CONTAMINANT INVESTIGATIONS WITH PISCES, 2008

Threemile and Sixmile Creeks in the vicinity of Griffiss Air Force Base
Rome, Oneida County, NY

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Front Cover: Two Hassett-style PISCES suspended from a wooden pole in Threemile Creek; Photograph credit - Corbin Gosier, BOH, NYSDEC.

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Introduction

Purpose

During the summer of 2008, passive in-situ chemical extraction samplers (PISCES) were deployed in Threemile (TMC) and Sixmile Creeks (SMC) in the vicinity of the Griffiss Air Force Base (GAFB), Rome, Oneida County, New York. Hassett-style PISCES (Figure 1) were deployed in TMC to trace polychlorinated biphenyl (PCB) contamination following several remedial projects. In addition, PCB uptake data for a downstream TMC site was compared to the 1995 PCB data prior to a contaminated sediment removal project. Hassett-style PISCES sampling in SMC was conducted primarily to locate a source responsible for elevated PCB levels in fish.

Background

TMC and SMC Creeks have a history of industrial contamination stemming from GAFB (Air Force Conversion Agency 2001). Since 1942, various national defense missions were carried out at this 3,552 acre parcel. Hazardous wastes were used, generated, stored and disposed at various sites on the installation. In 1993, GAFB was realigned, which resulted in deactivation of the 416th Bombardment Wing, leaving only GAFB's Rome Laboratory, Northeast Air Defense Sector, and Defense Finance and Accounting Services. Currently, much of the former GAFB is being developed as an industrial park with several area businesses with plans to include the Oneida County Airport.

Numerous studies and investigations have been carried out starting in the 1980s to locate, assess and quantify toxic and hazardous waste storage, disposal and spill sites on the GAFB property (Air Force Conversion Agency 2001). Results of these studies outlined 31 Areas of Concern (AOC) which were reported to the United States Environmental Protection Agency and the New York State Department of Environmental Conservation (NYSDEC). AOCs included several remediated landfills, spill sites and contaminated building sites located on GAFB property. Many of these sites have been remediated and are being monitored, others are still being cleaned up.

During June 1990, the New York State Department of Health (NYSDOH) issued a health advisory for TMC when elevated PCB levels were found in white sucker. This consumption advisory is still in effect today (NYSDOH 2008/09). To follow up on the health advisory, in

1995, a downstream TMC impoundment was sampled with PISCES by the NYSDEC (Spodaryk et al 1996). This study found "problematic levels" of PCB, particularly AR1254/60 in PISCES. Contaminated sediment has since been removed from this pond and it (TMC 5) was re-sampled for this 2008 PISCES study.

GAFB hired the FPM Group to collect fish from SMC in 2004 for contaminant analysis as part of their environmental sampling duties related to monitoring the efficacy of remedial activities at the air base (FPM 2006). SMC fish continue to show elevated PCB levels despite several remedial efforts.

At the start of this PISCES study, it was suspected that an electrical substation at GAFB remained a source of PCB contamination to groundwater and to TMC (personal communication - Corbin Gosier, NYSDEC). Other potential PCB sources or pathways included several capped landfills and a tributary to SMC known as Rainbow Creek (RBC). Air Force Conversion Agency, (June 2001) reports PCB contaminated oil and soil from a nearby locomotive building (Bldg. 20) were removed as was PCB contaminated sediment from nearby RBC (personal communication - Corbin Gosier, NYSDEC).

From the start of this PISCES study there was an urgency to gather and evaluate PISCES data because development plans are currently in place to direct the remaining open section of RBC through a culvert that is to be covered with "bio-dirt", i.e. remediated PCB contaminated soil, that originated on the air base. The City of Rome plans to develop this area for a bus station/terminal and parking area. The NYSDEC has concern that further remedial activities may be needed before new construction to fully eliminate PCB inputs from this area to SMC.

Methods

PISCES Study Area and Sampling

GAFB is bounded on the west by TMC and on the east by SMC (Figure 1). The air base has an elaborate storm drain system which includes flow from tributaries and wetlands, all of which ultimately drain southward via TMC and SMC to the New York State Barge Canal.

PISCES samplers were deployed at five sites in TMC and at nine locations in SMC drainage including one RBC site, and one Slate Creek site (Figures 2 - 4). Subsequent to the first exposure, additional samplers were deployed in RBC and at a new site, SMC 13, located upstream from SMC 4 and immediately below the 8,020 foot-long underground section of SMC that covers the confluence of SMC and RBC (Figure 5). Table 1 provides a brief description of PISCES sampling locations and coordinates. Samplers for the second exposure were deployed because of sampling problems at RBC and SMC 4 during the first exposure following a rush of storm water. Sampling locations were selected based on previously established FPM Group fish sampling sites, and on the locations of tributaries and landfills. As mentioned earlier, TMC 5 was selected because it was previously sampled with PISCES in 1995 and was the only station where pre and post-remedial comparisons could be made.

After measuring water temperature and recording site coordinates, two Hassett-style PISCES were deployed side by side at each station for a period of approximately three weeks beginning in mid-June. The exposure period was extended one week from the typical 14-day

exposure period because low ambient PCB levels were anticipated and the longer exposure period would allow for greater concentration in the samplers. Where sediment was soft, samplers were affixed in the water column by attaching them to a wooden pole driven in the bottom [TMC 1 - 4, and at SMC 13]. At other sites, samplers were suspended from an overhanging branch [SMC 2, 3 and 6] or suspended below an anchored float [at TMC 5]. Where the bottom was firm [SMC 1, 4, 5, Slate Creek, and RBC], samplers were attached to opposing sides of a concrete half-block that was set on the substrate. For the second exposure in RBC and at SMC 13, rather than using the concrete half-block, PISCES were attached to a wooden pole driven in the bottom sediment to keep them in place during storm water surges.

At deployment, PISCES were filled with ~180 mL of Ultra Resi-Analyzed® (J.T. Baker Co.) hexane and each was spiked with 50 uL of a trans-chlordane solution for quality control. The solution was prepared from a purchased solution (Ultra Scientific) of certified trans-chlordane at 100 ug (+/- 0.5 ug) /mL in methanol. The original solution was diluted 1:10 with a solution of acetone plus iso-octane to make a final 10 ng/uL solution of trans-chlordane.

Upon sampler retrieval, hexane samples were poured into new 250 mL I-Chem cleaned amber bottles and placed into a cooler with ice until transferred by the primary author later in the day to the walk-in cooler at the Hale Creek Field Station (HCFS). Within three weeks, the Analytical Services Unit at HCFS subjected samples to a Flurosil™ column cleanup and performed PCB Aroclors and organochlorine (OC) pesticides analyses with a gas chromatograph equipped with an electron capture device. Prior to chemical analysis, samples containing any water were placed into a separatory funnel which allowed the heavier water to be carefully drawn off. Method detection limits (MDLs) were 20 ng for AR1242 and AR1254/ 1260; 8 ng for 4,4' DDT, 2,4'-DDT and beta HCH ; 4 ng for 4,4'-DDE, 4,4'-DDD, mirex, photomirex, oxychlordane, cis-chlordane, trans-chlordane, heptachlor, aldrin, heptachlor epoxide, 2,4'-DDE, cis-nonachlor, alpha HCH and 2 ng for HCB. Preddice (2007 rev.) provides a more thorough description of Standard Operating Procedures (SOPs) used for PISCES studies conducted by HCFS staff (Appendix A).

PISCES Data Handling

Analytical data are presented for each PCB Aroclor and OC pesticide detected in PISCES. Data are represented as an amount measured in nanograms (ng) and for comparative purposes PCB Aroclor data were also presented as uptake rates measured as ng/cm^2/day. To calculate the uptake rate the amount measured in each sampler was divided by the surface area of permeable membrane of the Hassett sampler (45.6 cm^2) which in turn was divided by the number of days exposure.

PISCES Quality Control

Several quality control (QC) measures were taken to ensure acceptable standards were followed (Appendix A). In the field these included the trans-chlordane spike added to each PISCES and the solvent blanks both of which were used to compute percent recoveries. Appendix A also describes analytical measures taken at the laboratory to ensure acceptable quality control. A standard rule of thumb adopted for all PISCES studies is to disregard PISCES samples that lose more than 50% (> 90 mL) of the solvent or more than 50% (>5ng) of the trans-chlordane spiking material.

Rainbow Creek Fish and Invertebrate Survey

To supplement PISCES information, fish and benthic macroinvertebrate communities in RBC were qualitatively examined with the aid of a square-D aquatic dip net. We found that fish were absent and only a few tolerant invertebrate forms (midge larvae and aquatic worms) were present, and as a result, decided to return to conduct an in-situ fish bioassay.

Rainbow Creek In-situ Bioassay

On June 24, 2008, five 2 to 3 inch-long brown trout from the NYS Rome Fish Hatchery were placed in each of two plastic live cages. One was deployed at the RBC PISCES site and the other downstream at SMC 4. The fish were already acclimated to within two degrees of stream temperatures. Live cages were anchored to a concrete half-blocks and also were tethered to a shrub or PISCES anchor pole. The fish were inspected only at termination of the test at about 72 hours.

7-**Day Chronic Toxicity Tests**

7-Day chronic toxicity tests were conducted at HCFS with the water flea, *Ceriodaphnia dubia.* Ambient water samples were collected on June 24th from RBC and from SMC 4, and compared to control water. Testing protocol followed biological screening methodology (SOP #402-07) developed by the Division of Water for the Rotating Intensive Basin Sampling water quality monitoring program, a modification of methodology used by the United States Environmental Protection Agency (NYSDEC 2007 rev. 1.0).

Nine replicate exposures were set up in tray fashion with RBC, SMC 4 and control water. Each test cup began with one, less than 24-hour-old water flea, known hereafter as the parent organism, which was inspected daily to determine survival and total number of young produced during the 7-day exposure. A second toxicity test used duplicate water samples collected on July 15th from the main flow of Rainbow Creek and from an adjacent intermittent tributary which was nearly dry on June 24th when water was collected for the first exposure. The duplicate sample from each site was aerated overnight prior to the test in an attempt to remove any toxicity that may be due to volatile organic compounds (VOCs). Statistical analyses of data were performed with a one way analysis of variance (ANOVA), Dunnett's Test and Fishers Exact Test to determine significant difference in survival and reproductive rates from control water. A complete report of these tests is provided (Appendix B). The reader will notice this non-Agency report, prepared as a SUNY Cobleskill internship requirement, refers to Rainbow Creek anonymously, e.g. Creek X, to hide its identity for potential legal reasons.

Results

Precipitation Record

Rainfall data for the Rome area during the PISCES exposure periods were obtained from www.weather.com/weather/monthly/USNY1242 .

The two PISCES exposure periods extended from June 2 to July 15, 2008. During this 44-day period there was measurable rainfall during 24 days with two events (June 6 and 16) during the first exposure that exceeded one inch (Table 2). During the first exposure period, a

total of 5.36 inches of precipitation fell in the Rome area during 16 of 21 days. During one of these events (probably June 6) heavy precipitation fell in a very short period of time which resulted in a torrent of runoff that ultimately disturbed samplers at RBC and at SMC 4. As a consequence, a second PISCES exposure was conducted at RBC and at new SMC 13. The second exposure also turned out to be a rainy period with measurable rain on 7of 18 days. The largest rainfall of nearly one inch fell on July 13 just two days before the end of the second exposure. This time the samplers were secured sufficiently to withstand high flows. When these samples were retrieved, flows were higher but the water was less turbid.

Threemile Creek PISCES Samples

Ten PISCES samples from a 21-day exposure (June 2/3 - 23/24) at five stations (2/sta.) were delivered to HCFS for chemical analysis. All PISCES samples had greater than 50 % of the original solvent and ± 50 % of spike recovered (acceptable amounts according to SOP) and only three samples had minor amounts of water (Table 3). Water is not a great concern for PISCES studies because it is carefully removed prior to the analysis. *Cladophora* sp., a filamentous green alga, covered samplers at TMC 1, 2 and 5, and may have interfered with contaminant uptake.

