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Warfare Center**



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TECHNICAL REPORT 3236
AUGUST 2021

Toxicity Associated with PAHs in Navy Skeet Range Clay Targets

Kara Sorensen Ph.D
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UCSD

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EXECUTIVE SUMMARY

OBJECTIVE

DoD liability for PAH-impacted soils at skeet ranges is in excess of \$100M over more than 40 sites. Current PAH cleanup goals often assume that 100% of PAHs in soil are bioavailable for uptake, resulting in > \$1M per site and overly-protective cleanup approaches. Recent research indicates lower bioavailability of skeet-derived PAHs (Relative Bioavailability (RBA) of 10-80%), that, when applied on a site-specific basis, would reduce costs cleanups by \$100K-\$1M per site (Lowney et al., 2017; Ruby et al., 2016; Xia et al., 2016; Magee et al., 2014). In vivo studies in which rodents are fed contaminated soils, are used to quantify site-specific RBA. However, these studies are not cost and time effective for all sites (\$>200–300K/site; personal communications Schoolfield, 2017, Meyer, 2019). To that end, the overarching objective of this study was to develop, optimize and demonstrate simple and rapid in vitro approaches using benchtop animal-free methods that can be used to provide site-specific RBA estimates. Results of this study shows potential for these methods as low cost, robust, and rapid methods to evaluate RBA of PAHs in skeet-impacted soil across sites with different soil types.

To reach the overarching objective of this work, the four main sub-objectives (tasks) were as follows: (1) to provide an improved ability to discern clay target particles from soil particles; (2) to better inform PAH fate and transport processes of skeet impacted soils; (3) to demonstrate and calculate more realistic, site specific RBAs for PAHs instead of default RBAs; and (4) to provide defensible technical information that RPMs can use to negotiate lower risk-based clean-up levels.

RESULTS

This project began in October 2012 in response to Need N-0742-11 submitted by John Schoolfield (NAVFAC SE). Dr. Sorensen (SSC PAC) took over as PI in January of 2014 when Bill Major (NAVFAC EXWC) retired end of December 2013. Over the course of this effort, two In vitro assays were calibrated for PAH analysis and tested for their ability to better inform PAH fate and transport processes as well as develop a means of calculating site specific RBAs to aid RPMs in negotiating risk based soil PAH clean up levels. Study results indicate an improved ability to discern clay target particles from soil. Analysis method development included examination of 7 different vintage skeet types frequently used in military shooting ranges as well as 8 soil samples (both PAH contaminated and uncontaminated) from multiple skeet ranges. In vitro assays (PBET and passive sampling) were calibrated against in vivo feeding trial samples, which resulted in development of a well aligned correlation model. Together, these lines of evidence can be used to determine bioavailable concentration of PAHs in soil and a site-specific RBA that correlates well with RBAs determined from in vivo animal testing. Initial analyses of environmental samples indicate bulk soil analysis may overestimate risk by a factor of 11 (average passive sampling) to 75 (average PBET). While results are promising, testing of additional clay target impacted soils would improve confidence in this surrogate availability approach, clearing way for regulatory approval and adoption during risk-based remediation at dozens of DoD skeet ranges sites.

PRIMARY FINDING AND FOLLOW ON RECOMMENDATIONS

In vitro approaches evaluated in this project (PBET and passive sampling) are good chemical measures of digestive availability for B(a)P, which correlated well with *in vivo* measurements of RBA. Measurements were based on comparisons across a total of 5 soil concentrations, from one soil source (*in vivo*, *in vitro* comparison-IVIVC).

Next steps

Add data to the correlations via testing additional clay target-impacted soils from additional sites via *in vivo*, PBET, and passive sampling. This approach should include multiple soils that represent a range of PAH concentrations and soil characteristics.

Apply the PBET and passive sampling approach to additional soils contaminated with other PAH sources (i.e., petroleum, creosote, etc.) that have already been tested *in vivo*.

Results of this work show that PBET and passive sampling data can be used to predict PAH bioavailability and risk, however, current results focus only on digestive pathway and relative risk and RBA is based solely on Benzo pyrene (B(a)P)

Additional steps

Include additive risks from dermal absorption pathways

Include the other 6 carcinogenic PAHs using the PBET and passive sampling approaches

ACRONYMS

alpha iron	α Fe
average	AVG
background soil	BG
Base Realignment and Closure	BRAC
benzo[a]pyrene	BaP
black carbon	BC
Bronson field	BF
calcite	CaCO ₃
Cancer slope factor	CSF
Carbon Hydrogen Nitrogen	CHN
carcinogenic PAHS	cPAHS
centimeter	CM
Chemical Analyses	CA
commercial reference soil	CRM
concentrations in soil	Cfree
Cubic yards	CYD
degrees Celsius	°c
deionized	DI
deoxyribonucleic acid	DNA
Department of Defense	DOD
dichloromethane	DCM
Differential Thermal Analysis	DTA
dolomite	MgCO ₃
dry weight	dw
Environmental Protection Agency	EPA
feeding trial soil	FT
feet	ft
Formerly Used Defense Site	FUDS
Foster Air Force Base	FAFB
Fourier Transform Infrared Spectroscopy	FTIR
gas chromatography with mass spectrometry	GC/MS
gastric solution	GS
gram	g
Hydrochloride	HCL
Identification	ID
In vitro in vivo correlation	IVIVC
inorganic carbon	IC
Integrated Risk Information System	IRIS
Interim Program Review	IPR
Laredo Air Force Base	LAFB
Liters	L
Marine Corps Air Station	MCAS
Mega ohm per centimeter	m Ω -cm

microliters	μl
micrometer	μm
milligrams per kilograms	mg/kg
millimeter	mm
multi-incremental sampling	MIS
Munitions Response Area	MRA
Munitions Response Program	MRP
Nano gram/liter	ng/L
National Oceanic and Atmospheric Administration	NOAA
National Priorities list	NPL
natural organic matter	NOM
Naval Air Station	NAS
Naval Base Guam	NBG
Naval Facilities Engineering and Expeditionary Warfare Center	NAVFACEXWC
Naval Facilities Engineering Command Southeast	NAVFAC SE
Naval Facilities Engineering Command Southwest	NAVFAC SW
Naval Information Warfare Center - Pacific	NIWC
Naval Installation Restoration Information Solution	NIRIS
Naval Environmental Sustainability Development Integration	NESDI
NOAA Status and Trends	NS&T
Not applicable	N/A
Organic carbon	OC
particle-size distributions	PSD
parts per billion	ppb
percent weight	% wt
Performance Reference Compounds	PRCs
Physiologically-Based Extraction Test	PBET
polychlorinated biphenyl	PCB
Polycyclic Aromatic Hydrocarbons	PAH
polyethylene	PE
program manager	PM
quality assurance/quality control	QA/QC
range program managers	RPMs
Relative Bioavailability	RBA
regional screening levels for soil	RSLS
Relative Potency Factor	Rpf
Resource Conservation and Recovery Act	RCRA
rotations per minute	rpm
Scanning Electron Microscopy	SEM
selected ion monitoring	SIM
Shotgun range	SGR
site reference soil	SRS
skeet impacted soil	SA

sodium hydroxide	NaOH
soil partitioning	Koc values
Space and Naval Warfare Systems Center	SPAWAR
Space and Naval Warfare Systems Center Pacific	SSC PAC
standard deviation	SD
standard operation procedure	SOP
Strategic Environmental Research and Development Program	SERDP
Texas	TX
Thermal Gravimetric Analysis	TGA
total organic carbon	TOC
United States	US
United States of America	USA
United States Patent Trade Office	USPTO
University of Illinois	U of I
US Army Corps of Engineers	USACE
Whiting field	WF
World War two	WWII
X-ray Powder Diffraction	XRD

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CONTENTS

EXECUTIVE SUMMARY	v
ACRONYMS.....	vii
INTRODUCTION	1
1.1 PAHS.....	1
1.1.1 Benzo[a]pyrene (BaP)	3
1.1.2 Chemical and Physical Characteristics	5
1.2 BIOAVAILABILITY OF PAHS IN SOIL	7
1.3 SKEET RANGES	11
1.4 IMPACTS OF PAHS IN SOILS ON SKEET RANGES.....	16
1.4.1 Overarching Problem Statement	17
1.5 SCOPE OF WORK.....	17
1.5.1 Technical Objectives	17
1.5.2 Technical Approach.....	18
2. BACKGROUND.....	23
2.1 SCOPE OF SKEET MATERIALS AND IMPACT ON DOD/USN FACILITIES.....	23
2.1.1 Skeet Impacted DoD Sites	23
2.2 PAHS IN SKEET	24
2.2.1 Bioavailability of PAHs in skeet	24
2.3 PAH-SKEET SITES.....	24
2.3.1 Incorporating Relative Bioavailability at PAH-Skeet Sites.....	24
2.4 PAH RBA APPROACH	25
2.5 RBA EVALUATION METHODOLOGY.....	25
2.5.1 PBET Approach and Relationship to RBA.....	25
2.5.2 Passive Sampler Approach and Relationship to RBA.....	26
3. EXPERIMENTAL METHODS.....	27
3.1 OVERVIEW	27
3.2 STUDY SITES-SOIL COLLECTION (TASK 1)	27
3.2.1 General Soil Sampling Method and Processing for Analysis	27
3.2.2 Army Feeding Trial Soils	28
3.2.3 Additional Demonstration Sites	30
3.2.4 Soil Characterization (Task1)	34
3.2.5 PAH Contaminated Site Database (Task 1).....	36
3.3 <i>IN VITRO</i> ASSAY DEVELOPMENT (TASK 2).....	37
3.3.1 PBET Methodology and Details.....	37
Passive Sampler Methodology and Details.....	42
3.4 PAH CHEMICAL ANALYSIS.....	43

