aquatic sediments. Compounds from colored smokes also can deposit onto the water surface and increase the organic content of the water column.

It is critical, therefore, to assess the fraction of the S&O that can deposit on water surfaces from the atmospheric cloud, as this is the fraction that will have affect aquatic life. This PWTB investigates various collection media to determine optimal choices for collection and recovery of the most common types of S&O.

Materials and Methods

S&O Release

Field release experiments were conducted during May and August 2003 at Aberdeen Proving Grounds, MD. A central release point was designated for each type of S&O. In all the experiments, the collection media were placed in a straight line at different distances downwind from the point of release. The FO was released using a generation system mounted on the back of a vehicle. The generator slowly dropped FO onto a heated surface, which vaporized the oil into small aerosol droplets. A blower then ejected the droplets from the generator, forming a dense white cloud. The graphite smoke was emitted in a similar manner, but since the graphite flakes were already in particulate form, no heat was needed. Figure 1 shows both the FO and graphite smoke being emitted simultaneously from the same vehicle. HOC FO (Home Oil Co., Cowarts, AL) was used in these experiments.

Figure 1: FO and graphite smoke generation from one vehicle; FO smoke is white and graphite flake smoke is black.

Colored smoke grenades emit bright clouds from a small handheld canister. The grenade tab was pulled and the grenade was set on the ground at the release point. Any subsequent grenades were released sequentially from this identical release point. Figure 2 illustrates the release of a yellow smoke grenade.

Figure 2: Yellow signaling smoke being emitted from a single grenade.

Field release events

May — Media were compared for the collection of green signaling smoke, graphite flakes, and FO during May. Seven green smoke grenades were released sequentially with collection media set at 1 meter from the release point. Graphite flakes were released for 15 minutes. Since these are small particulates rather than chemical components, the filters have no influence on deposition, retention, and release. Further assessment of filter collection of graphite flakes was therefore eliminated. For the FO releases, samples were placed on the ground 5 meters from the generator release point. Two separate fogging times were used; one for 15 minutes of FO release and one for 18 minutes of FO release.

August — Media were compared for the collection of green and yellow signaling smoke during August. For the colored signal smoke releases, samples were placed on the ground 5 or 25 meters from the release point. In this case, 20 yellow or green smoke grenades were released sequentially.

Chamber release

Due to the difficulties of field testing and control of environmental conditions, an experiment was also performed within an enclosed chamber constructed at the Construction

Engineering Research Laboratory (CERL) specifically for S&O release. The environmental chamber at CERL is a 49.9 m^3 (2.65 m H x 4.05 m W x 4.65 m L) enclosure used for conducting experiments with military S&O to simulate field conditions under controlled conditions. Figure 3 shows the front wall of the chamber. The walls, ceiling, and doors were constructed with panels from U.S. Cooler (Quincy, IL) with smooth stainless steel interior surfaces. The floor was constructed in-house from plywood and spray foam insulated from the underside. The cooling system for the chamber was also from U.S. Cooler. The small door to the lower left of the picture reveals a smaller internal chamber (1 m H x 0.92 m W x 0.92 m L) that can be used for controlled releases of S&O. The small internal chamber has its own controllable damper system so that a user can release smoke into the large chamber or vent it out through an external filtration unit.

The larger chamber is equipped with a wall vent and fan that pull air into the chamber from outside the building, and a ceiling vent and fan that pull air out of the chamber and release it outside the building. This flow system is used for evacuation of smoke from within the chamber. Both vents can be opened and closed using dampers that, in addition to the fans, are controlled from outside the chamber. A third vent in the side wall can be opened to create a passageway between the chamber and the outside of the building.

Figure 3: Exterior of the environmental chamber.

Inside the chamber are 24 sets of ultraviolet (UV) lights separated into four banks that can be used to simulate different levels of UV radiation from the sun depending on how many banks are turned on. The temperature of the chamber is controlled with a radiator for heating and a built-in air-conditioning system for cooling. This arrangement allows for simulation of outside environmental conditions from winter to summertime conditions. Two real-time aerosol sensors (Model RAS-2 from Monitoring Instruments for the Environment, Inc.) are used to monitor the optical density of the smoke within the chamber during experiments. One is located approximately 1 ft off the floor, and the other is approximately 7 ft off the floor directly above the first sensor. The sensors are connected to an Omega data logger (Model 0M550) outside the chamber that is directly interfaced to a laptop. The computer program DataWorker LE for Windows (Omega Engineering, Inc., Stamford, CT) downloads and displays the sensor readings.

Environmental chamber protocol

The first step in using the environmental chamber is to set the internal chamber temperature. A temperature of 25 °C was used for the experiment below. A thermometer in the interior of the chamber lets the user know when the chamber has reached the desired temperature. A clean piece of aluminum foil is placed on the floor of the chamber. The samples to be tested are placed on the foil. The computer and the sensor data logger can be started at this point. Once the chamber has reached the desired temperature, the main door of the chamber is closed and rope insulation and duct tape are applied around the door to minimize leakage. The interior floor fan is turned on at this point to ensure mixing of fog throughout the chamber.

The fog generator (Figure 4) is moved outside of the building for use during experiments. A MasterFlex pump is connected to the generator to deliver HOC FO to the generator. As the generator warms up, the sensors can be tested to ensure they are receiving data from inside the chamber. Once the generator temperature reaches 450 °C, the oil pump is turned on. The chamber ceiling damper is opened and the ceiling fan is turned on to pull the fog into the chamber. When the generator is producing a steady stream of fog, an intake pipe is placed in front of the generator exhaust pipe for the desired fogging time for the experiment. In this experiment, the chamber was fogged with HOC FO for 2 minutes. The intake pipe directs the fog into the chamber through a vent in the wall of the chamber. After 2 minutes, the intake pipe is blocked to prevent further introduction of fog, the ceiling fan is turned off, and the ceiling damper is closed as quickly as possible. The oil pump is stopped and the generator is turned off to cool. The fog remains in the chamber for a set residence time. Once this time has expired, the ceiling and wall dampers are opened and their fans turned on to evacuate the chamber of fog. Readings from the aerosol sensors are used to determine when the chamber is evacuated to baseline levels. In this experiment, all of the fog within the chamber was allowed to settle for 9 hours.