All TMC PISCES samples contained measurable amounts of AR1242 and AR1254/ 1260 (Table 3) and four OC pesticides, p,p'-DDE; p,p'- DDD; cis-chlordane and trans-nonachlor (Table 5). Greatest mean total PCB uptake rate of 0.52 ng/cm^2/day was at TMC 4 located off Landfill Road near the transfer station. The smallest mean total PCB uptake rate of 0.20 ng/cm^2/day was at downstream impoundment, TMC 5. The most upstream sampling site TMC 1, located below drainage from the electrical substation, had a mean total PCB uptake rate of 0.37 ng/cm^2/day. Mean total PCB uptake rates progressively declined slightly downstream at TMC 2 and 3, and then increased at TMC 4 to the highest rate encountered. Downstream at TMC 5, the mean total PCB uptake rate decreased once again, even lower than upstream. The heavier Aroclor 1254/ 1260 predominated (54 - 65 %) at TMC 1, 2, 4 and 5 but only comprised 38 % of the PCB total at TMC 3.

Low residuals (up to 18.9 ng) of two DDT metabolites plus cis-chlordane (up to 13.4 ng) and trans-nonachlor (up to 6 ng) were detected but only at TMC 3-5 (Table 5). The latter was found only at TMC 4 where greatest amounts of the other three OC pesticides were also detected.

Sixmile Creek PISCES Samples

First Exposure (June 2/3 - 23/24; 21days) - Sixteen PISCES samples collected from eight stations (2 samples/ sta.) were delivered to HCFS. This total included two samples from RBC and two from the mouth of another SMC tributary, Slate Creek. The remaining 12 samples were from SMC. Four of the Hassett samplers leaked and contained ~ 10, 33.9, 51.8 and 100.6 mL of water (Table 4). The latter sample, 019 from SMC 2, although analyzed, lost more than 50 percent of the original solvent and spiking material, and following PISCES sampling protocol was disregarded. Samples from RBC and SMC 4 also lost solvent, probably due to a torrent of storm water but were still acceptable. Some of the Hassett samplers that leaked appeared to have a faulty Teflon™ membrane in the vented cap.

The lighter Aroclor 1242 was detected in all SMC samples. The heavier Aroclor 1254/ 1260 was detected in most samples with the exception of two samples from SMC 3 and one sample from Slate Creek (Table 4). Mean total PCB uptake rates ranged from a low of 0.14 ng/cm^2/day at SMC 3 to a high of 0.92 ng/cm^2/d at RBC. The two Hassett samplers in RBC with the greatest uptake rates were partially tipped over and the vent for one sampler at retrieval was above water so the data likely represent less than optimal uptake. AR1242 comprised from 78 - 92 % of the mean total PCB at all SMC stations. Of the OC pesticides analyzed, only low amounts (~ 4 - 11.3 ng) of two DDT metabolites, p,p'-DDE and p,p'-DDD, were detected in SMC samples (Table 5). DDE was present at SMC 6, 3 and 5, and DDD was detected at SMC 4 and 5.

Second Exposure (June 27 - July 15; 18 days) - The second PISCES exposure was conducted at RBC and at new SMC 13. The new site was located upstream from SMC 4, just below the long tunnel in which RBC and SMC join. Upon retrieval, one sampler (sample 039) at RBC was found to contain all water and was discarded. This problem was likely due to a faulty cap seal on the sampler. The other RBC sample and both SMC 13 samples were good samples despite a little water.

At sampler deployment and retrieval for the second exposure flows were estimated to be twice as great in RBC and SMC than for the first exposure during the first three weeks of June. Mean total PCB was 40 - 50 % less during this second exposure which may be due to the approximately two times greater dilution. Respective mean total PCB uptake rates (0.43 and 0.13 ng/cm^2/day) at the two sites also decreased by about 50 % (Table 4). Again, AR1242 predominated (85 and 87 %). OC pesticide amounts were less than MDLs.

PISCES Quality Control - Sample 019 lost more than 50 percent of the hexane and spiking material added at sampler deployment and, although analyzed, data were disregarded following PISCES sampling protocol (Appendix A). Also discarded was Sample 039, which contained only water. *[A relatively small amount of water in a PISCES sample is unimportant and is easily decanted with a separatory funnel during sample clean up procedures. However, a sample that is all water or one that has less than 90 mL of the original solvent is to be discarded. To be acceptable samples, the sampling protocol states that samples must contain greater than 50 percent of the original solvent and at least 50 percent of the spiking material.]* Percent recovery for the trans-chlordane spikes were all acceptable because they were within 5 ng (> 50 %) of the nominal 10 ng added at deployment. Both solvent field blanks were clean because they showed no detectable amounts of any of the analytes. Laboratory spike analyses performed on both analytical days for samples showed acceptable percent recoveries that ranged from 82.6 - 116 % and from 53.8 - 104 %, respectively. The three lowest percentages on the second day were for the HCH isomers. In addition, one method blank was performed on each of the two analytical days for samples from the first exposure and values for all analytes were less than the respective MDLs.

Rainbow Creek In-situ Fish Bioassay - A live cage with five fingerling brown trout was placed at the PISCES site in RBC and at SMC 4 for about three days. With the exception of one escapee to RBC, all fish were alive and appeared healthy at termination of the test. A fish

assumed to be the escaped trout was seen darting for cover in RBC several days later during retrieval of Hassett samplers for the second PISCES exposure.

7-day ChronicToxicity Testing- Appendix B provides the findings of the 7-day chronic toxicity tests with *C. Dubia* conducted by the junior author. As an integral addition to this PCB track-down investigation, an overview of the results and discussion are presented within this report.

First Exposure

RBC Main Flow and SMC 4 versus Control - During this toxicity test ambient water samples collected from SMC and RBC on June 24th were tested against control water. The control group produced 16 young without any parental mortality during the 7-day exposure. The SMC 4 group also had zero parental mortality but 4 of 9 parent organisms died in the RBC exposures. Reproductive rates in the SMC 4 group and in the RBC group were 12 and 8 young/ female, respectively. Analysis of variance (ANOVA) rejected the null hypothesis ($p= 0.05$) that reproductive rates in all groups were equal. Dunnett's Test indicated that only the mean reproductive rate for the RBC exposure group was significantly different from that for the control group. Fisher's Exact Test indicated that parental survival only in the RBC group was significantly different from that for the control group.

Second Exposure (aerated and non-aerated samples)

RBC Main Flow and Tributary versus Control - For this toxicity test ambient water samples collected on July 15th from RBC and the nearby tributary to RBC were tested against control water. Test cups were set up in duplicate with one group gently aerated to remove VOCs that might have contributed to the toxicity found in the first exposure. The other group was not aerated. After the 7-day test was completed, statistical tests found no significant mortality with parent organisms or differences in reproductive rates for aerated and non-aerated ambient samples compared with control exposures**.**

Discussion

Precipitation - June and July 2008 were abnormally wet months with plenty of rainfall to flush soil contaminants into nearby creeks where PISCES were deployed (Table 2). For some storm events, the runoff was too great, which caused samplers to be disturbed and, thus, some PISCES sampling was repeated. During sample deployment and retrieval in RBC, we had the opportunity to observe the creek at near low flow when it was turbid as well as at a higher flow when it was clear. Water samples collected under these different conditions allowed for 7-day chronic toxicity testing with water fleas to show that contaminant issues may exist in RBC under low flow conditions possibly when there is less dilution of contamination.

Threemile Creek - A 21-day PISCES exposure was completed at five TMC stations that extended from just below the electrical substation on GAFB to the downstream impoundment near Rt. 49, a distance of about 1.3 miles. All TMC PISCES samples had AR1242 and AR1254/

1260. AR1254/ 1260 comprised 54 - 65 % of the PCB total at 4 of 5 stations (Table 3). Low amounts of DDD, DDE, cis-chlordane and trans-nonachlor were also detected at the three downstream stations (Table 5).

TMC 1, located downstream from the electric substation at GAFB, had a mean total PCB uptake rate of 0.37 ng/cm^2/day (Table 3). To clearly implicate the substation or the immediate area around the substation as a PCB source, an upstream "clean control" station in the storm sewer system is needed but this was impossible to carry out when upstream flow at sampler deployment was practically nil. Should storm drain access becomes available, another PISCES exposure could be conducted provided there is at least a 10 to 14-day period with sufficient flow during Spring 2009.

Downstream at TMC 2 located below Landfill 5 and further downstream at TMC 3 near Landfill 6, there was a progressive and slight decline in the mean total PCB uptake rate from that at TMC 1. However, at TMC 4 off Landfill Road near the transfer station, the mean total PCB uptake rate increased to 0.52 ng/cm^2/day, a rate nearly double that at TMC 3 and even greater than upstream at TMC 1. TMC 4 was the only station with four OC pesticides and the amounts detected were greater than at other stations sampled. The increase in mean total PCB uptake rate at TMC 4 and the greater amounts of all four pesticides indicated a contaminant source located between TMC 3 and TMC 4. This may be due to leachate from Landfill 6 and should be investigated further.

The most downstream PISCES station, TMC 5, located in the impoundment along Rt. 49, had the lowest PCB uptake rate of 0.20 ng/cm^2/ day (Table 3). A low amount of AR1242 was detected in both samples but the heavier AR1254/ 1260 was found in only one sample. Both samplers at this location were moderately covered with *Cladophora* sp, a green alga, which could have reduced PCB uptake but the low uptake rate is more likely due to a remedial project that removed contaminated sediment from this impoundment. Previous PISCES sampling by NYSDEC has demonstrated that PCB contaminated sediment can contribute to the dissolved fraction in overlying water (Spodaryk et al 2005).

1995 versus 2008 PISCES Data for TMC 5 - In 1995, the inlet stream at the upper end of the impoundment, TMC 5, was sampled twice with Hassett-style PISCES; once for 27 days and once for 32 days. It should be noted that 1995 was only the second year for the primary author to use PISCES and during this early period, trials were occasionally conducted with different cleaning techniques and permeable membrane materials. One sampler (sample 086) deployed in 1995 at the TMC impoundment had a permeable membrane made of Duro-Seal™, a different material than normally used. It was determined that this thinner material stretched unpredictably and, for this reason, is no longer used on PISCES. The greater surface area of the stretched membrane probably accounted for the slightly greater PCB uptake in this sample. Table 6 compares 2008 PISCES results with those from 1995 which predate the contaminated sediment removal project. Slight differences (< 75 ft) in station locations between the two years is not expected to have any affect on the PISCES data. With the exception of DDD, OC pesticides were not included in Table 5 because amounts were less than MDLs.

In 1995, the lighter PCB Aroclor was undetected but in 2008 it occurred in both samples; 82.4 and 90.8, mean = 87 ng. During both years, the heavier AR1254/ 1260 was measured in all samples; mean = 40 ng in 1995 and 103 ng in 2008. In 2008, the mean total PCB uptake rate was

5 to 6 times greater than in 1995 (Table 6). PISCES data show this was due to the detection of AR1242 and a 2.5 fold increase in the mean amount of AR1254/ 1260. A difference in mean total PCB this large is considered by the primary author to be notable despite the limited sampling and expected maximum two fold variation among duplicate PISCES samples. NYSDEC (1991), reports replication for PISCES samples averaged ± 20 - 25 %. Although the TMC impoundment had the lowest total PCB uptake rate in 2008, PISCES data indicate that PCB amounts in the water column 13 years ago, prior to the sediment removal project, were several times lower. At this point in time, reasons for this are only speculative at best. For DDD it is difficult to make a comparison between the two years due to the low amounts detected, differences in MDLs and limited sampling.

Sixmile Creek - A 21-day PISCES exposure was completed in June 2008 for eight SMC stations including one site in RBC and one in Slate Creek. One sampler (sample 019) leaked badly and the data were disregarded. With the exception of two samples from SMC 3 and one sample from Slate Creek, all other PISCES samples from this exposure contained AR1242 and AR1254/ 1260 (Table 4). With the exception of SMC 3 where only AR1242 was detected, AR1242 comprised 78 - 92 % of the mean total PCB at SMC PISCES stations. The lowest mean total PCB uptake rate of 0.14 ng/cm^2/day was at SMC 3 and the highest of 0.92 ng/cm^2/day was at RBC (Table 4). Only very low residues of DDD and DDE were detected, the former at SMC 4 and 5 and the latter at SMC 6, 3 and 5 (Table 5).