3.4.1	Passive Samplers	43
3.4.2	PBET	43
4.	RESULTS AND DISCUSSION	45
4.1	CHARACTERIZATION OF SKEET IMPACTED SOILS (TASK 1).....	45
4.1.1	Sample Collection and Chemical and Mineralogical Analysis.....	45
4.1.2	Skeet Fingerprint evaluation.....	57
4.1.3	Skeet weathering analysis.....	60
4.1.4	PAH contaminated skeet range database	62
4.2	<i>IN VITRO</i> ASSAY DEVELOPMENT AND OPTIMIZATION (TASK 2)	64
4.2.1	Optimization of PBET Method Using Standard PAH Mixture Solution.....	64
4.3	DEVELOPMENT OF <i>IN VITRO</i> RBA MODEL AND DEMONSTRATION OF MODEL (TASK 3 AND 4)	72
4.3.1	Ability of PBET and Passive Sampling to Predict Mammalian Digestive Bioavailability of BaP in Soils Impacted by Clay Targets	74
4.4	DEMONSTRATION OF THE USE OF PBET AND PASSIVE SAMPLING TO EVALUATE THE RISK OF BAP IN SOILS IMPACTED BY CLAY TARGETS	75
4.4.1	Site Specific Results.....	78
5.	SUMMARY AND CONCLUSIONS	81
5.1	CONCLUSIONS	81
	REFERENCES	83

APPENDICES

A:	PBET AND PASSIVE SAMPLER DATA	A-1
B:	UNIVERSITY OF ILLINOIS REPORTS.....	B-1
C:	TABLES.....	C-1

FIGURES

1.	Chemical structure of seven cPAHS. Chemical of focus in assay development (benzo[a]pyrene).	5
2.	PAH enterohepatic cycling Process.	6
3.	Calculating soil screening levels for site.....	7
4.	PAH oral bioavailability process.	8
5.	PAH availability for oral or dermal absorption as a function of PAH source materials and soil chemistry.	9
6.	Soil-Chemical Interactions: Effect of Source Materials on PAH Partitioning.....	10

7. Example of potential physical or mechanical weathering of skeet fragments	10
8. WWII Skeet Target Practice.	11
9. Skeet Target Turret Training, WWII.....	12
10. Example of typical clay target “pigeon” before and after munitions impact as well as skeet fragments found at a site in Jacksonville.	12
11. Example single ½ circle firing point.	13
12. Aerial of Historic Skeet Range, Spanish Steps, Naval Base Guam (NBG).....	14
13. Example of overlapping historic skeet range on now developed areas.	15
14. Example of semi developed (golf course) with overlapping historic skeet range.....	16
15. Performance Objectives: Success Criteria.	18
16. Technical Approach: Tasks 1 and 2.	21
17. Technical Approach: Tasks 3 & 4) Note (** In progress - at time of brief referred to transition of technology and current ongoing demonstration at site in Florida).....	22
18. Former Laredo Air Force base. Red line approximately outlines the base. Light blue box approximates impact area of firing range.	29
19. Former Foster Air Force Base skeet shooting range location.	30
20. MCAS Miramar, CA Site 19C.	31
21. Spanish Steps Skeet Range.....	32
22. Finegayan Skeet and Trap Range, Naval Base Guam, Guam.	33
23. Naval Air Station Whiting Field.	34
24. Head over Tail Heated Tumbler (extraction device) for PBET procedure.	39
25. Physiologically Based Extraction Test (PBET) Methods Flow chart.	41
26. Example of SP3™ Passive sampler.	42
27. Summary of Total Carbon Content (TOC) for 7 EBay Skeet Samples.	49
28. Mössbauer spectroscopy Carbon/Mineral Analysis of EBay Skeets 1–4.....	50
29. Mössbauer spectroscopy Carbon/Mineral Analysis of EBay Skeets 5–7.....	51
30. Soil Particle Distribution from two sites in both background soil (BG) and skeet impacted soil (SA).	52
31. A Comparison of Total Carbon Content (TOC) for 2 Field samples and SRS Soil samples. BG indicates SRS or background soils while SA indicates field soils.....	53

32. Mineralogical Analysis of Field Soils.	53
33. Organic Carbon Analysis of Field Soils.	54
34. Total PAH Concentration of Base Soils including reference soils.	55
35. Comparison of Total PAH concentration from two sites.	56
36. Historic Skeet (EBay Skeet) Total PAH and Carbon Analysis.	57
37. Xray Diffraction Carbon Analysis, calibrated to Calcite comparison of Whitening Field.	58
38. Mössbauer spectroscopy Carbon/Mineral Analysis compared to 2 Field soil samples.	59
39. Mössbauer spectroscopy Carbon/Mineral Analysis compared to 1 Field soil samples.	59
40. Identification of Skeet Signature in FT Soils.	60
41. Mechanical Weathering of Vintage Skeet3 (EBay) as compared to skeet from two field soils.	61
42. Mechanical Weathering of Vintage Skeet3 (EBay) as compared to mechanical weathering of skeet fragments at Whiting Field (WF-SA).	62
43. Example of Vintage Clay Targets (Skeet) Purchased from EBay.	63
44. Sample Manufacturer Label.	64
45. PBET Assay extraction from matrix issue (* y axis (ppb, recovery %) while X axis is polycyclic aromatic hydrocarbon constitute (PAH).	65
46. Example of PBET Replicate inconsistency.	66
47 Example of Addition of Solvent. 10-20 ppb spiked solution w/addition of solvent for stabilization.	67
48 Example of Addition of Solvent. 1-2 ppb spiked solution w/addition of solvent for stabilization.	67
49 Optimized PBET Assay.	69
50 PBET analysis of FT soil (G3).	71
51 PBET analysis of ST Soil (G3) Negative control (gastric solution alone) results.	71
52 Schematic of RBA Model Components.	72
53. Concentration of bioavailable B _a P in soil versus the concentration of C _{free} B _a P in soil.	75

TABLES

1	Sources of PAHs based on primary origin.	1
2	Classification of PAHs by Category.....	3
3	Changes to BaP IRIS toxicity level and recalculated RSLs.....	4
4.	List of PAH mixture components in the dichloromethane matrix.....	38
5.	Field Soil Samples.....	46
6.	Skeet and Reference Soil Samples.....	47
7.	Summary of Mineralogical and Chemical Analysis for Soil Samples.....	48
8.	Bioavailable concentration of Benzo(a) Pyrene (BaP) in skeet impacted soil as measured by PBET.	70
9.	Summary of field soil samples collected and type of analysis performed on each	73
10.	Concentration of BaP, RBA, concentration of bioavailable BaP (RBA × concentration of BaP), and total organic carbon content (TOC) of the five test soils used in the mammalian feeding experiment.	74
11	Estimation of potential BaP risk in 8 example soils (using example BaP/kg soil risk-based criteria) using total bulk analysis of BaP in soil, analysis of BaP via PBET, and analysis of freely-dissolved BaP via passive sampling.	77
A-1.	Concentrations of PAHs in PBET matrix, as applied to soil.....	A-1
A-2.	Concentration of analytes in polyethylene (PE).....	A-2
A-3.	Concentrations of freely-dissolved (C _{free}) PAHs in soil, as measured by passive sampling.	A-7
C-1.	EXWC RANGE DATA FILE- List of Bases by Region.....	C-1
C-2.	Additional Data Included in Data Files.....	C-5

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INTRODUCTION

1.1 PAHS

The chemical family of Polycyclic Aromatic Hydrocarbons (PAHs) are a ubiquitous group of chemicals found in the natural environment (~100 substances). Sources of PAHs can be formed during the incomplete burning of garbage, petroleum products, coal, or other organics like meat and tobacco. Other sources of PAH released into the environment include, volcanoes, forest fires, coal burning, car exhaust, industrial site coking, and asphalt production. Environmental release of PAH is typically either a pyrogenic (e.g. incomplete combustion) or petrogenic process (e.g. nonaqueous phase liquid such as crude oil or petroleum distillates). Below

Table 1 from Ruby et al (2016) provides a nice summary of the primary PAH sources separated into natural, industrial, and nonindustrial origins. Most pyrogenic PAHS are present at the surface of matrix such as tar, pitch, soot or coal. Of the approximately 1,400 Environmental Protection Agency (EPA) compiled, National Priorities list (NPL) sites, almost half (~600) include some form of PAH mixture. (Brown et al; Lowney et al 2017)

Table 1 Sources of PAHs based on primary origin.