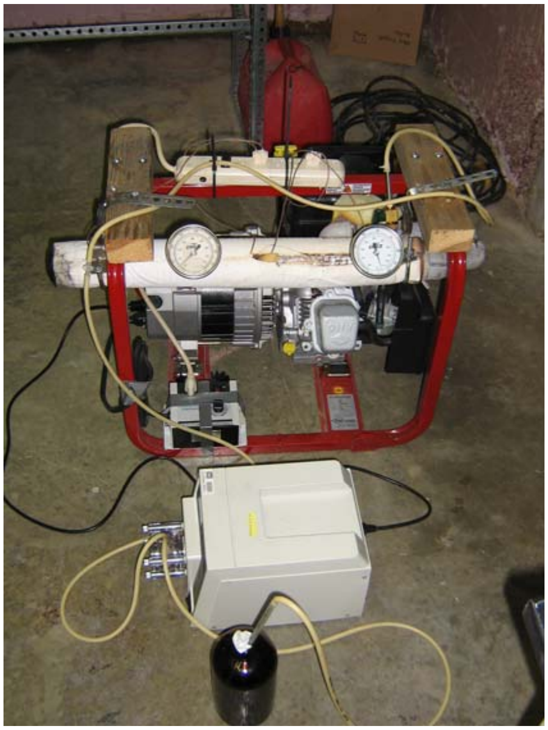

Figure 4: Fog generator and oil pump.

Type of filters

Consideration of sampling substrates is critical. For example, FO deposition on bird feathers is measurable (Driver et al. 1999); however, there was no deposition on aluminum foil coupons or glass fiber filters (GFF; Liljegren et al. 1988). This emphasizes the importance of the sample substrate character for collection. Detection on the bird feather likely reveals some adsorptive properties of the feather structure as opposed to the flat, inert surface of typical sample substrates. Sampling substrates will therefore include not only the usual aluminum foil and glass fiber filters, but also filters with different surface chemistries, as well as activated carbon fiber (ACF) filters. Volatile losses from these types of substrates will be minimized due to enhanced adsorptive properties. A comparison of collection efficiencies using these substrates will greatly enhance other field collection studies where volatility losses may have compromised the results.

Table 1 lists all of the collection media that were used in this study. Pall Scientific was chosen as a source of filter media due to the wide variety and availability of their inventory.

Table 1: Collection media used for experiments.

Type of Media	Surface Area (cm^2)	Shape of Media	Manufacturer	Description
Jars of Heptane	44.2	Circle	Sigma-Aldrich®	CHROMASOLV®, for HPLC, ≥99%
Glass Fiber Filters (GFF)	30.25 or 95.03	Circle	Fisher®	Borosilicate glass without binder
Jars of Water	44.2	Circle	DI water	From Millipore filtration system
Foil coupons	30.25 or 80.00	Square	Reynolds®	Aluminum Foil
ICE-450	78.54	Circle	Pall®	Polysulfone with nonwoven polyester support; hydrophilic cationic exchange
Tuffryn	83.00	Square	Pall®	Hydrophilic polyethersulfone
SB6407	78.54	Circle	Pall®	Polyethersulfone copolymer
PTFE	76.00	Square	Pall®	Polytetrafluoroethylene (PTFE) on a polypropylene support
Fiberfilm	85.00	Square	Pall®	Heat resistant borosilicate glass fiber coated with fluorocarbon (TFE)
Emfab	85.00	Square	Pall®	Borosilicate glass microfibers reinforced with woven glass cloth and bonded with PTFE
Nylaflo	85.00	Square	Pall®	Hydrophilic nylon
GHP	80.00	Square	Pall®	Hydrophilic polypropylene
Metricel	80.00	Square	Pall®	Hydrophobic polypropylene
Versapor	78.54	Circle	Pall®	Hydrophilic acrylic copolymer on a nonwoven support
Supor	78.54	Circle	Pall®	Hydrophilic polyethersulfone
FP-450	78.54	Circle	Pall®	Hydrophilic polyvinylidene fluoride (PVDF)
ACF-15	30.25	Square	EKOS®	Carbonized and activated phenolic resin coated glass fibers, high surface area
ACF-7	30.25	Square	EKOS®	Carbonized and activated phenolic resin coated glass fibers, low surface area
Basic ACF	30.25	Square	EKOS®	Carbonized and activated phenolic resin coated glass fibers, aminated surface
Oxidized ACF	30.25	Square	EKOS®	Carbonized and activated phenolic resin coated glass fibers, hydroxyl and carboxyl surface

Filters were used as received or were cut to the desired size. The 500-mL jars for solvents were purchased pre-cleaned from I-CHEM (Chase Scientific Glass, Inc., Rockwood, TN) and, when filled with liquid, had a surface area of $44.2cm^2$.

Jars were filled with either water or heptane and were placed at the desired distance from the release point. To prevent the wind from blowing the filters away, they were placed in Petri dishes on the test field as seen in Figure 5. After exposure to S&O, the filters were placed in a 40 mL pre-cleaned I-CHEM vial. The jars of heptane and water were uncapped only prior to and during exposure and were re-capped immediately following exposure. All exposed collection media awaited analysis at a walk-in freezer at CERL in Champaign, IL.

Figure 5: A grouping of collection media on the test field at one distance from the release point.

Grabbing an air sample from an S&O cloud will collect all of the components of the cloud, including volatile emissions that will not affect aquatic TES. Clearly, the passive sample arrangement used here allows the analysis of the fraction of S&O that settles from the atmosphere onto a surface to measure actual deposition.

Extractions and Concentrations

Filters

Filters exposed to the FO plume during the May and August field experiments were promptly rolled up and placed in I-CHEM 40 mL clear glass vials until extraction. All FO was extracted from the collection media using Sigma-Aldrich Heptane, Chromasolv® for HPLC, ≥99%. A 20 mL B-D Yale glass syringe (Becton, Dickinson & Co., Franklin Lakes, NJ) was used to inject approximately 10mL of heptane into the 40 mL vial. This initial step was to ensure that any FO vapor contained in the vial was collected by the heptane. The vial was then shaken, and the heptane was collected in a 200 mL Zymark concentrating vessel. The filter was rinsed three to four times with 10–15 mL of heptane, each time combining all heptane into the Zymark concentrating vessel. The contents of the Zymark vessel were then concentrated by a Zymark Turbo Vap II®, which used ultra-high purity nitrogen (S&J Smith, Urbana, IL) to approximately 0.5–1 mL. The resulting concentration was then reconstituted to exactly 2 mL and placed in a gas chromatography/mass spectrometry (GC/MS) vial for automated analysis.