Mean total PCB uptake rates for upstream stations SMC 1, 2 and 6 were similar and ranged from 0.26 - 0.30, mean = 0.29 ng/cm^2/day. The mean total PCB uptake rate for SMC 1 was expected to be closer to the background uptake rate of 0.14 ng/cm^2/day found at SMC 3 and the 0.13 ng/cm^2/day subsequently found at new SMC 13 (Table 4). This data suggests another PCB source may be located upstream from SMC 1. Mean total PCB uptake rate at SMC 3 was one-half that at SMC 6 located only 800 feet upstream. This decrease was likely due to increased flow and greater dilution although this was not apparent on this flat section of creek. About 500 - 600 feet below SMC 3 the creek flows into an 8,020-foot-long tunnel. Approximately 5,080 feet into this tunnel is where RBC has been redirected to join SMC.

PISCES samples from RBC had the highest mean total PCB uptake rate of 0.92 ng/cm^2 /day encountered in this study (Table 4). This rate is about three times that of upstream stations SMC 1, 2 and 6 which strongly implicates this tributary as a pathway for another PCB source. AR1242 comprised 88 % of the total PCB at this station. At SMC 4, located about 1,000 feet downstream from the tunnel, it was expected that the total PCB uptake rate in SMC would increase substantially from that at SMC 3 due to the influence of PCB from RBC but this was not the case. The uptake rate at SMC 4 decreased to 0.24 ng/cm^2/day, a rate slightly less than at upstream stations. This fairly low uptake rate suggests that the total PCB contribution from RBC is relatively small and diluted by SMC. Downstream in Slate Creek the mean total PCB uptake rate was 0.24 ng/cm^2/day, a rate identical to that at SMC 4. This data indicates the presence of a small upstream PCB source in the Slate Creek drainage. Further downstream about 1,600 feet at SMC 5, the PCB uptake rate increased to 0.63 ng/cm^2/day which provides fairly strong evidence for a larger and unknown PCB source to SMC located between SMC 4 and 5. This PCB input as

well as smaller contributions from RBC, Slate Creek and from a source upstream of SMC 1, contribute to the PCB burden measured in downstream SMC fish collected in 2004 (FPM Group 2006). The slight increase in DDE at SMC 5 strengthens the PCB data that indicates the presence of another contaminant source located between SMC 4 and 5 (Table 5).

A second PISCES exposure (18 days) was conducted beginning in late June 2008 at RBC and at new SMC 13 located at the downstream end of the long SMC tunnel. This exposure was performed primarily because at least one storm event during the first exposure period disturbed samplers in RBC and at SMC 4. As it turned out, rainfall during the second exposure was even greater (Table 6). Nevertheless, this time 3 of 4 PISCES samples were retrieved in good condition because they were fastened to poles driven in the substrate rather than attached to more mobile concrete half-blocks. Sample 039 from RBC contained only water and no solvent probably due to a faulty membrane in the cap of the Hassett sampler, and was discarded. The good sample from RBC contained both PCB Aroclors but the total PCB uptake rate was less than one-half that from the earlier exposure at this site. This uptake rate, 0.43 $ng/cm^2/day$, was still greater than at upstream SMC stations during the first exposure, and, again, implicated RBC as a PCB pathway for another source. The lighter AR1242 comprised 95 % of the PCB detected at this station. The total PCB uptake rate of 0.13 $ng/cm^2/day$ at new SMC 13 was the lowest rate encountered at any SMC PISCES station. OC pesticides were less than MDLs during this exposure. Lower PCB uptake rates and OC pesticides at less than MDLs probably reflect the greater dilution of contamination during this second exposure.

RBC In-situ Fish Bioassay - A 3-day in-situ bioassay test was performed to gain water quality and toxicity information not provided by PISCES testing. Results indicate that RBC will support young brown trout for a at least a few days and probably much longer. Stream temperatures were colder (13 and 14 °C) than expected but warmed to 20°C with increased storm water input.

Before the bioassay, the benthic macroinvertebrate population in the vicinity of the RBC PISCES station was examined and found to be nearly devoid of organisms. Only a few tolerant midge larvae and aquatic worms were observed. This condition in RBC could be caused in part by toxic conditions, intermittent flows, poor substrate type or a combination of these factors. 7-Day chronic testing determined there is a toxicity issue particularly at lower flows. In addition to a sparse invertebrate community, fish were absent. The reason for this is unknown, possibly some of the same reasons apply. In addition, the steep incline of the underground culvert to SMC is one factor not attractive or passable to upstream migrating fish during spawning. Seventy years ago (pre-1940s), before RBC was disrupted by development at GAFB, this creek was likely a small, cold water spawning and nursery stream for local brook and brown trout. Today, RBC would require major habitat improvements to return to its former stream status. This potential deserves to be investigated but is likely impractical because too much development/ growth has occurred and even more is planned.

7-day Chronic Toxicity Testing- The purpose for this testing was also to gain toxicity information about RBC not provided by PISCES sampling. The first exposure compared ambient water from SMC 4 and RBC with control water. Water samples were collected on June 24th when flows in both creeks were fairly low and turbid.

During this first test, only five of the parent RBC water fleas survived and, as a result, reproductive rates were less than that for the control water. The three statistical tests performed showed that survival and reproductive rates for RBC were significantly different from the control which indicated the presence of a toxicity. Results for the SMC 4 water sample collected on the same day showed no significant difference in survival or reproductive rates from controls.

For the second toxicity tests, duplicate water samples were collected on July 15th in the main flow at the RBC PISCES site as well as from the mouth of a nearby, adjoining tributary to RBC. This time the water level and flows in RBC were greater due to major storm activity a few days earlier. The water was much less turbid than during the first test probably because most of the initial surge of runoff had passed before the sample was collected. The tributary was not sampled for the first exposure because the flow was practically nil. For this second toxicity test, the duplicate water samples were aerated prior to testing in an attempt to remove any VOCs that may have contributed to the toxicity observed during the first round of RBC toxicity testing. For aerated and non-aerated samples, results and statistical tests demonstrated no significant difference from controls for survival or reproductive rates in RBC or tributary samples.

The two 7-day chronic toxicity tests performed indicated that at fairly low flow there is a toxicity issue in RBC. It is unclear if VOCs are related to this toxicity, and additional sampling and toxicity screening are recommended.

Summary

Sampling with passive in-situ chemical extraction samplers (PISCESs) was conducted in June and July 2008 for Threemile (TMC) and Sixmile Creeks (SMC), Rome, Oneida County, NY. Sampling at five TMC sites was performed for polychlorinated biphenyl (PCB) track-down purposes and to update PCB amounts in the water column after several remedial projects at the Griffiss Air Force Base (GAFB) and at a downstream impoundment, TMC 5. SMC sampling was performed at nine sites to determine the overall efficacy of remedial efforts at the air base but, more specifically, to determine the source for elevated PCB levels in downstream SMC fish. Some PISCES sampling for this study focused on an electric substation located near upper TMC and on a SMC tributary known as Rainbow Creek (RBC). In addition to PISCES studies and following an inspection of RBC showing the lack of fish and sparce benthic macroinvertebrate life, an in-situ bioassay test with fingerling brown trout was conducted for RBC and SMC 4. In addition, 7-day chronic toxicity tests with the water flea, *C. dubia*, were performed with water samples from RBC and its tributary, and for water samples from SMC 4.

TMC - PCB Aroclors 1242 and 1254/ 1260 were detected in PISCES samples at all five sites sampled. AR1254/ 1260 comprised 54 - 65 % of mean total PCB at four of these sites. PISCES data show the electric substation at Griffiss Air Force Base (GAFB) is likely to be a PCB source although the necessary upstream flow in the storm drain system was nil and could not be sampled. Highest total PCB uptake rate of 0.52 ng/cm^2/day was at TMC 4 on Landfill Road near the transfer station possibly implicating the nearby landfill. Although the total PCB uptake rate was lowest (0.20 ng/cm^2/day) at downstream TMC 5, located in a remediated impoundment, the 2008 PCB uptake rate did not reflect improvement compared with data

collected in 1995 previous to a contaminated sediment removal project. Additional PISCES sampling that brackets the electric substation and Landfill 6 are recommended during moderate Spring (May) flows.

SMC - PISCES sampling in SMC was performed at nine sites which included one site in Rainbow Creek (RBC) and one in Slate Creek. The lighter PCB AR1242 was detected at 8 of 9 sites and the heavier AR1254/ 1260 was found at all sites. Unlike at TMC where AR1254/ 1260 dominated, the lighter AR1242 comprised 78 - 92 % of the total PCB at all SMC PISCES stations. Lowest PCB uptake rates of 0.12 and 0.14 ng/cm^2/day at SMC 3 and at new SMC 13 likely reflect background conditions for the area. The PCB uptake rate at the most upstream site, SMC 1, and at Slate Creek was double background and indicated the presence of low level PCB sources to both creeks. The highest total PCB uptake rate of 0.92 ng/cm^2/day was in RBC. This elevated rate indicated that RBC is a PCB pathway but the effect was not detectable far downstream. However, further downstream below RBC and SMC 4, the PCB uptake rate at SMC 5 increased to 0.63 ng/cm^2/day which indicated the presence of another more significant and unknown source. All of the PCB sources described contribute to the PCB burden previously measured in SMC fish. Additional PISCES sampling is recommended to locate upstream PCB sources in SMC and Slate Creek as well as to better locate the PCB source to RBC and the unknown source located between SMC 4 and SMC 5. PISCES data indicate the PCB source between SMC 4 and SMC 5 is the most important contributor to locate.

During June 2008 field investigations found RBC to be a cold water stream. 72-Hr in-situ toxicity testing with fingerling brown trout determined that RBC should be able to support fish including trout provided flows are not limiting. However, the sparse benthic macroinvertebrate community and the present lack of fish suggests there may be other water quality issues. Additionally, 7-day chronic toxicity tests with the water flea, *C. Dubia,* were performed comparing the toxicity of ambient water samples from RBC, a nearby tributary to RBC and SMC 4 to control water. Results show a significant difference in parent survival and reproductive rates for RBC indicative of a toxicity, especially when flow is low and dilution of contamination is reduced. Water sampling in the upstream storm drain system and subsequent 7-day chronic toxicity testing are needed to sort this out.

Acknowledgements

This investigation was made possibly with the help and cooperation of several individuals. The Analytical Services Unit at HCFS under the supervision of Anthony Gudlewski deserves thanks for its prompt attention to PISCES samples and for the generation of good quality data. Others who assisted, particularly with access to sampling sites on the Griffiss Air Force Base, include staff from FPM Group: Daniel Baldyga, Josh Wenzel and Niels Van Hoesel. Corbin Gosier, Ecologist with NYSDEC's Bureau of Habitat, provided field assistance and made early site reconnaissance arrangements with FPM staff. Dr. Ed Kuzia and Nicole Wright,

Research Scientists with Division of Water, provided instruction to the junior author during 7-day chronic toxicity tests. Dr. Kuzia, Research Scientist II and, Corbin Gosier and Larry Skinner, both Ecologists with the Division of Fish, Wildlife and Marine Resources, provided critical review of this manuscript.

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Table 1. PISCES sampling locations for Threemile (TMC) and Sixmile Creeks (SMC), Rome, Oneida Co, NY, 2008.