Source Type	PAH Source	primary PAH-Bearing Materials
natural	forest fires	soot, char
	grass fires	soot, char
	volcanic eruptions	soot, char
	oil seeps	weathered crude oil
	sedimentary rock	kerogen
industrial	manufactured gas	coal tar, oil tar, pitch, coal, char,
	plants	soot
	coking operations	coal tar, coal, coke, soot
	aluminum production	coal tar or petroleum pitch
		(making and disposing of anodes)
	foundries	coal tar, creosote, fuel oil

- Ruby et al 2016

- Notes: NAPL= nonaqueous-phase liquid; PAH = polycyclic aromatic hydrocarbons

Table 1 Sources of PAHs based on primary origin. (Continued)

Source Type	PAH Source	primary PAH-Bearing Materials
		(used in making sand casts), soot
	wood treating facilities	creosote
	refineries	soot, various NAPLs
		(crude oil, fuel oil, diesel)
	carbon black	soot, oil tar
	manufacture	
	fuel spills and/or	various NAPLs (crude oil, fuel oil,
	disposal	waste oil, diesel)
nonindustrial	skate	coal tar pitch or bitumen (used as
		binder in targets)
	asphalt sealants	coal tar
	landfills	creosote (treated wood), soot, char
	incinerators (industrial,	soot
	municipal, hospital)	
	open burning	soot, char
	fire training	soot, char
	auto/truck emissions	soot

- Ruby et al 2016

- Notes: NAPL= nonaqueous-phase liquid; PAH = polycyclic aromatic hydrocarbons

Table 2 provides a breakdown of priority PAHs separated by carcinogenicity. Due to their carcinogenic potential, seven of the sixteen priority pollutant PAHs in Table 2 (benzo[a]-anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]-fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno-[1, 2, 3-cd]pyrene) are currently regulated by the U.S. Environmental Protection Agency (EPA). These seven carcinogenic PAHs (cPAHs) commonly drive human health-based cleanup goals at sites. For purpose of this study we focused on benzo[a]pyrene (BaP) because the toxicity of BaP has been better characterized than that of other cPAHs (Ruby et al 2016).

Table 2 Classification of PAHs by Category.

Carcinogenic PAHs	Noncarcinogenic PAHs
benzo(a)anthracene	acenaphthene
benzo(a)pyrene	acenaphthylene
benzo(b)fluoranthene	anthracene
benzo(k)fluoranthene	benzo(ghi)perylene
chrysene	fluoranthene
dibenzo(a,h)anthracene	fluorene
indeno(1, 2, 3-cd)pyrene	naphthalene
	phenanthrene
	pyrene

1.1.1 Benzo[a]pyrene (BaP)

Based on its high carcinogenicity potential, in addition to overall toxicity that has been well characterized (IARC, 1983, EPA 2017), the EPA uses Benzo [a] pyrene (C₂₀H₁₂) as its main index chemical for calculating relative potency factors (RPF) and setting clean up criteria. BaP has been classified as a reasonable human carcinogen (no direct link proven in humans but adequate evidence in animals) and mutagen. Its classification as reasonable mutagen is based in part of fact that its diol epoxide metabolites (e.g. 7, 8-diol-9, 10-epoxide) can react and bind to DNA, resulting in mutations and eventually cancer. It is a high public health concern due to its possible effects on industrial workers, as an environmental pollutant, and as a component of tobacco smoke.

In neat or purified form, BaP is a crystalline, aromatic hydrocarbon consisting of five fused benzene rings. It is commonly formed during the incomplete combustion of organic matter, and like other cPAHs it is found in gasoline and diesel exhausts, coal tar and pitch as well as charcoal broiled foods, soot smoke, creosote oil, asphalt and shale oils as well as certain amino acids, fatty acids and carbohydrate pyrolysis products (HMDB 2018; ATSDR 1995). “Benzo[a]pyrene is metabolized to approximately 20 primary and secondary oxidized metabolites and to a variety of conjugates. Several metabolites can induce mutations, transform cells and/or bind to cellular macromolecules” (IARC, 1983).

In January of 2017 the EPA, through its Integrated Risk Information System (IRIS) database, published updated toxicity values for BaP (EPA 2017). The main changes included addition of an inhalation route of exposure; a potential for non-cancer health effects; removal of dermal exposure in calculations, and an overall indication that BaP is now considered less toxic by the oral route. The reconsideration and update to toxicity levels included revisions to the EPA regional screening levels (RSLs) for soil, which are the main drivers for site-based cleanup goals.

Table 3 provides a summary of prior and current toxicity and RSL levels. The authors refer the reader to the EPA’s Toxicological Review of Benzo[a]pyrene (2017) and Development of a Relative Potency Factor (Rpf) Approach for Polycyclic Aromatic Hydrocarbon (PAH) Mixtures (2010) for a more detailed discussion of changes and methods used to calculate regional screening levels.

Table 3 Changes to BaP IRIS toxicity level and recalculated RSLs

	Prior To 2017			2017 Change			
	IRIS Toxicity (1E-6)*	RSL Soil (mg/kg)		IRIS Toxicity (1E-6)*	Current/Projected RSL (mg/kg)		Difference of RSLs
		Residential	Industrial		Residential	Industrial	
Cancer		0.15	0.29		0.11	2.1	~7x increase
OCSF ¹ (mg/kg/dy)	7.3E+00			1E+00			
IUR (µg/m³) ⁻¹	NC*			6E-04			
Non-cancer		NC*	NC*		17.9	220	~7x increase
OCSF ¹ (mg/kg/dy)	NC*			3E-04			
IUR (µg/m³) ⁻¹	NC*			2E-06			

- OCSF (Oral Cancer Slope Factor); IUR (Inhalation Unit Risk); RSL (Regional Screening Level); NC (no previous IRIS value/not calculated); 1E-6 (1 in 1 million)

1.1.2 Chemical and Physical Characteristics

While there are many types of PAHs, common physico-chemical characteristics include relatively low water solubility; low vapor pressure, high octanol:water partition coefficients, and generally exist in solid form with high melting and boiling points. PAHs degrade through chemical, photolytic and metabolic processes associated with microorganisms. Their ability to strongly adhere to particles entrainment in stormwater runoff and wind-blown dust potential makes this a transport mechanisms of concern, however volatilization and migration to groundwater not of concern. According to the ATSDR, direct contact is the principal concern through either ingestion, dermal absorption, &/or inhalation (ATSDR 1997).

The structure consists of molecules containing two or more fused six-carbon atom aromatic rings. Only hydrogen and carbon are present in the molecules. The chemical structure of the seven cPAHs is provided below (Figure 1).