Filters exposed to colored smoke grenades were extracted using exactly the same method; however, Sigma-Aldrich Dichloromethane, Chromasolv® for HPLC, ≥99.8% was used instead of heptane.

Jars

Jars of water exposed to the FO plume were extracted using heptane. The contents of the jar were quantitatively transferred into a 500-mL separation funnel and extracted three times with 20-30 mL of heptane. The jar and lid were also rinsed three times with 5-10 mL of heptane. The extraction solution and rinses were combined and concentrated to a final volume of 0.5-1 mL. The remaining solution was reconstituted to 2 mL using clean heptane and placed in a 2 mL GC/MS vial for analysis.

Jars of water exposed to colored smoke grenades were extracted using exactly the same method. However, Sigma-Aldrich Dichloromethane, Chromasolv® for HPLC, ≥99.8% was used instead of heptane.

Jars of heptane exposed to the FO plume were concentrated down to 2 mL by quantitatively transferring the contents of the jar into three separate Zymark vessels. The jar and lid were rinsed three times with 5-10 mL of heptane and added to the Zymark vessels. As the amount of heptane in each vessel sufficiently decreased, the remaining contents were transferred into one Zymark vessel. This solution was then allowed to reach approximately 0.5-1 mL, before being reconstituted to 2 mL and placed in a 2 mL GC/MS vial.

Jars of heptane exposed to colored smokes were extracted using exactly the same method as the ones exposed to FO; however, Sigma-Aldrich Dichloromethane, Chromasolv® for HPLC, ≥99.8% was used instead of heptane to rinse the jar and lid (three times), rinse the Zymark vessels as the contents were being transferred, and reconstitute the final solution back to 2 mL.

GC Analysis

Extracts of the above samples were analyzed on either an Agilent 6890 GC/5973 inert MS (GC/MS) with an Agilent 7683 autosampler (Agilent, Wilmington, DE) or a two dimensional GC x GC / flame ionization detector (2D GC/FID) made by LECO Corporation (St. Joseph, MI).

For GC/MS analysis, the FO samples were analyzed using the following parameters:

- An Agilent HP5MS capillary column (30 m x 0.25 mm inside diameter [i.d.] x 0.25 um film thickness);
- 2 µL splitless injection
- Injection port temperature set at 310 °C
- Oven temperature started at 100 °C for 3 minutes, ramped at 50 °C / minute to 310 °C, and held at 310 °C for 15 minutes.
- The GC /MS transfer line set at 310 °C.
- The MS mass range set from 35 to 550 amu.

For 2D GC/FID analysis, the FO samples were analyzed using the following parameters:

Columns	Primary (Phenomenex, Torrance, CA)	ZB-1 MS 30m, 0.25mm ID, 0.25µm df
	Secondary (Restek, Bellefonte, PA)	RTX-17 1.1m, 0.10mm ID, 0.1µm df
	Temp. program 1st column	40˚C (0.5min) - 300˚C @ 5˚C/min (34 min)
	Temp. program 2nd column	50˚C (0.5min) – 300˚C@ 5˚C/min (34 min)
	Modulator offset Temperature	20˚C
	Modulation time	5 sec
	Hot pulse time	0.8 sec
Injection	Split / splitless	4mm open Liner
	Temperature	310˚C
	1.0 µl, split ratio 20:1	
Flow	1.0 ml/min constant flow	Helium
Detection	FID	320˚C

For GC/MS analysis, the colored smoke samples were analyzed suing the following parameters:

- A Phenomenex 7HG-G002-11 capillary column (5% phenyl, 30 m x 0.25 mm i.d. x 0.25 um film thickness)

- 2 µL splitless injection

- Injection port temperature set at 250°C

- Oven temperature started at 50 °C for 3 minutes, ramped at 20 °C / minute to 300 °C, and held at 300 °C for 52 minutes.

- The GC/MS transfer line set at 310 °C.

- The MS was used in selected ion mode, using 273 atomic mass units (amu) when analyzing for yellow dye and 418 amu when analyzing for green dye.

- Resultant peak areas from GC/MS are expressed as relative arbitrary units (RAU). These peak areas can be directly compared to one another to determine relative abundance.

Graphite flakes settle from the atmosphere as particulate. This particular S&O was not examined further since a simple dish followed by gravimetric analysis will suffice to collect all flakes that will settle onto a water surface.

Results and Discussion

Green smoke

The May experiment with green signaling smoke collected the dye settling from the sequential release of seven grenades, 1 meter from the release point. Figure 6 shows the vials containing the extracted and concentrated solutions from collection media comparing the different types of ACF, aluminum foil, and GFF. All of these filters were cut to the same nominal size, 30.25 cm^2, as measured by a ruler along the edges.

Figure 6: Extracted samples from deposition of seven green signaling grenades. From left to right, the collection media were oxidized ACF, basic ACF, ACF-15, foil, GFF, and ACF-7.

Measurement of the green dye peak areas allows a direct comparison among these filters. The difference in the amount of green dye that is collected and extracted from these filters is striking. The oxidized ACF, basic ACF, and ACF-15 sample extracts contained no green dye, indicating that these filters either did not collect any green dye in the field or the dye could not be extracted using a dichloromethane soak. The green dye (Figure 7), also known as 1,4-bis[(4-methylphenyl) amino] anthracenedione, may be strongly bound to the surface modified oxidized and basic ACF. It may also get trapped in the porous

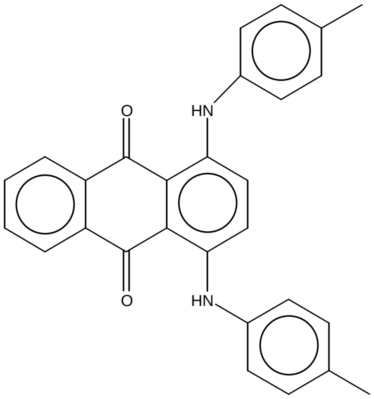

Figure 7: Green dye chemical structure.