Station No.	Coordinates	Location Description
Threemile Creek TMC 1	18T 0467908; UTM 4783242	~ 250 yard downstream from drainage ditch that borders electrical substation on Griffiss Air Force Base
TMC 2	18T 0466804; UTM 4784682	downstream from Landfill 5, ~ 30 ft below stainless piping near fish sampling station
TMC 3	187T 0467227; UTM 4784325	opposite Landfill 6 near fish sampling station
TMC 4	18T 0467793; UTM 4783604	~ 125 ft north of stream crossing on road to landfill transfer station
TMC 5	18T 0467909; UTM 4783239	middle of remediated impoundment along Rt. 49
Sixmile Creek SMC 1	18T 0468856; UTM 4784701	upstream from weir, ~ 200 yards behind and upstream from residence off Cemetery Road
SMC 2	18T 0466634; UTM4787768	below Landfill 1 at fish sampling station
SMC 6	-	opposite wetland pond along air base road below arms storage facilities
SMC 3	18T 0466979; UTM 4787063	along runway below nuclear storage bunkers
Rainbow Creek (RBC)	18T 0467707; UTM 4785457	~ 20 feet downstream from junction of main flow and nearby intermediate flow ditch
SMC 4	18T 0468616; UTM 4784894	below field where air stripping is being used to remove VOCs from soil
new SMC 13	18/T 0468502; UTM 4785043	immediately downstream from 8,020-foot-long tunnel/culvert for SMC, below jct. with Rainbow Creek
Slate Creek	18T 0468914; UTM 4784729	near mouth, off small stony point, at bend in road below Family Dollar Warehouse
SMC 5	18T 0468804; UTM 4784425	most downstream SMC station, at fish sampling sta.

Table 2. Rainfall data (*inches*) for June/July at Rome, NY, 2008.

JUNE

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
1 *0.0*[1]	2 *0.0*	3 *0.03*	4 *0.03*	5 *0.02*	6 ***1.63***[2]	7 *0.0*
8 *0.24*	9 *0.0*	10 ***0.43***	11 *0.0*	12 *0.0*	13 *0.0*	14 *0.04*
15 *0.16*	16 ***1.09***	17 *0.13*	18 *0.08*	19 *0.05*	20 *0.07*	21 ***0.41***
22 *0.19*	23 ***0.76***	24 *0.0*	25 *0.0*	26 *0.22*	27 ***0.40***	28 *0.16*
29 *0.67*	30 *0.15*					

JULY

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
		1 *0.0*	2 *0.0*	3 ***0.43***	4 *0.0*	5 *0.0*
6 *0.0*	7 *0.0*	8 *0.0*	9 *0.0*	10 *0.0*	11 *0.11*	12 *0.0*
13 ***0.98***	14 *0.0*	15 *0.0*				

[1] Numbers in italicized print are rainfall events

[2] Numbers in larger italicized bold print are rainfall events ≥0.4 inches

Source: http://www.weather.com/weather/monthly USNY1242

Table 3. PCB data for Hassett-style PISCES samples collected from Threemile Creek, Rome, Oneida Co., NY, 2008.

Station No.	Sample Jar No.	Total Liquid (mL)	Water (mL)	Solvent (mL)	% Recovery T-chlordane	AR1242 (ng)	AR1254/60 (ng)	Mean Total PCB (ng)	No. Days Exposure	Mean Total PCB Uptake Rate ($ng/cm^2/day$)
TMC - 1	003	172	0	172	133	136	304	359	21	0.37
	004	148	0	148	98.2	124	154			
TMC- 2	005	193	23.6	169	106	158	144	327	21	0.34
	006	175	4.3	171	122	130	222			
TMC - 3	007	172	0	172	79.4	127	97.2	286	21	0.30
	008	164	0	164	105	232	116			
TMC - 4	009	122	0	122	78.2	164	337	494	21	0.52
	010	148	0	148	95.9	183	303			
TMC - 5	001	192	34.5	158	91.3	82.4	82.3	190	21	0.20
	002	142	0	142	98.2	90.8	124			

Table 4. PCB data for Hassett-style PISCES samples collected from Sixmile Creek, Oneida Co., Rome, NY, 2008.

Station No.	Sample Jar No.	Total Liquid (mL)	Water (mL)	Solvent (mL)	% Recovery T-chlordane	AR1242 (ng)	AR1254/1260 (ng)	Mean Total PCB [1] (ng)	No. Days Exposure	Mean Total PCB Uptake Rate (ng/cm²/day)
1st exposure SMC - 1	021	177	0	177	111	204	54	274	20	0.30
	022	170	0	170	92.3	242	47.2			
SMC - 2	019	170	100.6	69	38.9	81.2	25.5	Failed QC: lost > 50 % of solvent and spike - disregard data		
	020	175	0	175	111	194	46.4	240	20	0.26
SMC - 6	017	200	33.9	166	86.8	218	45.2	271	20	0.30
	018	171	0	171	89.1	220	58			
SMC - 3	015	162	51.8	110	65.6	198	< 20	130	20	0.14
	016	161	0	161	77.6	63.2	< 20			
Rainbow Creek (RBC)	023	150	0	150	86.2	600	189	879 [2]	21	0.92 [2]
	024	109	0	109	96.2	868	101			
SMC - 4	025	102	0	102	56.1	173	43.6	226 [2]	21	0.24 [2]
	026	172	0	172	95.6	186	50			
Slate Creek	013	170	< 10 [3]	170	95.8	230	47.6	227	21	0.24
	014	167	0	167	98.5	177	< 20			
SMC - 5	011	134	0	134	90.4	588	115	602	21	0.63
	012	134	0	134	104	400	101			
2nd exposure Rainbow Creek (RBC)	039	Sample - all water and no solvent - discarded								
	040	170	0	170	113	304	52.4	356	19	0.43
new SMC- 13	037	192	56	136	80.5	96.8	23	107	19	0.13
	038	168	21	147	91.8	94.4	< 20			

[1] zero used to calculate mean total PCB where AR1254/ 1260 was less than MDL of < 20 ng

[2] both samplers were tipped over on side and could represent less than optimum uptake

[3] small amount of water observed upon return to HCFS but not during sample clean up

Table 5. Organochlorine pesticide data (ng) for Hassett-style PISCES samples collected from Threemile and Sixmile Creeks, Rome, Oneida Co., NY, 2008. [1]

Station	Sample Jar No.	p,p'-DDE	p,p'-DDD	cis-chlordane	trans-nonachlor
	Threemile Creek				
TMC - 3	007	5.0	4.0	< 4	< 4
	008	6.5	5.3	4.3	< 4
TMC - 4	009	12.1	18.9	13.4	6.0
	010	10.5	16.0	11.4	5.0
TMC - 5	001	< 4	5.3	< 4	< 4
	002	< 4	7.5	5.2	< 4
	Sixmile Creek - 1st exposure				
SMC - 6	017	< 4	< 4	< 4	< 4
	018	4.3	< 4	< 4	< 4
SMC - 3	015	4.6	< 4	< 4	< 4
	016	< 4	< 4	< 4	< 4
SMC - 4	025	< 4	6.92	< 4	< 4
	026	< 4	4.88	< 4	< 4
SMC - 5	011	7.2	11.3	< 4	< 4
	012	4.3	7.6	< 4	< 4

[1] Data for samples with amounts of OC pesticides greater than MDLs

Table 6. Comparison of 1995 and 2008 PCB and DDD data for Hassett-style PISCES samples from the impoundment (TMC 5) on lower Threemile Creek, Rome, Oneida Co., NY.[1]

Year	Sample No.	Duration (days)	AR1016 or AR1242 [2] (ng)	AR1254/ 1260 [2] (ng)	Mean Total PCB Uptake Rate [3] ($ng/cm^2/day$)	DDD [2] (ng)
1995	003	27	<20	38	0.03	8
	004	27	<20	42		6
	086[4]	32	<20	69	0.04	7
	087	32	<20	44		3
2008	001	21	82.4	82.3	0.20	< 4
	002	21	90.8	124		< 4

[1] sampling location: 1995 - head of impoundment; 2008 - middle of impoundment [no expected differences in contaminantion due to slight difference in site locations (sites within 75 ft)]

[2] Method Detection Limits:
PCB Aroclors - 20 ng - 1995 and 2008
DDD: 2 ng - 1995; 4 ng - 2008

[3] zero was used to compute mean total PCB uptake rate where AR1242 was less than MDL of < 20 ng

[4] equipped with Duro-Seal membrane instead of normal 4 mil low density polyethylene membrane

Figure 1. Hassett-style PISCES used for Threemile and Sixmile Creeks contaminant track-down studies, 2008.

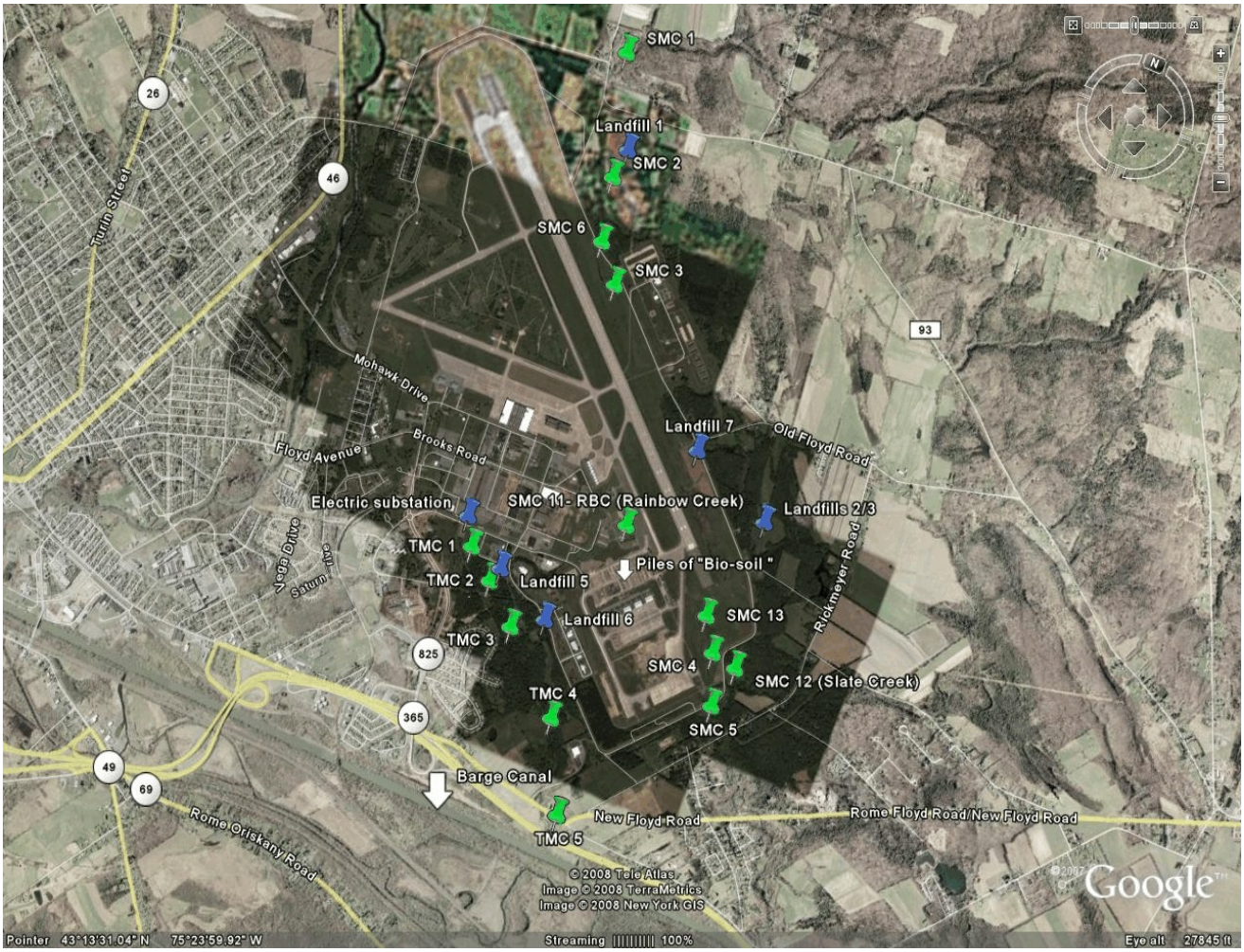

Figure 2. PISCES sampling locations for Threemile and Sixmile Creeks, Rome, Oneida Co., NY, 2008.

Figure 3. PISCES sampling locations for Threemile Creek, Rome, Oneida Co., NY, 2008.