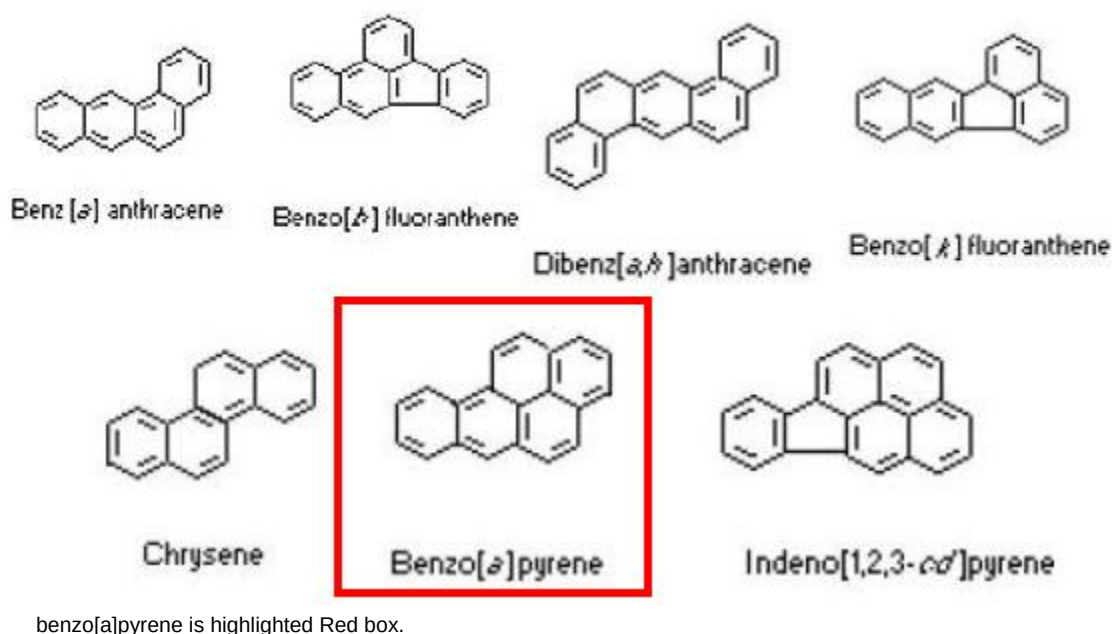


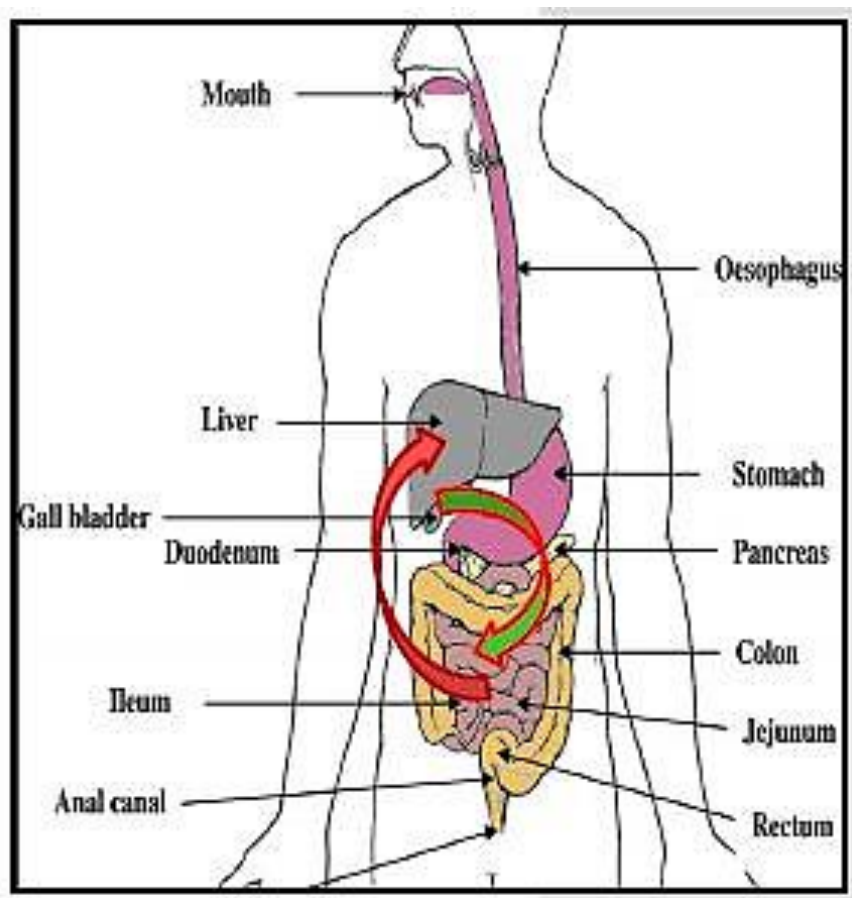
Figure 1. Chemical structure of seven cPAHs. Chemical of focus in assay development (benzo[a]pyrene).

1.1.2.1 Gastrointestinal absorption

While there are other exposure pathways of concern from an ecotoxicology and/or occupational perspective, this study focused on human health ingestion as primary risk-based exposure, as it is the main driver for human health-based cleanup goals at sites (EPA 2010 & 2017). There have been several recent publications that provide a nice summary related to the PAH absorption process. For purposes of this effort a brief summary is provided below. For a more detailed description of the PAH absorption process please refer to Ruby and Lowney (2012), Ruby et al (2016), Lowney et al (2017); Van Schooten et al (1997).

Fat-soluble organics such as PAHs are metabolized in the liver and excreted from the small intestines via fat globules in the form of bile. However these same excreted PAHs and their

metabolites can be re-absorbed in the small intestine in a process known as enterohepatic cycling (Figure 2) thereby increasing overall exposure. PAH metabolites can also be excreted in the urine.



- (Magee et al 2014)

Figure 2. PAH enterohepatic cycling Process.

1.1.2.2 Human Health Risk Factors

As mentioned previously, site-based PAH clean up criteria are based on potential risk factors to human health. A relative potency factor(s) or (RPFs) are utilized to assess the toxicity of an individual PAH. The RPF approach takes the doses of individual components acting through a similar mechanism of action and then sums them after scaling to the relative potency of an index chemical within the group of chemicals that has the greatest /most complete dose response characterization data available. In the case of the chemical class of PAHs benzo[a]pyrene (BaP) is that index chemical (EPA 2010; Lowney et al 2012). The selection of BaP as the index chemical is four fold: (1) it has the most robust toxicological dataset to include a formal dose-response assessment in rodent models; (2) it is typically found present in environmental settings where one would suspect presence of PAHs; (3) it is the most potent carcinogen of all PAHs tested thus far; and (4) it has a large database of in vivo and in vitro studies directly comparing its potency (Lowney et al 2017).

The U.S. Environmental Protection Agency uses risk-based screening values that are intended to be protective of human health and/or the environment. These are often defined as chemical

concentrations in a target media (e.g. soil), which if found to be below concentration, no additional regulatory attention to that site would be required. If the concentration is found to be above that screening value, further regulatory attention (e.g. clean up of site) might be required. These screening values are derived by combining exposure assumptions with toxicity data. For purpose of this study we will focus only on soil screening levels, as that would be the primary exposure path associated with skeet impacted soil (ITRC, 2005).

Regional Screening Levels (RSLs); based on the EPA's Soil Screening Guidance: A User's Guide (EPA 1996); provide a standard methodology to calculate risk-based soil screening levels for contaminants in soil (EPA 1995). Many states have adopted their own screening values for managing hazardous waste. These screening values are based on an acceptable risk level (e.g. one in one million cancer risk as default value for conservative exposure). An example of how a soil based screening level, including assumptions used for a particular site, is provided below (Figure 3). For BaP (PAH index chemical) current RSLs used to evaluate a site are provided in Table 2.

Risk-based Assumptions

$$\text{Soil Screening Level (mg/kg)} = \frac{\text{Target Cancer Risk} \times \text{Body Weight} \times \text{Averaging Time}}{\text{CSF} \times \text{RBAF} \times \text{Intake} \times \text{Exposure Assumptions}}$$

1. Target Cancer Risk – Typically 10^{-6} or 10^{-5}
2. Body Weight – 15 kilograms (kg) for child and 70 kg for adult
3. Averaging Time – 365 days per year (d/yr) over 70 years
4. Exposure Assumptions – Typically 350 d/yr over 30 years
5. Intake – 200 mg/d for child and 100 mg/d for adult
6. CSF – Cancer Slope Factor – 7.3 per mg/kg-day for B[a]P & Relative Potency Factors (RPFs) for other PAHs
7. RBAF – Relative Bioavailability Factor – Typically assumed to be 1

* Bioavailability is the only input available to apply site-specific data





Environment, Energy Security & Sustainability Symposium & Exhibition

- (Magee et al 2014)

Figure 3. Calculating soil screening levels for site.

1.2 BIOAVAILABILITY OF PAHS IN SOIL

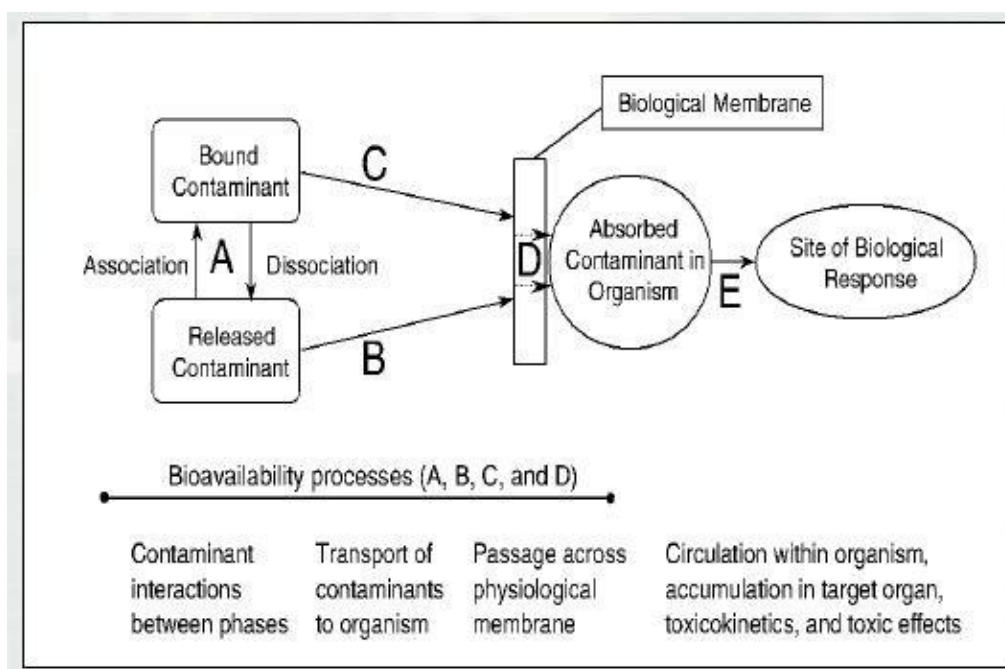
There have been several recent publications which have gone into great detail describing the bioavailability pathway of PAHs in soils (Magee et al 2016; Xia et al 2016; Ruby and Lowney 2012; Ruby et al 2016; Lowney et al 2017), in particular a recently funded SERDP effort focused on the bioavailability of PAH in soil (Lowney et al 2017). The authors refer the reader to the Lowney et al (2017) effort in particular for a very detailed description of different variables associated with

bioavailability. As such, for purpose of this report a very brief description will be summarized in this section.

In short,

- Bioavailability is complex and is based on:
 - How well PAHs is bound to skeet
 - How well PAH material is bound to soil
 - What happens when clay target fragments erode and degrade
- Source material of clay targets is important
- Skeet impacted soils generally have higher PAH concentrations, and PAHs are more tightly bound overall

As discussed above, PAHs are deposited in soil from different source materials (e.g., soot, char, coke, coal, pitch, coal tar, creosote, oil tar, crude oil, or petroleum products). These materials subsequently interact with various soil components, which in turn affect their oral bioavailability, resulting in limited human exposures. Figure 4 provides a general overview of the process. Note that A, B, and C can also occur internal to organism such as in the lumen or the gut (Meyer 2011).