ACF-15 where it cannot be removed easily by a solvent rinse. Only a complex thermal desorption experiment would determine the actual amount of dye present, but the application of an electric field may degrade the dye before extraction. In contrast, the foil had a green dye peak area of 650,000 RAU, the GFF had a green peak area of 1,000,000 RAU, and the ACF-7 had a peak area of 2,500,000 RAU. The foil and GFF are inert substrates and will collect deposited chemicals without confounding issues of chemical interactions. While foil is a nonporous surface, GFF will have more surface area for trapping dye. The numbers illustrate that GFF can trap, hold, and release more dye than the foil, illustrating that porous substrates are better than foil. Under the same conditions, however, ACF-7 is the best performer. It can collect and release the largest amount of green dye. The activated carbon surface, together with the numerous pores for increasing the filter surface area, creates the best media for organic dye collection. It has a larger pore size than ACF-15, which can hold the chemical but will also allow the dichloromethane to easily remove the dye for analysis. The pores and the sorptive surface serve to trap chemicals and prevent volatile or mechanical losses due to wind. Based on these numbers, ACF-7 represents the best substrate for green dye collection.

Unfortunately, these ACFs are difficult to fabricate and acquire. Therefore, commercial filters that are readily available were tested. The August experiment with green signaling smoke collected the dye settling from the sequential release of 20 grenades, 25 meters from the release point. Figure 8 shows the vials containing the extracted and concentrated solutions from collection media comparing the different types of filters. These vials are arranged in visual order, from clear to greenest. This is also the order in which they were analyzed by GC/MS.

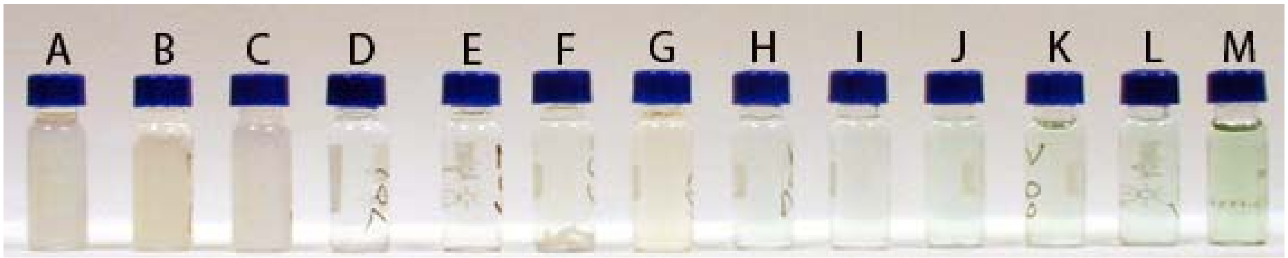

Figure 8: Extracted samples from deposition of 20 green signaling grenades onto different filters. A=Supor, B=ICE450, C=SB6407, D=Fiberfilm, E=FP450, F=Versapor, G=Tuffryn, H=Nylaflo, I=GFF, J=Metricel, K=foil, L=Emfab, M=PTFE.

Figure 9 shows the green dye peak areas collected and extracted by these filters. The peak areas are divided by the filter nominal size. Only Metricel, Emfab, and PTFE showed any collection of green dye at 25 meters away from the release point. From Table 1, it is noted that these filters are hydrophobic substrates, Emfab and PTFE, due to the presence of the fluoroethylene. PTFE collects and releases the most green dye; more than ten times the amount observed in Emfab and Metricel. The dichloromethane extraction process completely degraded Supor, ICE450, and SB6407. These samples became viscous and cloudy, and are filled with the monomer from the filter substrate and support structure. Due to this contamination and from the lack of green color, these samples were not analyzed further.

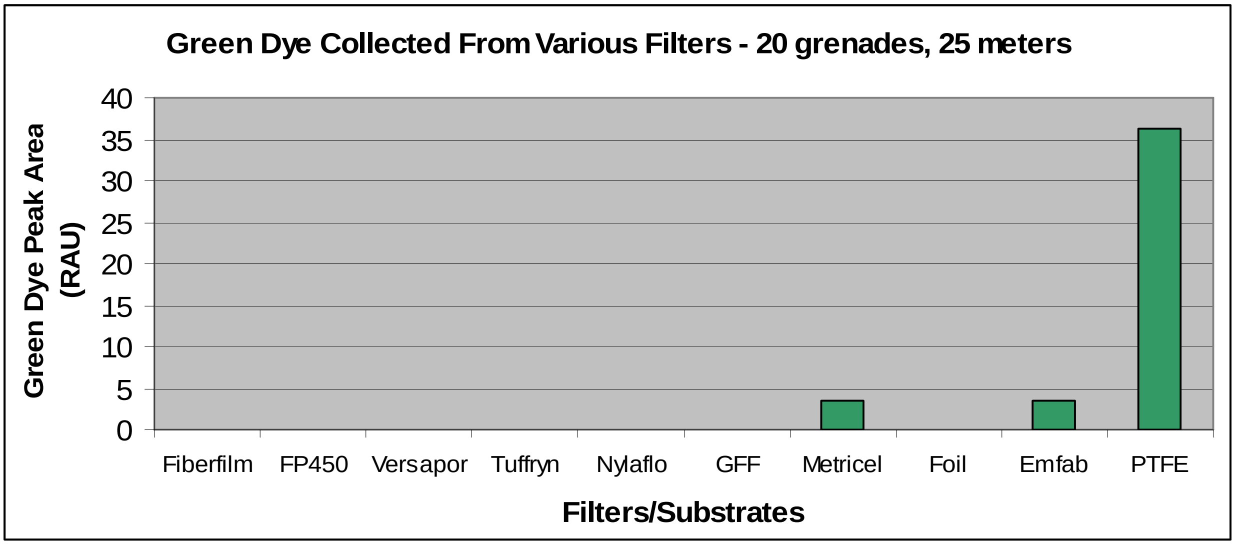

Figure 9: Green dye peak area collected from different substrates using 20 grenades 25 meters from the release point.

Yellow smoke

Based on wind turbulence during the August testing, a decision was made to perform a deposition collection at both 5 and 25 meters. As seen in figure 2, the ejection force of the grenade is great enough to propel dye particulates directly at the filter media. Figure 10 shows a bar graph of the yellow dye peak areas. All of the solid substrates have nearly the same nominal size, 78-80 cm^2, but heptane in the jar has an available surface area of only 44.2 cm^2.