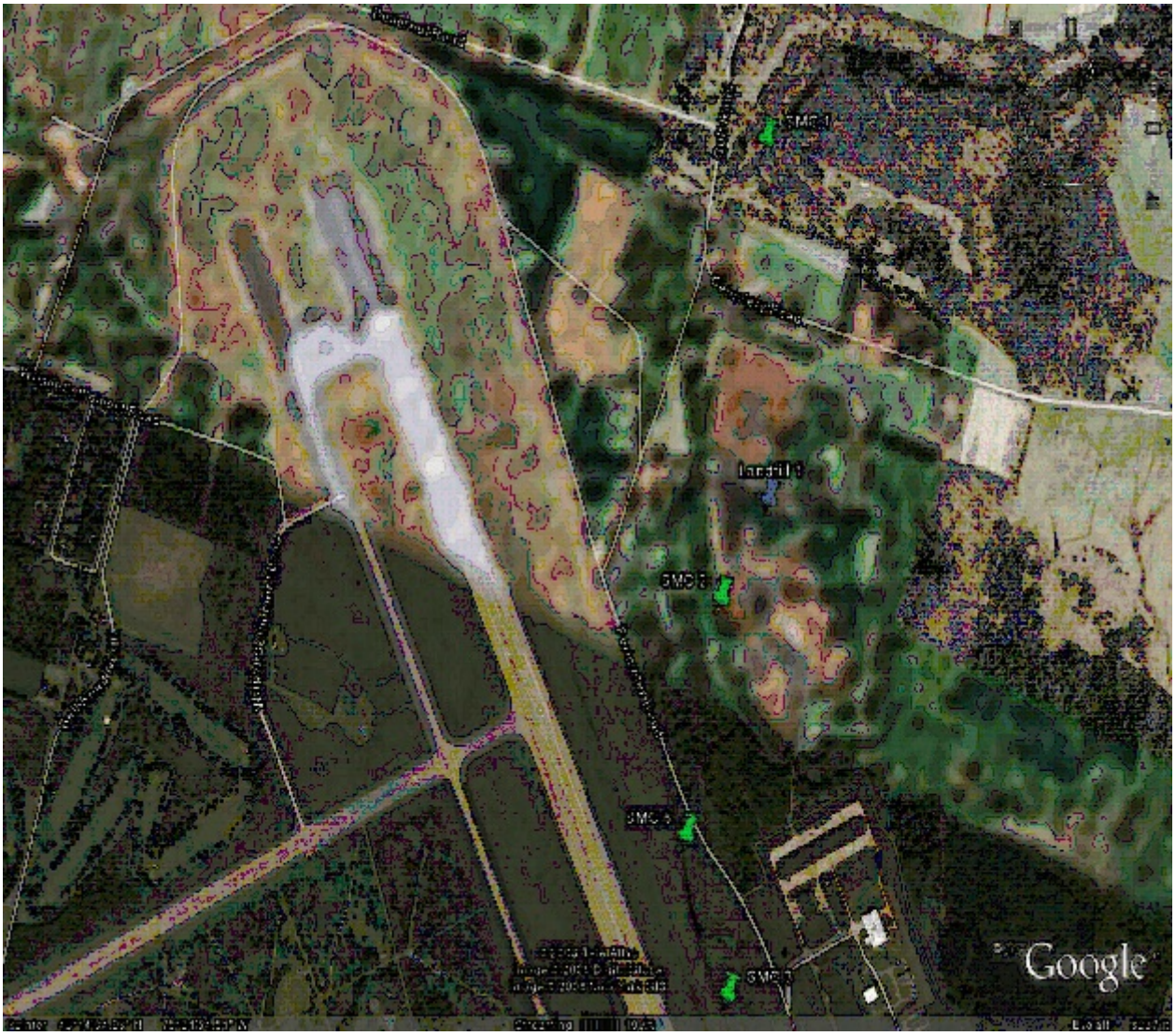

Figure 4. PISCES sampling locations for Sixmile Creek stations 1, 2, 3 and 6, Rome, Oneida Co., NY, 2008. (Figure intentionally blurred for military reasons)

Figure 5. PISCES sampling locations for Sixmile Creek stations 4, 5, 13, and Rainbow and Slate Creeks, Rome, Oneida Co., NY, 2008.

Appendix

List of Appendices

A. Preddice, T, 2007 rev. Contaminant track-down with PISCES - Standard Operating Procedures -. Hale Creek Field Station, Bureau of Habitat, Division of Fish, Wildlife and Marine Resources, New York State Department of Environmental Conservation, Gloversville, NY.

B. Oliver, D, 2008. Toxicity of a remediated stream to the water flea, *Ceriodaphnia dubia*. Student Internship report for Department of Fisheries, SUNY Cobleskill, Cobleskill, NY.

Appendice A

Contaminant Track-down With PISCES

- Standard Operating Procedures -

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June 2007

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DISCLAIMER

Mention of trade names, commercial products or scientific vendors does not constitute endorsement or recommendation for purchase.

ACKNOWLEDGMENT

This document is the second revision of our Standard Operating Procedures for studies using passive in-situ chemical extraction samplers (PISCES) performed by staff at the Hale Creek Field Station. Much of the latest revision was taken directly from previous versions by the author and Mr. Joseph G. Spodaryk. Mr. Spodaryk retired in 2003 but deserves acknowledgment for his previous contributions.

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Introduction

This document updates standard operating procedures (SOPs) for contaminant track-down studies using passive in-situ *concentration* (or chemical) extraction samplers (PISCES) conducted by staff of the New York State Department of Environmental Conservation's (NYSDEC) Hale Creek Field Station (HCFS). The previous revision was eight years ago (Spodaryk, et al.,1999). The most important change since then was to retire the Litten sampler in favor of the commercially available Hassett sampler (Figure 1) and the newer bag sampler developed at HCFS (Figure 2). The latter two samplers are preferred because they have fewer leaks, a larger permeable membrane surface and because they can be deployed in warmer waters with less fear of membrane rupture. This SOP includes methods specific to the Hassett sampler and bag sampler preparation, implementation of environmental monitoring, quality control steps and summaries for analytical procedures.

Basically, PISCES are a solvent container with a permeable membrane. Hydrophobic compounds such as polychlorinated biphenyls (PCBs) and other nonpolar compounds with an affinity for the solvent including several organochlorine pesticides (OCs), and are able to diffuse through the polyethylene membrane and accumulate in the solvent. PISCES are intended to somewhat simulate a fish's ability to bioaccumulate hydrophobic contaminants and, as a result, can concentrate very low levels of contaminants from water that could not otherwise be detected with most conventional sampling methods. The name PISCES is based on the commonly recognized Latin word pisces for fish. This type of sampler is unaffected by analytes bound to dissolved organic carbon particle (Litten, 1996) but is affected by dissolved organic matter, i.e., humic acids (Luckey, 1998). PISCES analytical data, unlike fish data, represent amounts of contaminants concentrated at a fixed location during the exposure. Also, unlike biota samples, PISCES samples have the added advantages of requiring no extraction of lipids and need much less preparation in the laboratory before analysis.

Brief History of PISCES Studies

NYSDEC began using PISCES over 20 years ago using a few different designs which staff at HCFS have labeled as Litten samplers, named after Dr. Simon Litten with NYSDEC's Division of Water (Litten et al., 1993 ; Litten, 1996). In 1993, the author of this SOP and then co-worker, Joseph G. Spodaryk (retired 2003) became interested in contaminant track-down studies as a means of locating sources of PCBs and organochlorine pesticides responsible for sportfish consumption advisories (NYSDOH, 2007) in New York State. Their first study in 1994 began on the lower Mohawk River in the vicinity of Schenectady, NY with Litten style PISCES constructed of common brass plumbing parts which they modified to make more reliable (Preddice et al., 1996). Modifications included filing and sanding brass parts to make the samplers less prone to leak, development of a sampler vent, trials with different membrane materials, trials with different cleaning procedures and the adoption of leak testing procedures.

About 1995, the first Hassett PISCES were purchased and used in several contaminant track-down studies, sometimes in conjunction with the Litten PISCES. Eventually, Litten

PISCES were phased out, favoring the Hassett's patented vent, larger membrane and better reliability. In early 1996, we began development of the bag sampler which has since been used successfully in several NYS DEC contaminant track-down studies.

Sampler Location

PISCES sites are selected with the aid of topography maps and often after an initial reconnaissance trip to determine site accessibility, water characteristics such as depth and current and, if necessary, permission to access private property. Often it has been necessary to notify and work with town and city maintenance supervisors for access to storm water manholes, especially if access is via a manhole cover located in the middle of a busy street.

PISCES samplers are placed at irregular intervals in rivers and streams with non-turbulent current of about 0.5 to 3.0 feet per second (turbulence at the membrane can erroneously increase uptake), and occasionally in lake systems with localized areas of concern. PISCES have also proven useful in city storm drains to determine sections of town or cities where problems might originate. Sampling sites are often selected to bracket landfills, hazardous waste sites, sewage treatment facilities, storm sewer discharges, industrial sites and tributaries suspected to be pathways for contaminant transport. Other factors such as distance from suspected source or from other PISCES sites, current, flow patterns, channels and accessibility are taken into account when establishing sampling sites. Samplers in streams are deployed inconspicuously and without an attention-grabbing, identifiable float to help ensure that they are not stolen, moved or tampered with during the exposure. For stream sites prone to "people" problems, a NYSDEC sign is sometimes posted nearby to caution and educate. Stream samplers susceptible of being washed away during a major storm are tethered to a nearby woody bush or tree. Samplers in deep water are always deployed with an identifiable float to make them easy to retrieve and easy to be avoided by boaters.

Hassett Sampler

Hassett PISCES shown in Figure 1 can be purchased from Dr. John Hassett by calling 315-470-6827 or writing Dr. Hassett at 5892 Mercedes Lane, Jamesville, NY 13078. The unit price has remained the same at about $70. From the beginning, we attached our own hanger to facilitate sampler deployment, and a brass bracket across the bottom to help protect the sampler membrane and keep it from contacting the substrate. Our hanger is made from a length of 5/32 inch vinyl-covered wire (purchased at local hardware store) secured to the sampler body with one #56 (3 1/16 - 4 inch) stainless steel hose clamp. The membrane guard is made from a brass strip (8 inches long x ½ inch wide x 1/16 inch thick) bent at 3/4 inch and 2 ½ inches from each end (Figure 1). Each strip is drilled (3/16 inch hole) on the tabs to match diagonal holes used to secure the bottom plate, O-ring and permeable membrane with supplied machine bolts.

The Hassett sampler has a U.S. Fish and Wildlife Service patented vented cap that allows the sampler to be deployed in warm water temperatures. Past experiences have shown that the membrane of an unvented Litten samplers is vulnerable to micro tears and ruptures at water temperatures in excess of about 23 °C. The upper temperature limit of the Hassett sampler is unknown but the sampler has worked well at 28°C.

The Hassett sampler is reusable but requires extensive cleaning and a new permeable membrane for each use. The inexpensive 4 X 4 inch membranes are cut from 4-mil low density

polyethylene sample bags (VWR Catalog No. 6255-0918). Membranes are extracted overnight in a pesticide-grade hexane soak to ensure they are free of contaminants that might interfere with chemical analysis and interpretation of results.

Hassett Sampler Cleaning

Used and new metal sampler parts are soaked overnight in a common dish detergent solution and scrubbed with a nylon brush. These parts are then rinsed with warm tap water and placed into a soak tub with a powdered laboratory cleaner solution. Here caution should be used because some laboratory cleaners are very caustic and can react with the acid-core solder used to make Hassett samplers, causing leaks. After 24 hours, metal parts are again scrubbed and rinsed in warm tap water. Sampler parts are then soaked for two days in a Micro^{R} (International Products Corp.) solution and rinsed with warm tap water. Metal sampler parts receive two 1-day soaks in de-ionized water, followed by a final rinse with de-ionized water before being air dried. Each Hassett sampler is provided with a Viton™ O-ring, used to seal the sampler body and membrane. O-rings get soaked for 24 hours in a common dish detergent solution and scrubbed with a nylon brush. After a warm tap water rinse they receive two 1-day de-ionized water soaks and a final de-ionized water rinse before being air dried.