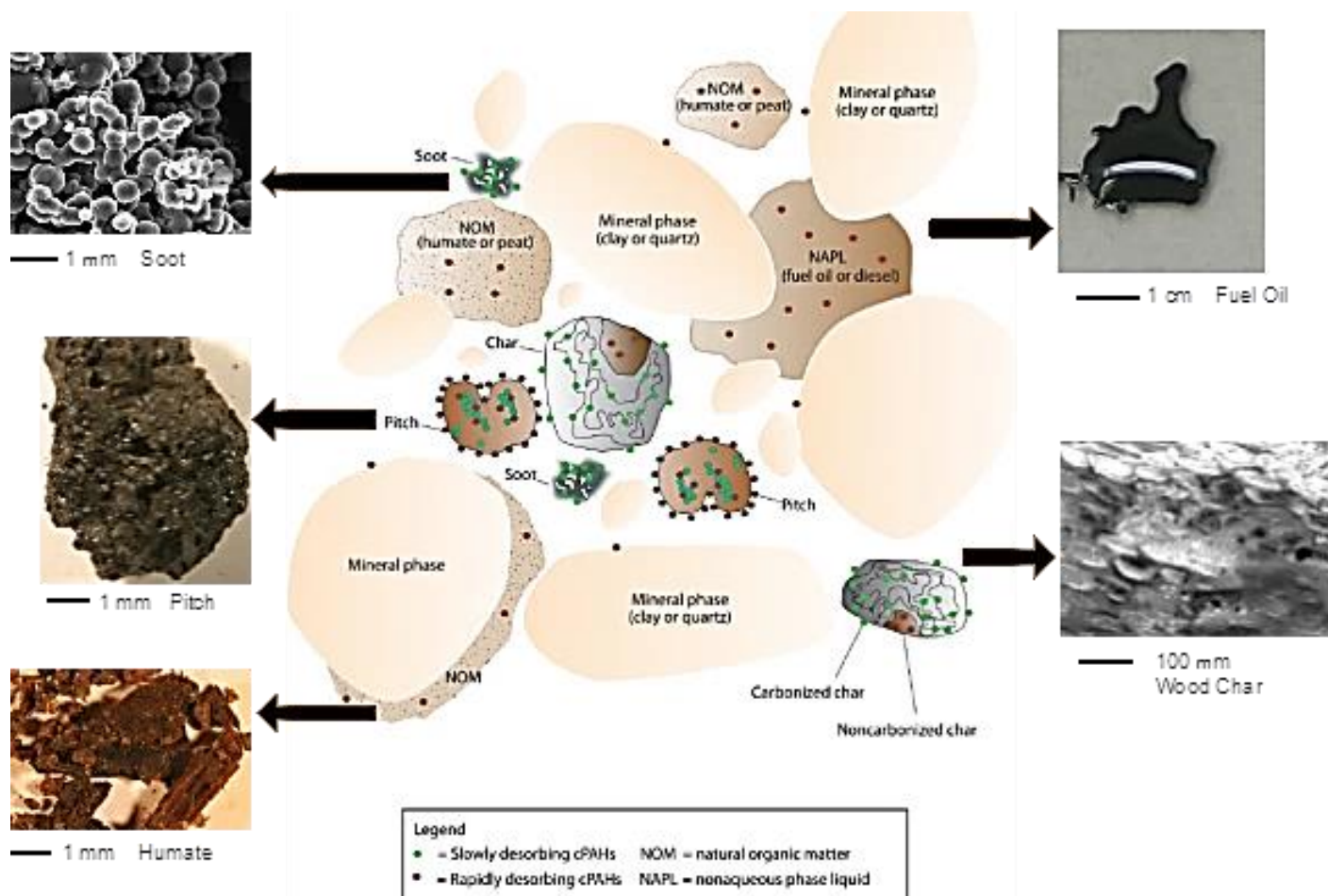
- (Meyer 2011; NRC 2003)

Figure 4. PAH oral bioavailability process.

Sorption of PAH within a soil environment can be roughly described as a mixture of sorption to black carbon and natural organic matter (NOM) spheres (Ruby et al 2016. Based on work completed under the SERDP effort (SERDP Project ER-1793, Lowney et al 201).

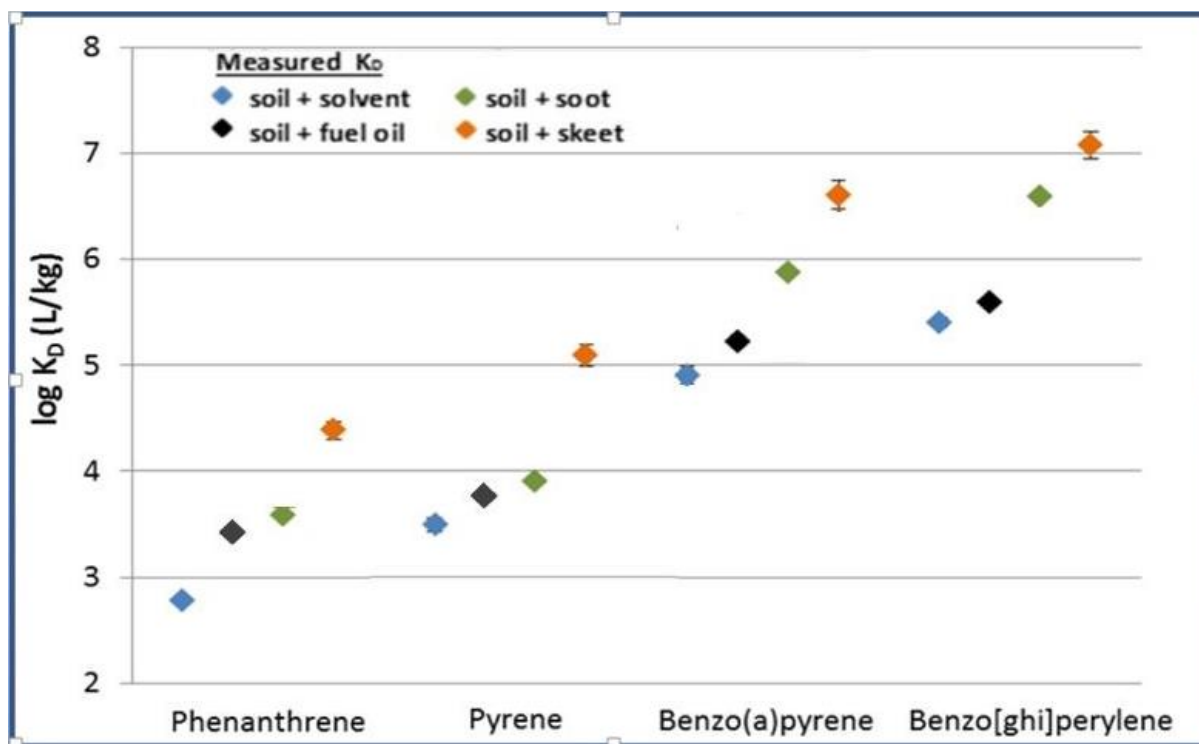
Figure 5 (Ruby et al 2016) summarizes the impact of different types of organic carbon like NOM impact the potential bioavailability of PAHs, for which Ruby et al (2016) postulated the type of PAH source material such as crude oil or petroleum vs. black carbon or pitch determines the rate and

desorption potential of PAHs into the soil. For instance, the PAHs found in crude oil or petroleum type products more rapidly desorb PAHs while black carbon sources such as soot or char contain more slowly desorbing PAHs, and some mixture based carbon sources such as pitch will contain both rapidly desorbing and slowly desorbing PAHs, as well as non-desorbing PAHs. The concept of source material impacting bioavailability was explored by Xia et al (2016), during an equilibrium partitioning study as part of the SERDP effort, which showed that source material impacted the binding of PAHs to soil, and that soot or soot in particular as a PAH source resulted in much stronger binding of PAHs to soil with lower dissolution.



(Source: Ruby et al 2016)

Figure 5. PAH availability for oral or dermal absorption as a function of PAH source materials and soil chemistry.



(Source Xia et al 2016)

Figure 6. Soil-Chemical Interactions: Effect of Source Materials on PAH Partitioning.

Weathering

An additional consideration when determining the bioavailability of PAH source materials in soil is the role that aging or weathering might play on this source material. As stated by Ruby et al 2016 “in this context, weathering is associated with losses by biodegradation, leaching, or volatilization of the rapidly desorbing fraction of PAHs, and the continuous diffusion and retention of PAH molecules into remote and inaccessible regions within the soil matrix”. Weathering can lead to both the breakdown of source materials (e.g. skeet fragments) and potentially increase the surface area allowing for chemical reactions (Figure 7), and/or altering the movement of PAH molecules into areas of the soil matrix, making them either more or less available.