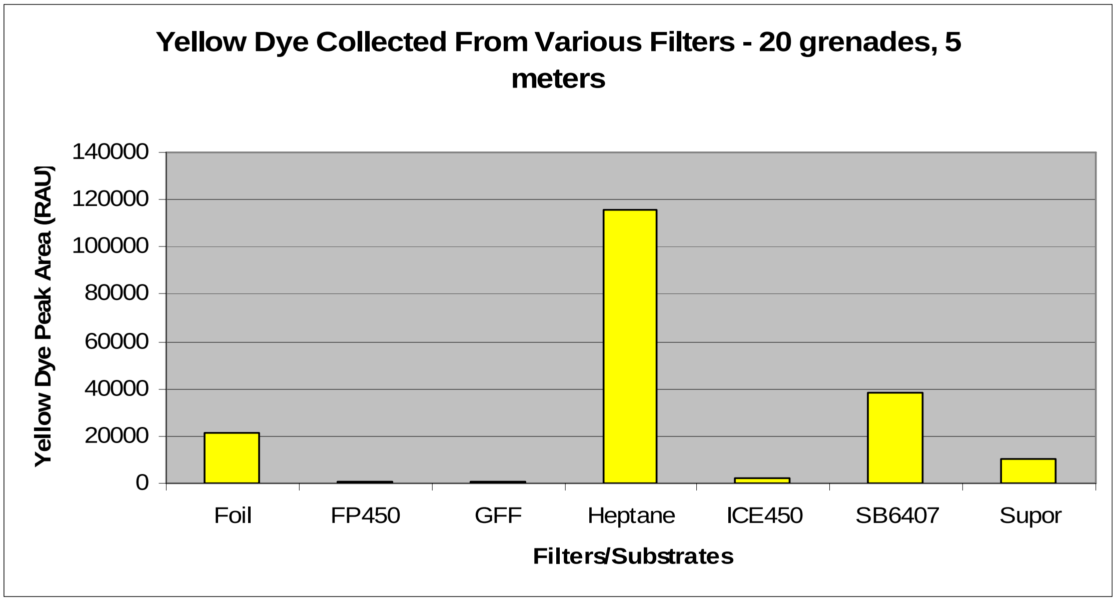

Figure 10: Yellow dye peak areas collected on different substrates using 20 grenades at 5 meters from the release point.

Of the solid substrates, only SB6407, Supor, and aluminum foil collected an appreciable amount of yellow dye. After the green dye experiment described above, the SB6407 and Supor samples were filtered with 0.22 µm filters to remove the viscous component. This allowed injection of these samples to occur. A jar of heptane, however, does the best job of collecting yellow dye (Figure 11), also known as 1H-indene-1,3(2H)-dione, 2-(2-quinolinyl). Since heptane is a nonpolar liquid, it is a reasonably good solvent for the yellow dye, and it will have essentially unlimited capacity to collect and store dye, compared with solid substrates, which are limited by size and surface area. It is recognized that the transport and application of heptane can limit the use of this solvent in the field.

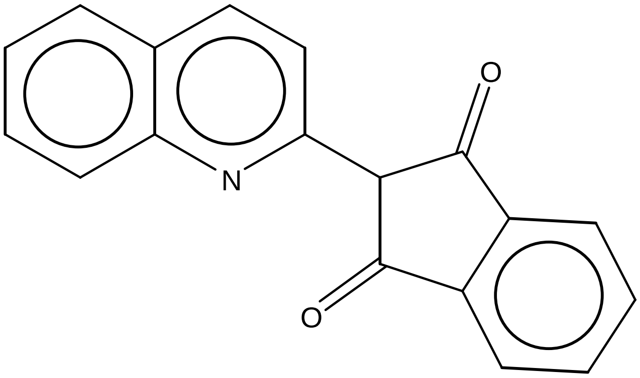

Figure 11: Yellow dye chemical structure.

A second experiment was performed using 20 yellow signaling grenades with collection substrates arranged 25 meters from the release point. At 25 meters from the release point, the yellow cloud is expected to be more dilute and the fraction of settleable components to be proportionately less. Figure 12 shows a bar graph of the yellow dye peak areas collected and extracted during this experiment.