Hassett Sampler Assembly

Although Hassett sampler parts are interchangeable, to minimize potential leaks it is recommended to identify major parts so there is better assurance that parts match. To help with this, each new sampler is identified with a successive number that is scratched onto the sampler body, cap and bottom plate. Sampler assembly is self-explanatory and requires only simple hand tools, e.g. flat-headed screw driver, wrench or T-handle nut driver and awl. For each deployment, a new, clean permeable membrane is sealed across the bottom of the sampler with a 3/16 inch thick x 3 1/8 inch O.D. Viton™ O-ring (McMaster-Carr, Catalog No. 9464K62) secured in place with the brass bottom plate, brass membrane guard and four brass machine bolts and nuts supplied with the sampler. Care must be taken to center the O-ring and to not over tighten the nuts which can cause the O-ring to distort resulting in a leak. For each deployment, a new 25 mm disk filter (VWR, Catalog No. 28155-182) made of polypropylene laminated polytetrafluoroethylene (PTFE) is installed in the vented screw cap and held in place with a 1/8 inch thick x 1 1/16 inch O.D. Viton™ O-ring, (McMaster-Carr, Catalog No. 9464K32) or similar sized piece of Viton™ gasket material cut in a ring. The duller surface of the filter disc must face upward when installed. The PTFE filter disk is not listed in the newest McMaster-Carr catalog. Mr. Hassett should be contacted to determine what he is currently using. It is recommended to have extra small and large O-rings on-hand should the originals supplied with the sampler become distorted after repeated usage.

Hassett Sampler Leak Testing

Each assembled Hassett sampler is leak tested at the laboratory prior to deployment. About 15 mL of hexane (J.T. Baker Catalog No. 9262-03, Ultra Resi-analyzed^{R}; Fisher Scientific Catalog No. H300-4 pesticide grade or H307-4 HPLC grade) is poured into the sampler from a dedicated dispenser. The sampler is capped, gently rotated to rinse the inside and immediately inspected for leaks. Gentle shaking and warming the sampler by hand will help to

locate any leaks when the solvent expands creating internal pressure. If no leaks are found, the sampler is hung on a ring stand for 1 - 2 hours after which the membrane is again inspected for small leaks, particularly around the large O-ring where the membrane is prone to wrinkle. If none are found, the sampler is inverted and the cap end is inspected for leaks. If micro leaks exist, a faint hissing sound may be heard or wetness detected. If leaks are found, tightening the cap or bottom plate screws may solve the problem. Samplers that continue to leak must be dismantled, and reassembled with a new O-ring and membrane depending on where the leak is found. If no leaks are discovered, the 15 mL of solvent is discarded. A second 15 mL of solvent rinse is added, and again the unit is resealed, gently rotated and checked for leaks. If no leaks are found, this second 15 mL of hexane is also poured off to a waste container. It is very important that the sampler is allowed to hang on the ring stand until any remaining solvent has completely evaporated. The cap is loosely replaced before the sampler is wrapped for storage or field use. This latter safety step may prevent a latent flammable situation or ruptured membrane during storage *[Leak testing should always be performed in a fume hood while wearing solvent resistant gloves, laboratory coat, and eye protection or face shield.]* Leak-tested Hassett samplers are wrapped in heavy duty, restaurant grade aluminum foil and placed into a one quart Ziploc^{R} freezer bag. Units are stored and transported into the field in clean five-gallon plastic pails with lids.

Hassett Sampler Deployment

At the deeper sites, the boat motor is first shut off to prevent possible contamination from exhaust. Water temperature is then measured and recorded. Hassett samplers are unwrapped and opened only when on site and ready for deployment. First, a small amount of hexane is used to rinse the dedicated filling beaker, which is discarded into a waste container. About 180 -185 mL of hexane is then measured in this beaker and 20 - 30 mL is poured into the sampler. The sampler is again checked for leaks and if none are found, the remaining hexane is added. The dedicated solvent beaker is covered with aluminum foil when no longer needed. The spiking solution is then carefully added from a clean glass syringe before the sampler is tightly capped. Typically this involves adding 50 uL of a 10 ng/uL spiking solution of trans-chlordane into the PISCES, which is subsequently recovered quantitatively during chemical analysis. The spiking solution is bottled in a small glass septum vial with enough solution for up to ten samplers. These vials are prepared once or twice per sampling season and are stored at 4 °C until transferred to a cooler with an ice pack for field use. The entire process is repeated for the second sampler to be deployed at the same site.

Samplers to be deployed from a boat in deep, non-wadeable water are clipped to a brass snap clip tied to a rope 1- 3 feet below a float. This same rope extends to an 8 x 8 inch concrete block anchor that rests on the bottom. At least 3 - 4 feet of extra rope is allowed for increases in water level following storms. Our float is made from a one-gallon plastic bottle partially filled with foam packaging peanuts and aerosol sprayed insulating foam, and tightly sealed. The float is previously labeled with a NYSDEC sticker, a flammable liquid decal, and the name, address and telephone number of project staff. A second sampler can be hung from the same snap clip or, if preferred, attached to a second clip tied at another depth.

Samplers (two) for shallow stream sites are secured directly to opposing sides of an anchor block with a length of polypropylene rope. The anchor block is rested on the bottom of an inconspicuous pool at least 12 inches deep with both samplers exposed equally to the flow. Again, for these sites, no float is used which could attract unwanted attention. It is important to not place samplers in very turbulent flow of some riffles, or below dams and spillways as this will artificially increase uptake of contaminants. When it is especially important that stream samplers not contact the bottom, samplers have been tied directly to a steel fence post that has been hammered into the bottom. When necessary to ensure that samplers are off the bottom in deep areas, a second float is tied to the anchor line about three feet from the bottom, and a clip for attaching one or two samplers is tied below this submerged float.

To mark sampling sites, especially for very remote areas, surveyor tape tied to a tree limb or bush near the samplers makes it easier to find the samplers should the water level be significantly higher and turbid during sampler retrieval. A 6-foot-long boat hook has also proven to be an invaluable tool to locate and retrieve samplers in roily water.

Hassett Sampler Retrieval

A typical exposure period is 14 days (± 1 - 2 day). Similar to deployment, the initial steps are to shut off the boat motor to prevent possible contamination from exhaust, and then to measure and record water temperature. Hassett samplers are located, un-clipped from the float rope and gently wiped clean with paper towel to remove vegetation, algae, detritus, silt and aquatic organisms. Samplers deployed in shallow streams are untied, un-clipped from the anchor block and wiped clean in a similar manner. Care is taken to hold samplers by the hanger to prevent damage to the fragile membrane. Before opening, the cap and top are wiped a second time with a second paper towel to remove any remaining water droplets and debris. It is important to not spill any solvent or allow any extraneous materials to get into the sample. The sample is poured directly into a labeled, 250 mL, chemical-clean, amber, glass jar and placed on ice in a cooler for transfer to the laboratory. At the laboratory, immediately after returning from sample retrieval, the level of solvent is marked on each bottle. While still on a level surface like the laboratory chemistry bench, the volumes of solvent and any water are estimated from a second jar of the same size with volumes marked on the label. This is a precautionary step should samples happen to loose solvent before processing when solvent and water are measured. Samples are stored in a walk-in refrigerator pending processing for chemical analysis.

Dirty samplers and hardware are placed into devoted 5-gallon pails with lids and returned to the laboratory for cleaning. Floats are placed into large plastic bags, and later detergent washed and air dried along with the anchor blocks to prevent transfer of aquatic organisms such as zebra mussel between locations. Used rope is discarded.

Bag Sampler

Figure 2 shows the bag sampler developed and fabricated by Joseph G. Spodaryk, retired Environmental Chemist II, and the author. A rugged, inexpensive, disposable sampler with a fairly large membrane was desired that could be made from easily obtained materials. The bag sampler that was developed has a permeable membrane nearly twice the surface area (45.6 versus

90 cm^2) of the Hassett sampler and, because it is disposable, nearly eliminates time-consuming clean up steps and minimizes chances for cross contamination inherent with Hassett samplers. The bag sample, which costs < $4 to make, has proven very dependable in several different field situations since 1996.

Bag Sampler Parts and Laboratory Assembly

The main component of the bag sampler is a 2.25 mil thick Whirl-Pak^R polyethylene sample bag (VWR Catalog No. 11216-012) which serves as the permeable membrane. In the laboratory, two solvent-rinsed butterfly paper clips are inserted into the Whirl Pak^R bag (previously hexane-extracted) to keep it from collapsing when subjected to water pressure. One is a large clip (Viking 624-ID-1) with the tips aligned and spread about 3/4 inch. This is placed into the bag, flat side down. The second is a medium clip (Viking 624-ID-2) with tips spread about 1 inch, and inserted between the tips of the larger clip. The bag's wire seal is folded over several times to reseal the bag. Several bags are prepared in this manner and transported to the field in a Ziploc^R re-sealable plastic bag.

The body of the sampler, which is also prepared at the laboratory, is made from the upper one-half of a disposable 50 cc polypropylene centrifuge tube having a polyethylene screw cap with a large rim seal (Corning 25322-50). This centrifuge tube is no longer available but Fisher Scientific offers (Catalog No. 05-538-60), a Corning brand polypropylene centrifuge tube with a new Centri Star® cap that may be a good substitute or perhaps VWR's centrifuge tube with a screw cap (Catalog No. 82018-052) will work just as well. The tube is cut at the 25 mL mark and two 3/16 inch holes are drilled opposite each other between the 35 and 40 mL marks. A skirt of polyethylene mesh webbing (McMaster-Carr 9314T33) cut into ~ 8 x 5 inch rectangles is wrapped around the tube body and attached at the two holes with 5 inch electrical ties and a 0.5 x 13/16 x 1.5 inch stainless steel hose clamp (McMaster-Carr Catalog No.3913561). Corners of the webbing are trimmed when the sampler is assembled. The black webbing, last purchased in 1998 (opening 0.25 inch, 0.075 thick x 36 inch wide), is no longer listed in the McMaster-Carr Catalog. Perhaps the polyethylene sheeting (McMaster-Carr 2110T2) nominal opening 0.25 inch, 0.086 inch thick x 48 inch wide or the 2.5 - 3 inch diameter elastic polyethylene mesh sleeve, 0.072 inch thick (McMaster-Carr Catalog No.5969K26) can be substituted. The centrifuge tube provides rigidity and a means to seal the sampler, and the webbing protects the fragile bag membrane. Two 4 inch electrical ties placed side by side under the hose clamp are used to form a loop to secure a 3 inch bronze, swivel-eye bolt snap clip (McMaster-Carr Catalog No.3913T61). This clip is used for securing the sampler with rope to the anchor block or float rope. A 2 or 3 ounce lead egg sinker is attached to the bottom edge of the plastic webbing with a 5.5 - 5.75 inch electrical tie to make the sampler hang vertically. A flammable sticker is attached to the top of the cap as a warning.

Bag Sampler Field Assembly, Deployment and Retrieval

Immediately before sampler deployment, a Whirl-Pak® bag with butterfly clips inside is selected from the transport bag and the bag's wire sealing strip is cut off. The upper portion of the bag is inserted into the bottom of a plastic centrifuge tube body and is formed over

the upper threaded end of the tube body. Using the same technique used to fill Hassett samplers, a dedicated beaker is rinsed and filled with 70 mL of solvent that is poured into the bag sampler. For bag samplers, isooctane (2,2,4- trimethylpentane (TMP), Ultra Resi-analyzed®, J. T. Baker Catalog No. 9335-03, VWR Catalog No. 0297-4 pesticide grade) is used instead of hexane because it has a lower boiling point and is not quite so volatile. Hexane was tried but bag samplers, especially those exposed to faster flows, have a tendency to lose hexane probably from around the cap seal. PISCES with TMP are reported to take up only chemical compounds with log K_{ow} values > 3.5 (Leonard et al., 2002). Chemical compounds with a logarithm of the octanol-water partition coefficient exceeding 3.5 includes the PCBs and OC pesticides most likely to bioaccumulate and cause problems.