PAH bioavailability varies by compound, studies would reduce uncertainty. Relative bioavailability may range from 0.1 to 0.76, with 0.3 being typical

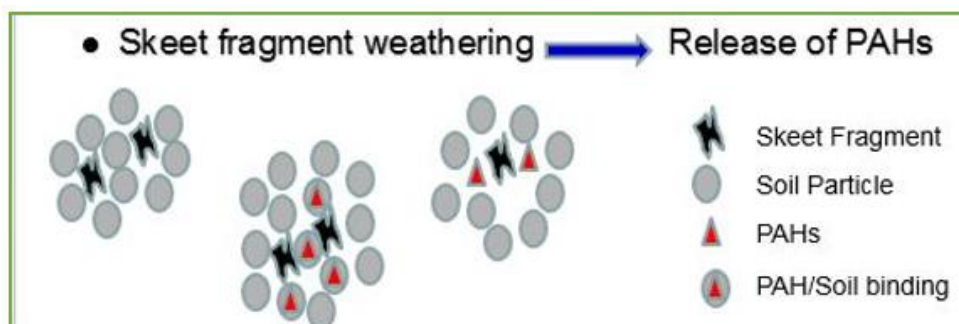
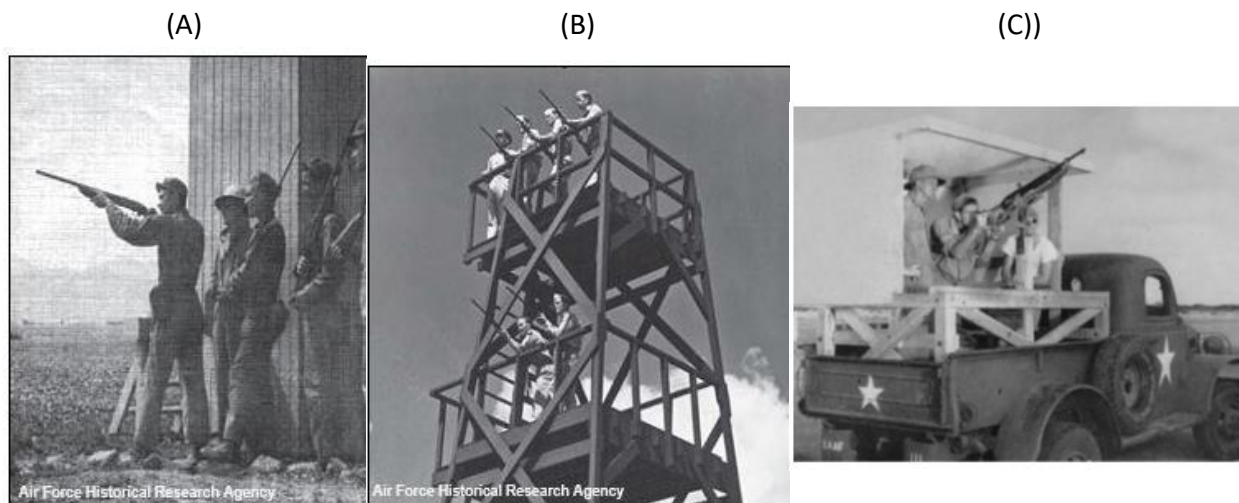


Figure 7. Example of potential physical or mechanical weathering of skeet fragments

1.3 SKEET RANGES

Navy Skeet Ranges were used for training WWII forces to shoot at moving targets (Figure 8). Types of training scenarios varied based on mission needs, however a typical example of training during that time-frame was to educate military personnel on how to operate turrets as they fired on clay pigeons, which were released from high towers (40 ft, Figure 9).



- (A), and (B) Photos of Air Force Historical Research Agency
- (C) Photo of Kingman Army Airfield Historical Society

Figure 8. WWII Skeet Target Practice.

Since WWII the use of US skeet targets averaged 50 million targets per year. While many military ranges are no longer in use, more than half of all US Naval and Marine Corps Installations (35 of 60 Navy and 10 of 18 Marine Corps) contain at least one historic skeet range, while many installations also contain multiple skeet range sites. While the distribution of both lead from the ammunition and the scattering pattern of clay target fragments from the shattered pigeon (Figure 10) generally occurred in a predictable pattern, the total area of impact per skeet range can vary considerably depending on number of shooting points at each site. For example, a simple range site, with only one half-circle firing positions will have on average 6 acres of skeet impacted surface soil (Figure 11). However, multiple firing points per range were common and resulted in a larger acreage of soil impacted by skeet.

In addition, historic shotgun range sites used to train aerial gunners in WWII would have between 10 and 20 firing point locations and typically each firing point “half circle” or “fan” would overlap each other, thus clay target fragment patterns would overlap among adjacent firing positions (note, the highest density in a fan from a single firing position is between 65 to 260 feet). Thus, a skeet range containing multiple firing positions can have an impacted surface soil area of 20 acres or more (Figure 12). In fact, there are some installations within the NAVFAC SW region of the country where impacted surface soil area is reaching 68 acres. As most of these sites were used for training purposes during WWII, many of these sites are no longer in use. In some instances the land has been repurposed for other beneficial uses, such as golf courses, residential use through leasing, or other infrastructure has been built atop the land (Figure 13 & Figure 14). In some instances, due to the presence of other hazardous material (e.g. lead from gunshot pellets) or a location not suitable for other uses based on topography and/or landscape, several sites have remained untouched since being decommissioned (Figure 11 and Figure 12).



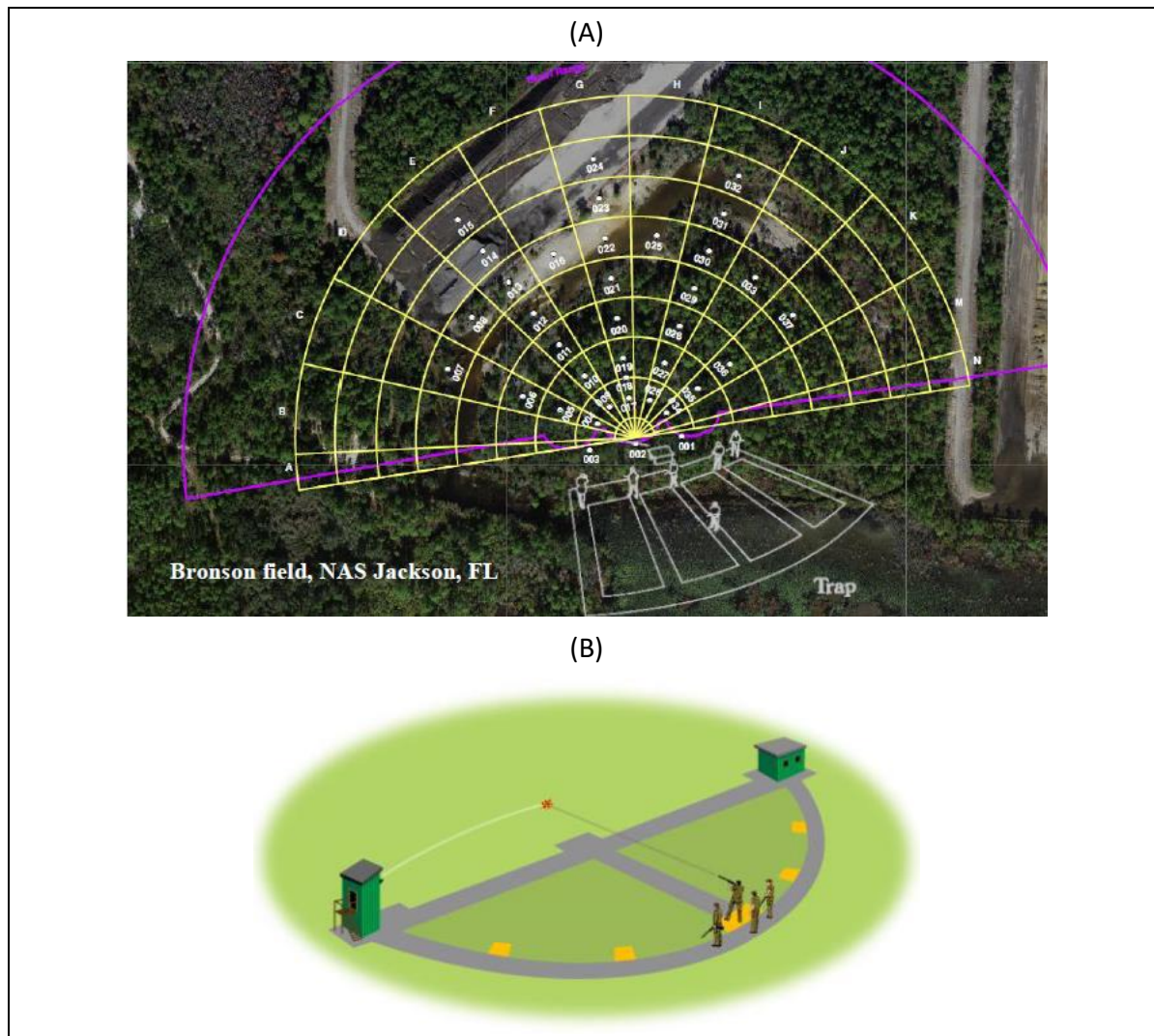
- Photos from Kingsman Army Airfield Historical Society

Figure 9. Skeet Target Turret Training, WWII.



- (George, 2017)

Figure 10. Example of typical clay target "pigeon" before and after munitions impact as well as skeet fragments found at a site in Jacksonville.



- Photo provided by John Schoolfield, NAVFAC SE RPM
- Aerial view with historic firing point and dispersant pattern overlay grid (A)
- Graphic Overlay of typical firing layout (B)

Figure 11 Example single $\frac{1}{2}$ circle firing point.