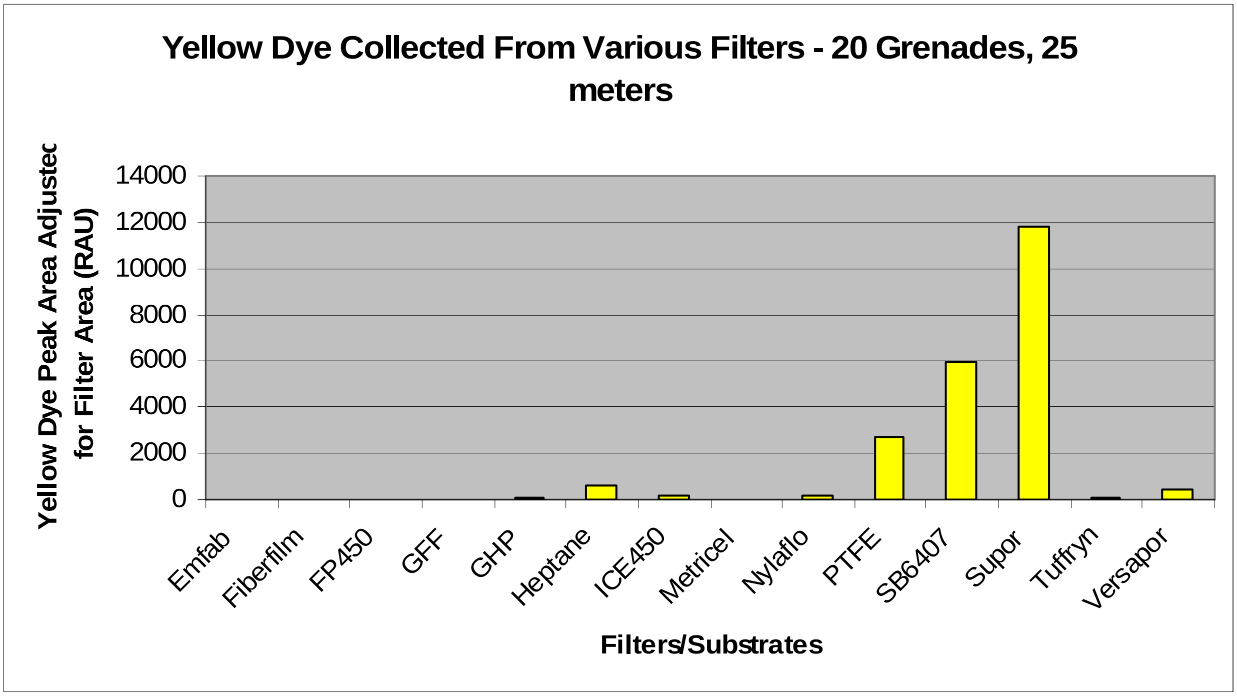

Figure 12: Yellow dye peak areas collected on different substrates using 20 grenades at 25 meters from the release point.

The amount of yellow dye that settles at 25 meters is approximately an order of magnitude less than that which deposits at 5 meters. Foil was not included in this series. Again, Supor and SB6407 were among the two best performers, and similar to the green dye data, PTFE can also collect yellow dye. Curiously, Supor collected nearly the exact amount at 25 meters as it did at 5 meters (a peak area of 11000). One possibility is that Supor is completely saturated at 5 meters and collects yellow dye so well at 25 meters, that it is also saturated at this distance as well. In this instance, it is suggested to use a substrate with higher capacity at close distances and the superior collecting power of Supor at distances farther from the grenade release point. At 25 meters, it is also noted that heptane is no longer the best substrate. It collects far less than the solid substrates at this distance. This could be due to a physical process where the deposition of chemicals over a jar of heptane is disrupted by the heptane volatility, or it could simply denote the difficulties of the uncontrollable nature of field studies.

Fog oil - field

The May FO experiment collected the hydrocarbon components settling at 5 meters from the release point using either a 15- or 18-minute fogging time. Figure 13 shows the FO collected by and subsequently extracted from the ACFs, aluminum foil, GFF, and both water and heptane.

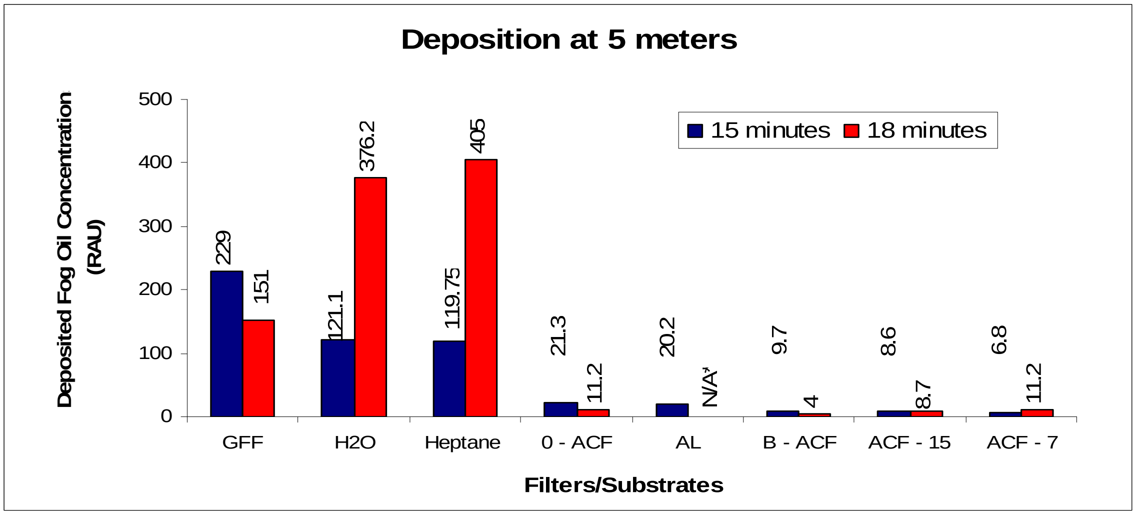

Figure 13: FO peak areas collected on different substrates using 15- and 18-minute fogging times at 5 meters from the release point.

Both water and heptane were examined in this experiment. Heptane does an excellent job at reproducing the exact amount of oil that deposits and collects on a water surface. The volatility of FO may limit glass fiber filter’s effectiveness, while inert substrates such as aluminum foil coupons do not collect or retain the FO deposition. The ACFs likely retain the FO too strongly and give poor recovery.

Fog oil - chamber

Field release of S&O is uncontrollable. Drift, diffusion, and deposition characteristics are likely to fluctuate under the vagaries of weather conditions. In an effort to better control the amount of S&O that each filter experiences and, further, to ensure that each filter experiences identical deposition conditions, a set of filters was submitted to FO released within the fogging chamber. An experiment was conducted using 2 minutes of fogging and a 9-hour settling time. A set of filters was placed on the floor of the chamber as shown in Figure 14 so that all were subjected to the same amount of fog.

Figure 14: Filters placed on the floor of the chamber for a fogging event.

Table 2 lists the amount of FO that was extracted from the filters. The concentration of FO was determined by GC/MS using a calibration curve made from known concentrations of FO in heptane. The filter results are listed from the smallest to the largest concentration in column two. Column three calculates the total amount of FO extracted from the filter. Column four is the amount of FO collected per filter area. In this experiment, and as seen in Figure 14, the size of some of the filters was increased to 20.3 cm x 25.4 cm sheets. Therefore, the values listed in column four show the most relevant parameter. If the sorbents are ranked from least to most FO collected, foil and Fiberfilm are the worst performers, while Metricel easily outperforms all others. GHP, SB6407, and heptane are the next best collectors of FO. Metricel and GHP are polypropylene and this polymer seems to work very well. Metricel is hydrophobic, however, as compared to the hydrophilic GHP, which may be the reason for the large difference in collecting the hydrophobic FO.

Table 2: FO extracted from filters from the fogging chamber.