Bag samplers are spiked similarly to Hassett samplers, after which the opening is first covered with a ~ 2 inch-diameter disk cut from 3 mil, military grade sealant Teflon™ PTFE tape (McMaster-Carr Catalog No. 6802K77) followed with an ~ 2 inch-diameter disc cut from a sheet of 2 mil FEP Teflon™ (McMaster-Carr Catalog 84955K14 or 85905K64) before the centrifuge cap is screwed on tightly. This arrangement provides a good seal and allows the cap to be securely tightened without tearing the PTFE liner. Discs of sealant materials are precut at the laboratory and kept separated with paper disks in plastic containers. Sealing materials are handled only with clean forceps. Different sealing arrangements were tried but the one described has worked effectively for three sampling seasons under a variety of flow and temperatures conditions. Each bag sampler is inspected carefully for leaks before deployment.

Bag samplers are also retrieved after 14 days. Samples are poured into clean 150 mL amber glass bottles and treated in a fashion similar to Hassett samples. Later at the laboratory, the stainless steel hose clamp and lead sinker are removed for cleaning and reuse, and the rest of the bag sampler is discarded.

SAMPLE PREPARATION

Samples are cleaned, evaporated and diluted to a known volume before analysis by gas chromatography (GC). The cleanup step is performed primarily to remove any water that may have gotten into the sample as well as any interfering co-extractables from the membrane. If any water is observed in the sample bottle, the sample is quantitatively transferred to a 500 mL glass separatory funnel. After layers separate, water is withdrawn, measured and discarded. The solvent layer is then quantitatively transferred to a glass chromatography column (22 mm ID x 350 mm - Kontes PN 420280-0242) previously filled with 10 g of activated Florisil™ that is topped with 10 g of Na_2SO_4. The sample is eluted into a 250 mL Erlenmeyer flask at a rate of 2 - 5 mL/min. After most of the sample is transferred, 50 mL of 2 % ethyl ether in petroleum ether (v/v) is added to the column and collected in the same flask. Ten drops of a keeper solution (1 mL paraffin oil in 100 mL acetone) are added to the flask. The flask is fitted with a 3-ball Snyder condenser and evaporated to less than 100 mL on a steam bath. The sample is then evaporated to dryness on a rotary evaporator (40 °C). The residue is diluted to 1 mL in iso-octane and transferred to a small septum vial for GC analysis.

GC ANALYSIS

Sample preparation and GC analyses are usually performed by the Analytical Services Unit at the Hale Creek Field Station using a Hewlett-Packard 5890 II electron capture GC equipped with a DB-1 (60 m x 0.25 mm x 0.25 μm) capillary column. Parameters reported include Aroclor (AR) 1242 and AR1254/60 and 20 organochlorine pesticides which include DDT forms, chlordane forms, mirex, photomirex and hexachloro benzene (HCB). Generally, detection limits are 0.020 μg for Aroclors 1242 and 1254/60 and 0.002 μg for the other parameters with the exception of 0.005 μg for photomirex.

QUALITY ASSURANCE/ QUALITY CONTROL

Necessary steps taken to assure good quality samples are interspersed in this SOP. Chain-of-Custody for samples is not a major concern because the samples usually remain in the custody of HCFS staff. However, a Chain-of-Custody form is used for the rare study when PISCES samples are sent to a contract laboratory for analysis. Generally, these situations are related to remedial investigations for a specific hazardous waste site where other analytical funding is available. In the ASU laboratory, accepted practices are followed that are routinely used for the NYSDEC's Toxic Substances Monitoring Program. Analytical quality control includes using laboratory and field blanks, sample spikes and internal standards added directly to the cleanup column and GC.

Data control limits are based on recommendations in "Guidance for Assessing Chemical Contaminant Data for Fish Advisories (USEPA, 1995). Analyte control limits for recovery accuracy are established at 50 to 150 %. The control limit for precision is a relative standard deviation (RSD) of ≤50 % for sample duplicates. The method detection is the level used to assess potential contamination. Matrix spikes and internal spikes are used to determine accuracy and precision for results. The 50 uL spike of a 10 ng/ uL trans-chlordane solution added to each sampler prior to deployment enables the determination of percent recoveries, a measure of sample escapement during deployment or loss during analytical procedures. Additionally, the remaining approximately 100 mL from each of the solvent bottle(s) used to fill PISCES is analyzed to detect potential contamination during field and analytical procedures.

PISCES samples that loose ~ 30 % of the solvent (Hassett - ≥50 mL; bag - ≥20 mL) or loose greater than 50 % of the spiking material (≥5 ng) are generally not submitted for chemical analysis. Also discarded are samples from PISCES heavily covered with vegetation or shallow stream/river samples partially buried and in contact with contaminated sediment. During previous sampling, when one of two samplers simultaneously exposed at a site was affected by a dense cover of vegetation or was in contact with contaminated sediment, the data for the two samples were very different. Vegetation limited contaminant uptake and the corresponding data were low, whereas contaminated sediment caused just the opposite with data sometimes an order of magnitude higher.

DATA HANDLING

PISCES analytical data for each analyte are usually reported as nanograms (ng). Data in this form is sufficient to make comparisons among sites for contaminant track-down purposes

when samplers have been exposed for the same number of days. However, when exposures differ a day or more, uptake rates as ng/cm^2/day are calculated to facilitate comparisons. To help explain occasional data anomalies, PISCES data have sometimes been corrected to adjust for loss of solvent or spiking material.

SAMPLER VARIABILITY

PISCES were never intended to be precise quantitative instruments. As a result, difference of about 25 % among replicate samplers exposed for the same time and at the same location are very acceptable for contaminant track-down purposes. PCB Aroclor data variability among replicate pairs of Hassett samplers from several PISCES studies conducted by the author found mean relative percent difference (RPD) to be about 23 %. A mean RPD of 25 % was observed from 27 pairs of PISCES deployed from the same buoy at the same time (Litten, 1997). Others conducting similar studies report mean RPDs of about 27 %. The author has not experimented to determine why this difference occurs but (Luckey, 2000) reports that flow and orientation are considered unimportant provided the membrane remains in full contact with the solvent and the sampler remains completely submerged.

ESTIMATION OF ANALYTE CONCENTRATION IN WATER

PISCES studies have reported estimates of analyte concentrations in the water or wastewater sampled based on the amounts detected in samples (Litten, 1996; Luckey, et al., 2000). The process used by Luckey (2000) and Litten (1996) is a three step calculation developed from laboratory experiments with PCB Aroclor 1242. The estimated sampling volume(L) of each PISCES is calculated based on water temperature (T) as absolute temperature in degrees K, duration of exposure as days (d) and membrane surface area (cm^2). Membrane surface area for our latest order of Hassett samplers is 45.6 cm^2 and that for our bag samplers is 90 cm^2. Luckey (2000) measured a surface area of 46.96 cm^2 for his Hassett samplers. First, the sampling rate (S) as L/cm^2/day is calculated based on the formula $S = \exp[(-6591/T) + 19.269]$**.** The sampling volume is then calculated following the formula L = S x membrane area x days exposure. Finally, divide the estimate for the amount of water sampled (liters) by the amount of analyte measured in the PISCES to obtain a concentration as ng/L. Litten(1997) indicates this process can be used for PCBs and some of the pesticides like DDTs, dieldrin, chlordane and BHCs but has been calibrated only for PCB. NYSDEC has since calibrated for some PAHs and for the insecticide DDT.

SAFETY

A personal floatation device is always worn when working from a boat. Chemical-resistant gloves and safety glasses or face shield are worn when handling solvents and spiking materials during sampler deployment and retrieval. HCFS has an approved and up-to-date Health and Safety Plan which addresses chemical exposure and periodic medical monitoring, and a Hearing Conservation Plan.

To reduce potential chemical hazards during transport to study sites, no more than two hexane and two TMP 4 L glass solvent bottles are transported at one time. These are carried in separate commercial acid/ petroleum ether shipping containers made of heavy cardboard with molded foam inserts to receive the bottles. Only one 4 L waste solvent bottle is transported at one time and between trips this is emptied to a solvent waste container at HCFS. PISCES samples are carried in coolers with cardboard separators between sample jars to prevent breakage. For each deployment trip, 2 - 4 spiking material vials are put into a vial rack secured in a designated six pack cooler with foam inserts to keep vials from moving. To further reduce the potential for chemical hazards, most shallow PISCES sites are reached by vehicle making it unnecessary to physically carry solvent bottles afield for sampler deployment. Likewise, at retrieval most PISCES are emptied into sample jars at the vehicle which is generally close by.

OTHER

Check lists are used detailing deployment and retrieval supplies/equipment before leaving HCFS. In addition, a sampler deployment/retrieval log is maintained summarizing sampler location, date, membrane condition, sample condition, sample number and an estimate of solvent volume noting the presence of any water in the sample.

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Table 1. Parts list for PISCES bag sampler used by Hale Creek Field Station staff, New York State Department of Environmental Conservation.

Part	Source	Catalog No.	Size	Quantity
Whirl Pak™ bag	VWR	11216-012	2.25 mil	1
X paper clips	Viking	624 ID - 1 & 624 ID - 2	large and medium	1 each
Centrifuge tube	Corning	25322-50	50 mL	1
plastic electrical ties	electrical supply		5 - 6 inch (2 widths)	5 or 6
PTFE tapeTeflon™ film	McMaster-Carr	6802K77	~2 inch dia. cut	1
FEP Teflon™ tape	McMaster-Carr	84955K14 or 85905K64	~2 inch dia. cut	1
bronze swivel-eye bolt snap clip	McMaster-Carr	3913T61	3 inch	1
2,2,4-trimethylpentane Ultra Resi-analyzed® (isooctane)	J.T. Baker or VWR	9335-03 0297-4 (pesticide grade)		
lead egg sinker	fishing supply store		2 or 3 ounce	1
stainless steel hose clamp	McMaster-Carr	3913561	0.5 x 13/16 x 1.5 inch	1
polyethylene mesh webbing	McMaster-Carr?	9314T33	~5 x 8 inch trimmed 0.25 inch openings, ~0.70 inch thick	1
concrete anchor block	masonry supply		8 x 8 inch	1
float (plastic bottle)			gallon	1
braided polypropylene rope	Nylon Net	91361	1/4 inch green	
Ziploc® plastic bag	grocery store		quart	1

Figure 1. PISCES Hassett sampler (approx. actual size) with added green hanger and protective membrane strap, Hale Creek Field Station, New York State Department Environmental Conservation.
Photo credit - J. Spodaryk

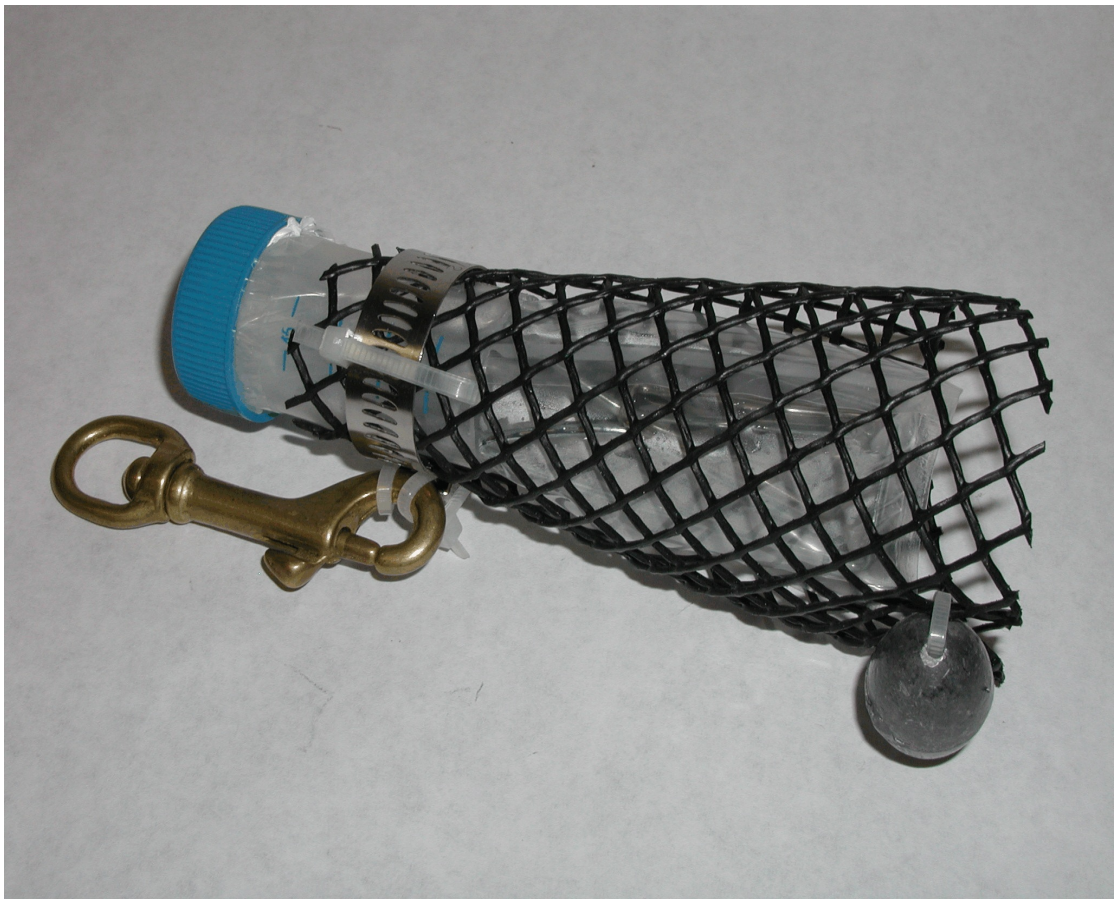

Figure 2. PISCES bag sampler (approx. actual size) developed at the Hale Creek Field Station, New York State Department Environmental Conservation. Photo credit - J. Spodaryk