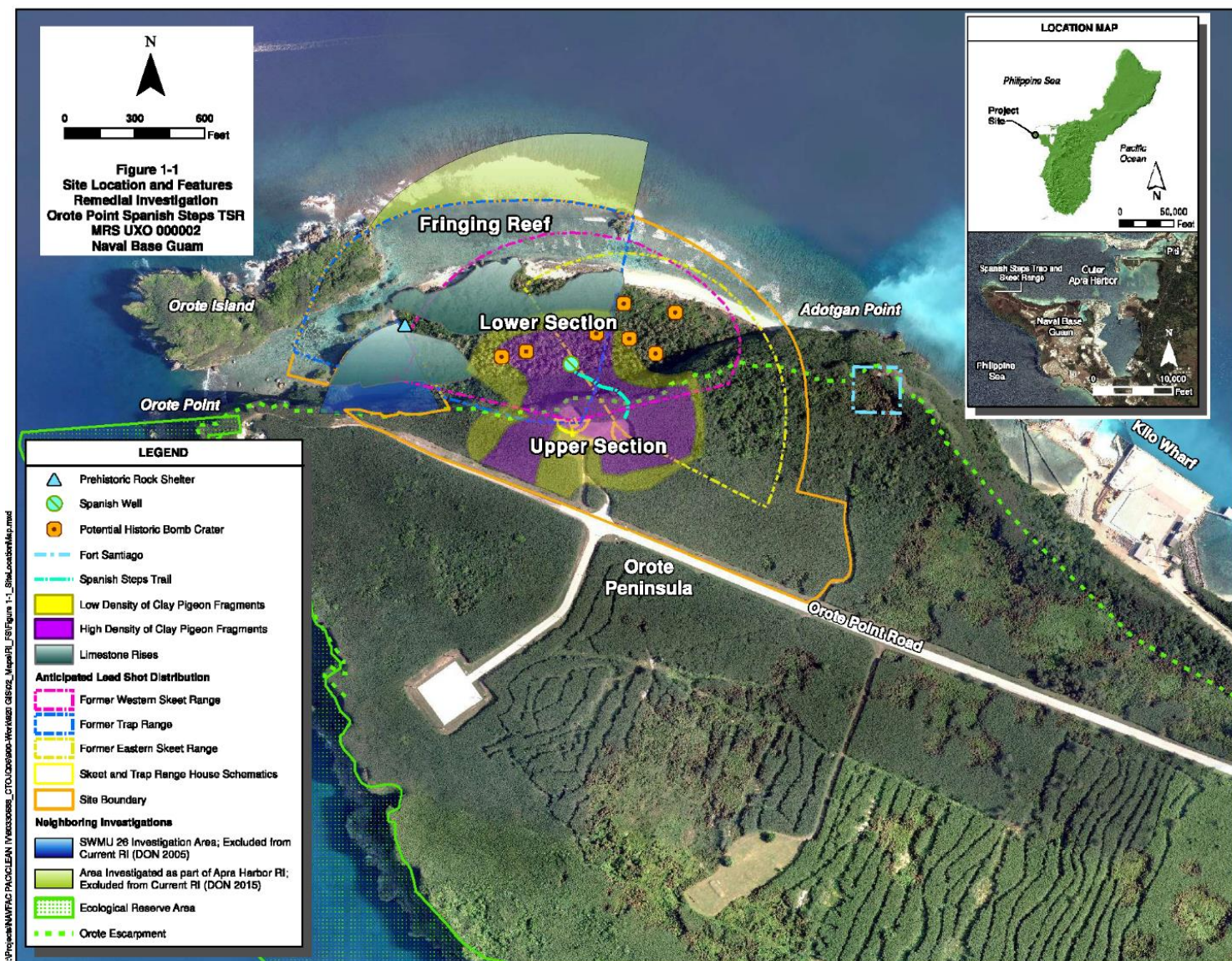
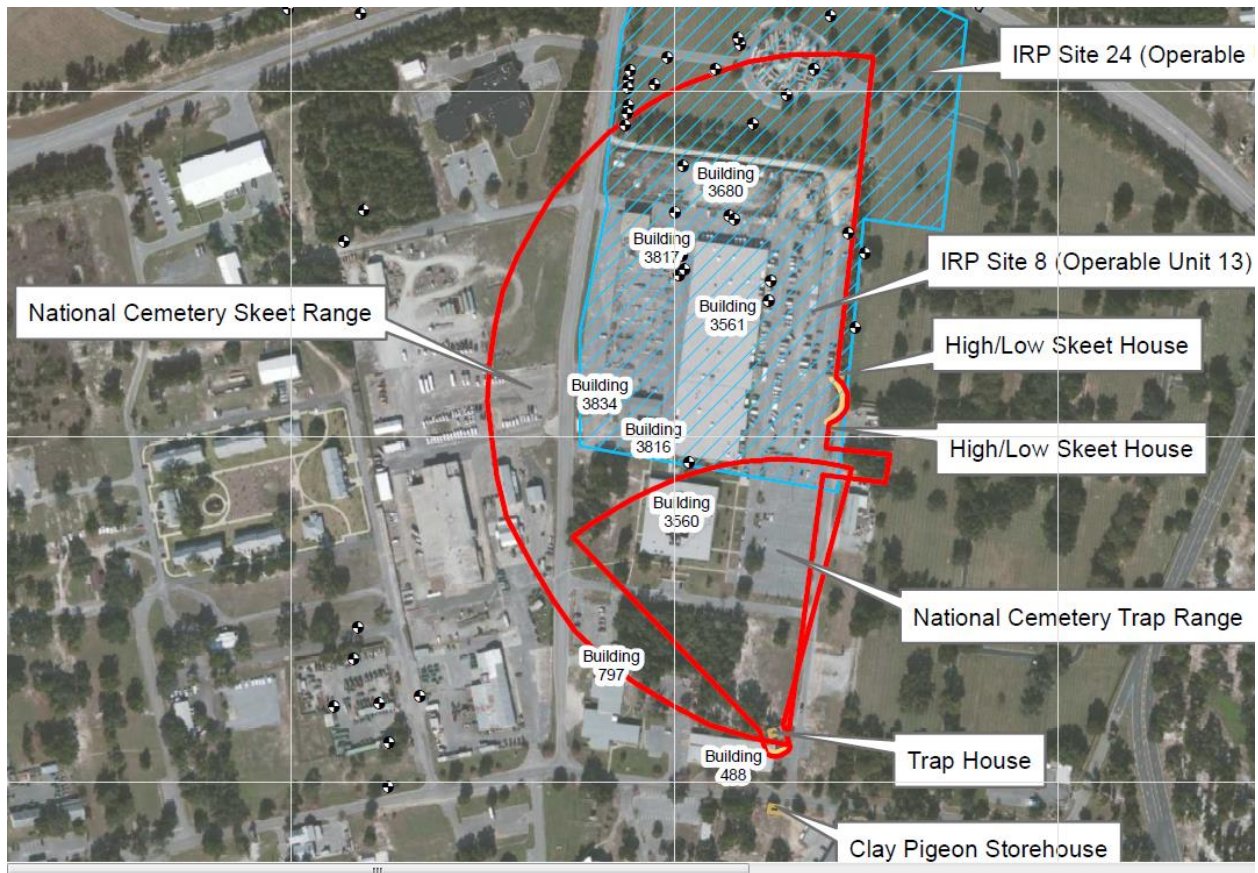


Figure provided by Vincete Ada, RPM, NBG.
Source for figure was provided by Guam RPM .

Map projection: WG8 1984 LITM Zone 55N.
Base Map Orthophoto: Orote Peninsula, 2009.

Figure 12. Aerial of Historic Skeet Range, Spanish Steps, Naval Base Guam (NBG).



Aerial of NAS, Pensacola

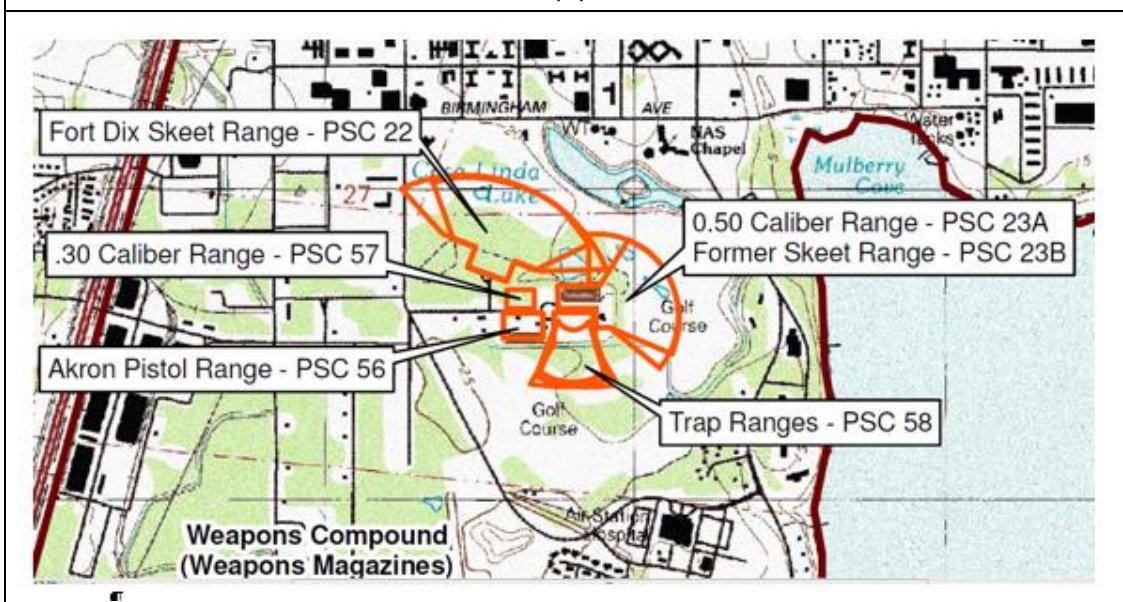
Figure provided by John Schoolfield, RPM, NAVFAC SE

Figure 13. Example of overlapping historic skeet range on now developed areas.