Filter	Concentration [mg/ml]	Amount on filter [mg]	Amount/filter area [mg/cm2]
GFF small	0.2	0.4	0.0042
ICE 450	0.3	0.5	0.0064
SB 6407	0.3	0.5	0.029
FP 450	0.3	0.6	0.0076
Foil	0.4	0.8	0.0016
Fiber Film	0.7	1.4	0.0027
Heptane	0.8	1.6	0.036
Emfab	0.9	1.7	0.0033
PTFE	1.2	2.4	0.0048
Tuffryn	1.2	2.4	0.0048
GFF large	1.4	2.7	0.0052
Versapor	1.4	2.9	0.0056
Nylaflo	2.4	4.8	0.0096
Supor	3.3	6.6	0.013
Metricel	7.3	14.5	0.18
GHP	7.3	14.6	0.028

Two-dimensional separations

FO is an exceedingly complex hydrocarbon mixture that may contain as many as one million components. Typical GC/MS analysis of FO results in an unresolved hump where individual components are unable to be extracted for identification. New techniques in separation science are enabling separations in two-dimensional (2D) space where the first dimension uses differences in volatility among compounds and the second dimension uses differences in polarity. Analysis of FO using 2D GC/FID provides a glimpse of the sheer sample complexity. Figure 15 shows a 2D GC/FID separation of HOC FO. Each peak represents, at best, a single component of FO. The axis that reaches from foreground to background is the volatility dimension. Lighter, more volatile compounds elute toward the foreground, while heavier denser compounds elute toward the background. The axis from the right to the left side of the figure is the polarity dimension. Nonpolar compounds appear toward the right side and more polar species elute toward the left side of the figure. The goal in this type of analysis is to spread the peaks out as much as possible in this 2D space to resolve the compounds from one another.

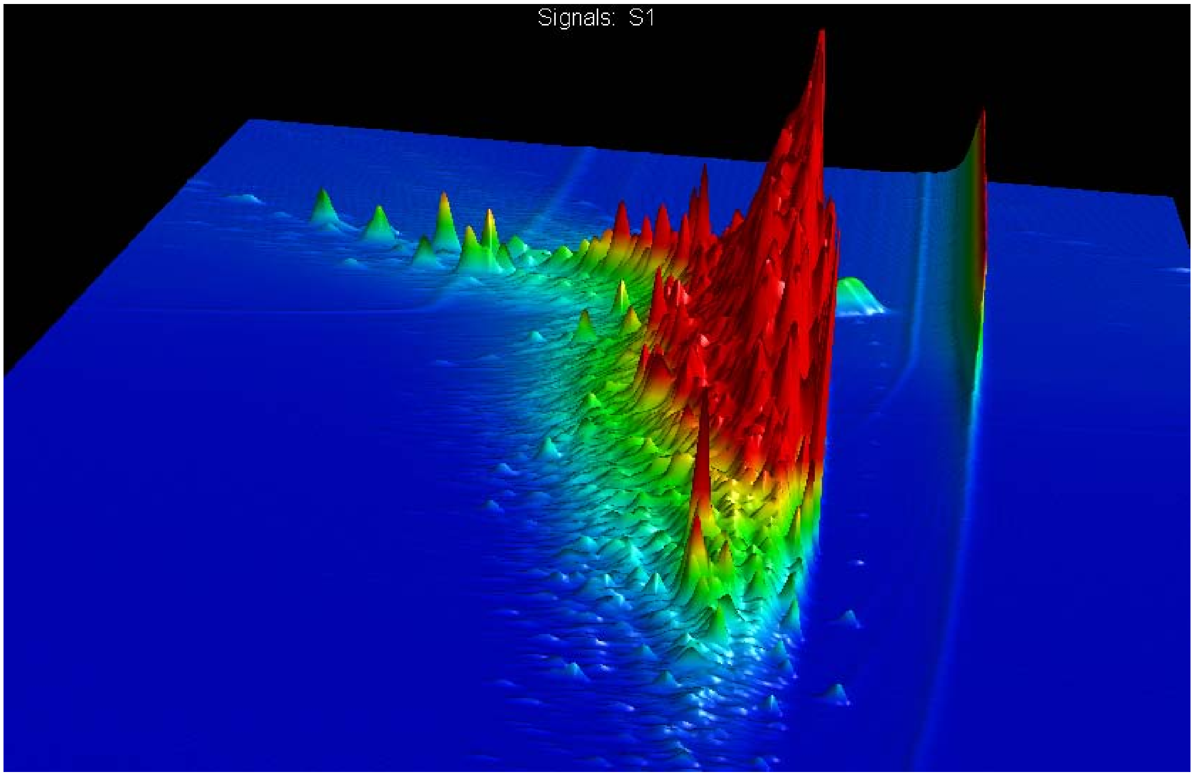

Figure 15: 2D GC/FID analysis of HOC FO.

Analysis of the sample extracts from the filters after chamber deposition of FO can be performed by 2D GC/FID. If the data are plotted as a surface plot, differences can be seen in the oil fractions that are collected on each filter. Figure 16 illustrates the surface plots of oil extracted from each filter sample. The x axis is volatility and the y axis is polarity. Dark blue is background, while lighter blue to green to yellow and finally to red indicates a progressive increase in the peak intensity.