Appendice B

Toxicity of a Remediated Stream to The Water Flea, (*Ceriodaphnia dubia*)

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Abstract: This report describes the results of a 7-day chronic toxicity study with the water flea, *Ceriodaphnia dubia*. Ambient water samples were collected from the remediated Creek X on June 24, 2008 and on July 15, 2008. An ambient water sample was also collected from the receiving stream on June 24, 2008. The results from Test 1 showed toxicity in Creek X, but not in the main stream downstream from confluence. Test 2, with ambient water samples were collected during greater stream flows, showed no toxicity in Creek X or its tributary.

Introduction

This report describes the results of a 7-day chronic toxicity study with the water flea, *Ceriodaphnia dubia*. Toxicity tests were performed with water samples collected from Creek X, tributary to Creek X and receiving stream. Samples were collected after a polychlorinated biphenyl (PCB) track-down study with passive in-situ chemical extraction samplers (PISCES) (Preddice and Oliver, 2008). This toxicity test was done to complement PISCES results.

In 1942 the area around Creek X was transformed into an area of shipment, maintenance and storage of government supplies. Later an electronics center was added and in the 1980's it began to be used as an industrial park (AFCA 2001). During this period several hazardous and toxic materials were used which resulted in environmental contamination. A site to the southeast of Creek X had 157, 55-gallon drums of hazardous material that were removed properly by contributing agencies (AFCA 2001). Similar hazardous material was previously discharged to a waste drain in a nearby railroad building. The material contained PCB (109 ppm), lead (700 ppm) and oil/grease (446,000 ppm) (AFCA 2001). In the early 1990's a remedial investigation was performed. During this investigation four volatile organic compounds (VOC'S), 7 semivolatile organic compounds (SVOC's), 8 pesticides, 21 metals and petroleum hydrocarbons were found in monitoring wells (AFCA 2001). Some of the contaminants identified in groundwater exceeded regulatory levels. The metals particularly hazardous to aquatic life included thallium, chromium and aluminum (AFCA 2001). The SVOC's included benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene and indeno (1,2,3-cd) pyrene (AFCA 2001).

Identification of leachates from discarded electrical devices has typically been accomplished through chemical testing (Vann et. al. 2006). Bioassays have become an alternative for track-down of potential aquatic toxicity (Townsend et. al. 2007). Daphnia sp. are a

common organism used in toxicity tests because they are susceptible to a large variety of pollutants and have a short propagation cycle (Lin et. al. 2005).

Materials and Methods

Water samples for Test #1 were collected on June 24, 2008 downstream from a small tributary and from the receiving stream downstream from the confluence with Creek X (Figure1). Samples were taken in one-half gallon, acid washed polyethylene bottles. On July 15, 2008 water samples for Test #2 were collected from the tributary and Creek X (Figure1). PISCES sampling was performed at this same location (Figure 1). Four samples were collected for Test #2, two from Creek X and two from the tributary (Figure 1). One sample from each location was aerated for about 24 hours to remove VOC'S. Procedures used for the 7-day chronic toxicity test using the water flea (*Ceriodaphnia dubia*) followed those used by the Division of Water (NYSDEC 2007). The test was set up on a tray with each water sample in a row containing ten 30 mL cups. Each cup (exposure) contained 15 mL of sample water with one, less than one day old test organism. Each column contained young from the same parent. Number of young and mortality were recorded daily. Water changes were performed on days three and five. Statistical data analysis was performed using one-way Analysis of Variance (ANOVA), Dunnett's test and Fishers exact test. The one-way ANOVA identified the significant difference among exposure groups. Dunnett's Test was used to identify significant difference in reproductive rates from the control. Fisher's exact test was used to identify the significant difference in survival amongst the different groups and control.

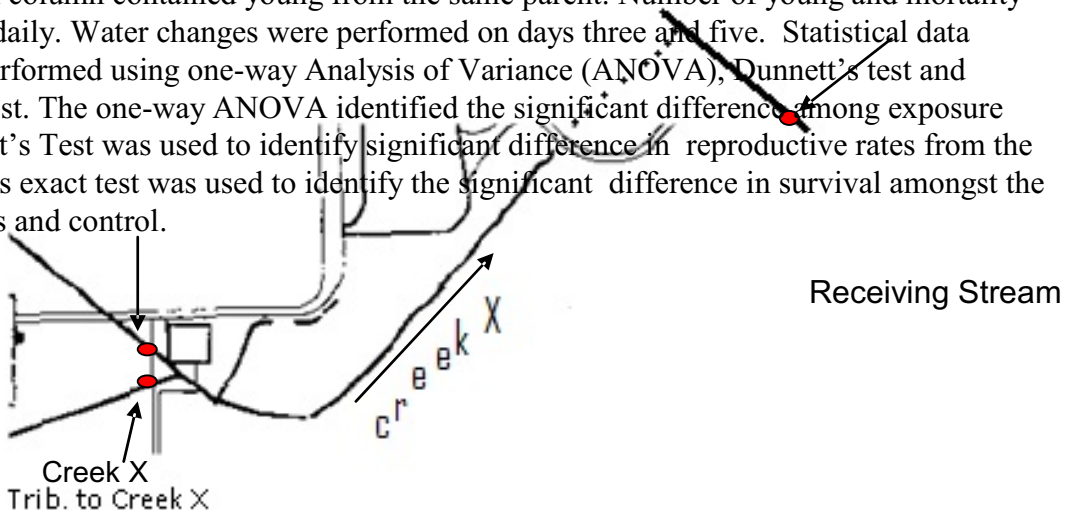

Figure 1- Creek X (PISCES sampling stations marked in red)

Results

Test #1

Mean reproduction in Creek X was slightly less than one-half that of the control (Table 1). Only nine replicates were available because one parent organism was lost from the control during the first transfer (Table 1). All parents in that column were eliminated from statistical analyses.

Table 1- Mean reproduction in the Creek X, Receiving Stream and the control – Test #1

Exposure	Test reproduction ● 2 3 4 5 6	● 8 9 mean
Control Creek X	● 27 13 15 20 9	● 16 18 16.1
Receiving Stream	● 15 1 0 15 10	● 6 13 7.9
	● 18 16 18 15 11	● 0 14 11.4

Analysis of Variance performed with a null hypothesis that all reproductive rates were equal had a critical F value of 4.49 (Table 2). The null hypothesis was rejected.

Table 2- Analysis of variance amongst Creek X, Receiving Stream and Control - Test #1

ANOVA TABLE

Source	DF	SS	MS	F
Between	1	320.889	320.889	9.053
Within (Error)	16	567.111	35.444	
Total	17	888.000		

Critical F value = 4.49 (0.05,1,16)

The Dunnett's Test showed a significant difference only between Creek X and the Control (Table 3).

Table 3- Dunnett's Test comparing reproductive rates in Creek X, Receiving Stream and Control – Test #1

Dunnett's Test

Source	Number of Exposed	Minimum Sig. Difference	% of control	Difference from control	Control
	9	-	-		Receiving
stream	9	6.445	40.6	4.000	Creek X 9
	6.445	40.6	8.444		

P = .05 (16,1)

There was a significant difference between Creek X samples and the control because the total number of live adults was equal to the critical Fisher's value of 5 (Table 4).

Table 4- Fisher's Exact Test comparing survival amongst Creek X, Receiving Stream and Control – Test #1

Fisher's Exact Test			
Source	Number of Exposed	Number Alive	Number Dead
Control	9	9	0
Creek X	9	5	4
Receiving Stream	9	6	3

Critical Fisher's Value = 5; P = .05 (16,1)

Test #2

[This test involved aerated and non-aerated ambient water samples from Creek X and its tributary.]

Mean reproductive rates are presented in Table 5. The F value for the test was 0.746 (Table 6). The test failed to reject the null hypothesis that all groups were equal (Table 6).

Table 5- Mean reproduction in the Creek X samples and the Control – Test #2

Exposure	Test reproduction 1 2 3 4	5 6 7	9 10 Mean
Creek X Aerated			19 15 17.7
Creek X Tributary			21 20 18.6
Aerated Tributary			15 19 16.7
Control	18 14 17 20 13 21		3 17 14.9
	19 20 27 22 17 16		1 17 17.1
	20 15 22 20 14 13		
	12 15 18 19 22 12		
	18 14 23 27 20 18		

Table 6- Analysis of Variance amongst Creek X, Tributary and the Control – Test #2

ANOVA TABLE					
Source	DF	SS	MS	F	
Between	4	75.600	18.900	0.746	
Within (Error)	45	1140.400	25.342		
Total	49	1216.00			

Critical F value = 2.61 (0.05,4,40)

There was no significant difference between the Test #2 samples and the control (Table7).

Table 7- Dunnett's Test comparing reproduction for Creek X and Tributary to Control – Test #2

Source	Number of Exposed	Dunnett's Test	% of control	Difference from control
Control	10 10 10 10 10	Minimum Sig. Difference	•	•
Aerated Creek X		•	3.4 33.4	0.600
Non-aerated Creek X		.718	33.4 33.4	-1.500
Aerated Tributary		5.718		0.400
Non-aerated Tributary		5.718		2.200
		5.718		
		5.718		

P = .05 (23,4)

There was no significant difference between Creek X samples and the control because the total number of live adults was greater than or equal to the critical Fisher's value of 4 (Table 8).

Table 8- Fisher's Exact Test comparing reproduction for Creek X and Tributary to Control – Test #2

Fisher's Exact Test

Source	Number of Exposed	Number Alive	Number Dead
Control	10	9	1
Aerated Creek X	10	10	0
Non-aerated Creek X	10	10	0
Aerated Tributary	10	10	0
Non-aerated Tributary	10	9	1

Critical Fisher's Value = 4; P = .05

Discussion

The results from Test #1 showed toxicity, but the cause was unknown. Although remediated, Creek X and the hazardous waste located to the southeast of Creek X may still have contaminants that contribute to the toxicity.

Test #2 showed no toxicity in Creek X or its tributary. This may be related to the great amount of precipitation the area received a few days previous to sample collection (Preddice and Oliver 2008). This measured precipitation may account for the difference in results between Test #1 and Test #2. The toxicant may have been more concentrated in Test #1 which affected mortality and reproduction. Increased flow likely diluted the toxic affects in Test #2.

Test #1 results indicate the need for additional toxicity testing and chemical analytical testing. Water samples for further testing should be taken during a low flow period. Toxicity identification evaluation efforts which combine toxicity testing methods and chemical analysis are recommended. It is also recommended that samples be collected further upstream in the storm drain system through which Creek X flows.

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