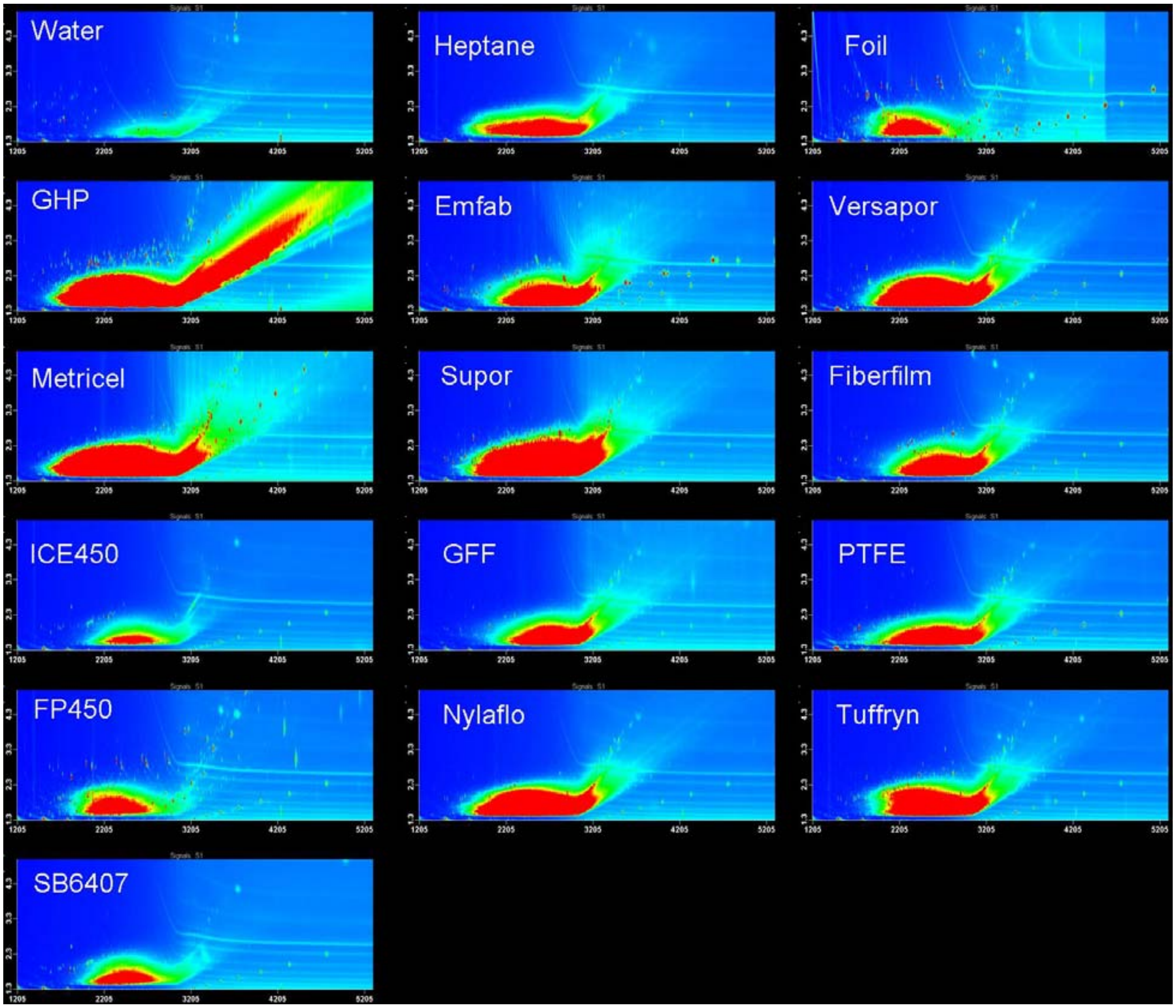

Figure 16: Surface plots of the 2D GC/FID analysis of oil extracted from fibers from chamber deposition.

Several characteristics can be noted when the data are displayed in this manner. The green area, signifying oil that deposits on water, elutes from 2205 to 3205 seconds on the volatility (x) axis and extends up to only 1.8 seconds on the polarity (y) axis at 2800 seconds. Most of the filters collected a far greater fraction of oil, including the more volatile fraction below 2205 seconds. As the most extreme examples, GHP and Metricel collected not only the most volatile species below 2205 seconds but can also collect more of the denser compounds that elute after 3205 seconds. So, while these two filters collected the most fog oil, they did not perform well at predicting the fraction that will deposit on water. To a lesser degree, Nylaflo and Tuffryn collected compounds that are more polar, as illustrated by an oil peak that extends to 2.3 seconds in the polarity dimension at 2800 seconds. While the oil peak in water is centered around 2700 seconds, foil and FP450 are centered near 2400 seconds with a tendency toward collecting the lower boiling point compounds of oil. By visual comparison, the filters that best reproduce the water deposition peak are GFF, Fiberfilm, and Emfab, where GFF is the best substrate. Curiously, all three of these filter types are predominantly borosilicate glass fibers, which seem to have the ideal behavior for mimicking the deposition of hydrocarbons on water.

Conclusions and Recommendations

Based on the data presented, each type of S&O examined has an optimal filter collection. For green colored smoke, ACF-7 is the best filter to collect the green deposited dye. However, it may be difficult and expensive to acquire. For commercial filters, PTFE performs best and would be readily available. It is suspected that ACF-7 would also work well for collection of yellow dye, as green and yellow dye are similar in size on a molecular scale and the functional groups are similar. If the sampling area is close to the release point, SB6407 performed best since it had a higher capacity for dye collection. Farther away from the release point, Supor was best since it can collect more dye in dilute conditions.

For FO, the recommendations are slightly more complex. If the goal is to collect the deposited oil fraction that best represents what would deposit onto a water surface, then GFF works well, and it is inexpensive. To collect all the oil that can deposit onto surfaces, Metricel, a hydrophobic polypropylene, works best.

Table 3 ranks the ability of the substrates to collect green dye, yellow dye, and FO. Two columns are shown for FO; one ranks the filters for the total collection of deposited oil while the second column ranks them according to how well they replicate deposition on water. Lower numbers indicate better performance. At a glance, this table dictates proper choice of filter for field use.

Table 3: Collection media rankings for green dye, yellow dye, and FO; from 1 (best) to 15 (worst).

Substrate	Green Dye (25 m)	Yellow Dye (25 m)	FO (total deposition)	FO (water deposition)
Emfab	3	8	13	4
Fiber Film	4	8	14	1
Foil	4	-	15	6
FP 450	4	8	7	6
GFF large	4	8	10	1
GFF small	4	8	12	-
GHP	-	7	4	11
Heptane	-	4	2	8
ICE 450	4	6	8	2
Metricel	2	8	1	10
Nylaflo	4	6	6	7
PTFE	1	3	11	3
SB 6407	4	2	3	2
Supor	4	1	5	9
Tuffryn	4	7	11	5
Versapor	4	5	9	7

These recommendations will be useful for site characterizations to minimize the amount of materials and equipment needed in the field. Transportation of jars of solvents is eliminated. Solid filters can be placed in difficult to access areas such as tortoise holes or in tree branches to determine the S&O that can deposit in these unusual geometries. The appropriate solid substrates can by used at installations to determine the amount of chemical that deposits from an S&O cloud during a training event This data will be important to correlate deposition with adverse effects on aquatic TES.

Finally, the need to test each type of S&O deposition independently is recognized. It is strongly encouraged to use an enclosed chamber for controlled release and equivalent deposition for direct comparison of filters.

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