(A)



(B)



- Aerial of NAS Jacksonville golf course (A)
- Detail Map of golf course (B)
- Figure provided by John Schoolfield, RPM, NAVFAC SE

Figure 14. Example of semi developed (golf course) with overlapping historic skeet range.

1.4 IMPACTS OF PAHS IN SOILS ON SKEET RANGES

Under the Munitions Response Program (MRP), the United States (U.S.) Navy is required to address and remove hazardous munitions constituents from soils under certain conditions. Polycyclic aromatic hydrocarbons (PAH) is a known constituent observed on skeet and target practice ranges service-wide. High levels of PAHs in soil can be found at sites where no re-development has

occurred and soils with visible clay target fragments are present, or at historic sites that have since been re-developed. While there are many different forms of skeet present, general composition of clay targets (skeet) consist of a dolomitic limestone and some form of binding agent such as coal tar pitch or petroleum. As stated previously, coal tar and petroleum pitch contain high molecular weight PAHs, which are listed by the EPA as priority chemicals of concern. A more detailed description outlining the overall impact of skeet PAH contaminated soils within the DOD as well issues associated with remediation are discussed in Section 2 below.

1.4.1 Overarching Problem Statement

DoD liability for PAH-impacted soils at skeet ranges is in excess of \$100M over more than 40 sites. Current PAH cleanup goals often assume 100% RBA, resulting in > \$1M per site and overly-protective cleanup approaches. Recent research indicates that lower bioavailability of skeet-derived PAHs (RBA of 10-80%), when applied on a site-specific basis, would reduce costs cleanups by \$100K-\$1M per site (Magee et al 2014; Lowney et al 2017; Ruby et al 2016; Xia et al 2016). In vivo studies are not cost and time effective for all sites (>\$300K/site); and recent efforts (Lowney et al 2017) have shown the potential of an in vitro approach to predict RBA.

1.5 SCOPE OF WORK

This project began in October 2012 in response to Need N-0742-11 submitted by John Schoolfield (NAVFAC SE). Dr. Sorensen (NIWC Pacific, formerly SSC PAC) took over as PI in January 2014 when Bill Major (NAVFAC EXWC) retired in December 2013. The primary technical objective of this work was to determine the polycyclic aromatic hydrocarbon (PAH) composition of clay targets and their relative bioavailability in soil. The intent of this effort was to evaluate potential approaches and technologies for low cost, robust, and rapid methods to evaluate RBA of PAHs in soil from skeet-impacted sites,

1.5.1 Technical Objectives

To achieve the primary objective, work under this effort included four main technical objectives.

1. To improve the ability to discern clay target particles from soil particles
2. To better inform PAH fate and transport processes
3. To calculate more realistic/site specific RBAs for PAHs instead of relying on default RBAs that lead to overly conservative cleanup goals
4. To provide technical information that range program managers (RPMs) can use to develop more accurate and effective risk-based clean-up levels based on 3, avoiding clean-up levels that assume 100% RBA

1.5.1.1 Performance Objectives

The overall success of meeting our technical objectives was measured against 3 main quantitative performance objectives. A summary of these performance objectives including data requirements and metrics for success is provided in Figure 15.

Qualitative Performance		
Performance Objectives	Data Requirements	Success Criteria
Develop method to identify clay target particles within soil matrix	Compare lab prepared soil/clay target mixtures to Navy skeet range PAH contaminated soils	Method developed capable of separating and identifying clay target particles vs. soil particles for a variety of sampled skeet ranges soils. Size distribution estimates made from separated clay target particles
Calibration of <i>in vitro</i> assay to <i>in vivo</i> assay	<i>In vitro</i> assay replicates are tight enough and consistent enough to where appropriate calibration coefficients can be applied	<i>In vitro</i> data and <i>in vivo</i> data show relevant correlations to make comparison meaningful
Determination of PAH Relative Bioavailability (RBA) for clay target contaminated soils	Comparison of <i>in vitro</i> method to <i>in vivo</i> rat models developed & tested under Army Corps and tested under NESDI program	<i>In vitro</i> test (e.g., PBET, passive samplers, chemical extraction, etc.) provides significant statistical correlation to <i>in vivo</i> models

Figure 15. Performance Objectives: Success Criteria.

1.5.2 Technical Approach

To achieve the technical objectives outlined above, this effort was split into four main tasks. As part of this tasking, a series of methodologies considered essential in completing the objectives was developed and optimized, which enabled us to complete our assessment. This section provides a general overview of methodologies developed (1.5.2.1), as well as main tasking (1.5.2.2).

1.5.2.1 Primary Methodologies Developed for Assessment

Methodologies developed/optimized under this effort enabled us to:

1. better understand the environment and difference between contaminant of concern vs. background
2. provide tools to more accurately assess area of concern. The battery of tools generated to accomplish our goals can be broken down into three subgroups:
 - a. tools to assess soils and skeet material (the environment)
 - b. assays to determine bioavailability
 - c. tools to recalculate relative bioavailability (RBA).

Methods used and/or developed under each subgroup are outlined below. A more detailed description of methods used is provided in Section 3.

1.5.2.1.1 Subgroup 1 (Skeet and soil particle analysis)

This subgroup included a compilation of base/range information (Excel Database-EXWC) and tools to identify differences in skeet material as well as initial weathering analysis (University of Illinois). Methods used/optimized included:

- Excel spreadsheet based database using NIRIS database
- Chemical Analyses (PAH, Black Carbon)
- Scanning Electron Microscopy (SEM)
- X-ray Powder Diffraction (XRD)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Differential Thermal Analysis (DTA) & Thermal Gravimetric Analysis (TGA)
- Mossbauer Spectroscopy

1.5.2.1.2 Subgroup 2 (Bioavailability Assay Development)

This subgroup focused on the development and optimization of in vitro assays as well as the identification of a suitable in vivo model to use for comparison. Methods used included:

- in vivo methods - rodent models (SERDP/ Army Corp Study)
- In vitro methods - Physiologically-Based Extraction Test (PBET) & mild-solvent extraction methods as well as Passive Samplers (Geosyntec / NIWC Pacific, formerly SSC PAC)

1.5.2.1.3 Subgroup 3 (IVIVC Model)

This subgroup included the development of an in vitro in vivo comparison model that could be used to relative bioavailability (RBA). The developed model utilized following information:

- In vitro assays (PBET and Passive sampler)
- In vivo RBA data (Army Corp Data)
- Koc values (soil partitioning- Xia et al., 2014)
- Calculated C_{free} (ng available PAH/L, equivalent to an aqueous concentration) C_{free} represents most available fraction of PAHs in soil.

1.5.2.2 Main Tasks

The overall technical approach was comprised of four main tasks with subsequent subtasks under each. The main tasks and general purpose of tasks is described below. Figure 16 and 17 provide an outline of tasking including subtasks as presented at the final NESDI IPR in March of 2017.

1.5.2.2.1 Task 1: Identification and Characterization of Skeet

The main goal of this task was to better understand the source material (skeet and soil) as well as provide a baseline characterization of soil and skeet from samples/sites used under this effort.

Subtasks included:

- a. collect soil samples from a variety of Navy skeet ranges and analyzing concentrations of PAH in skeet material, skeet impacted soil and non-skeet impacted soil
- b. determine means of differentiating skeet material from soil and “fingerprint the most widely used types of clay”
- c. conduct a baseline analysis of skeet material under “weathered” conditions;
- d. determine manufacturers and varieties of targets used (Database) on Navy ranges.

1.5.2.2.2 Task 2: In vitro Assay Development

The main goal of this task was to develop and calibrate a low cost, robust, and rapid in vitro method that simulates mammalian digestion to evaluate RBA of PAHs in soil from skeet-impacted sites. Two in vitro assays were developed/calibrated under this effort and subtasks included:

- a. develop both a physiologically based extraction test (PBET) and polyethylene based Passive Sampler assay;
- b. calibrate both assays to ensure reproducible data
- c. validate the assay using real world samples compared to in vivo assay data.

A more detailed description of each assay is described in methods section of this report.

1.5.2.2.3 Task 3: Develop In vitro /RBA Model

The main goal of this task was to develop an in vitro/in vivo comparative (IVIVC) model. The purpose of the model is to provide a means of predicting the bioaccessible concentration of an index chemical representing PAHs (BaP) in soil using in vitro measurements (passive sampling) and (PBET) and show that these measurements are predictive of measures of bioavailability developed from animal feeding trial (develop a numerical relationship between in vivo and in vitro measurements). Subtasks included under this task included:

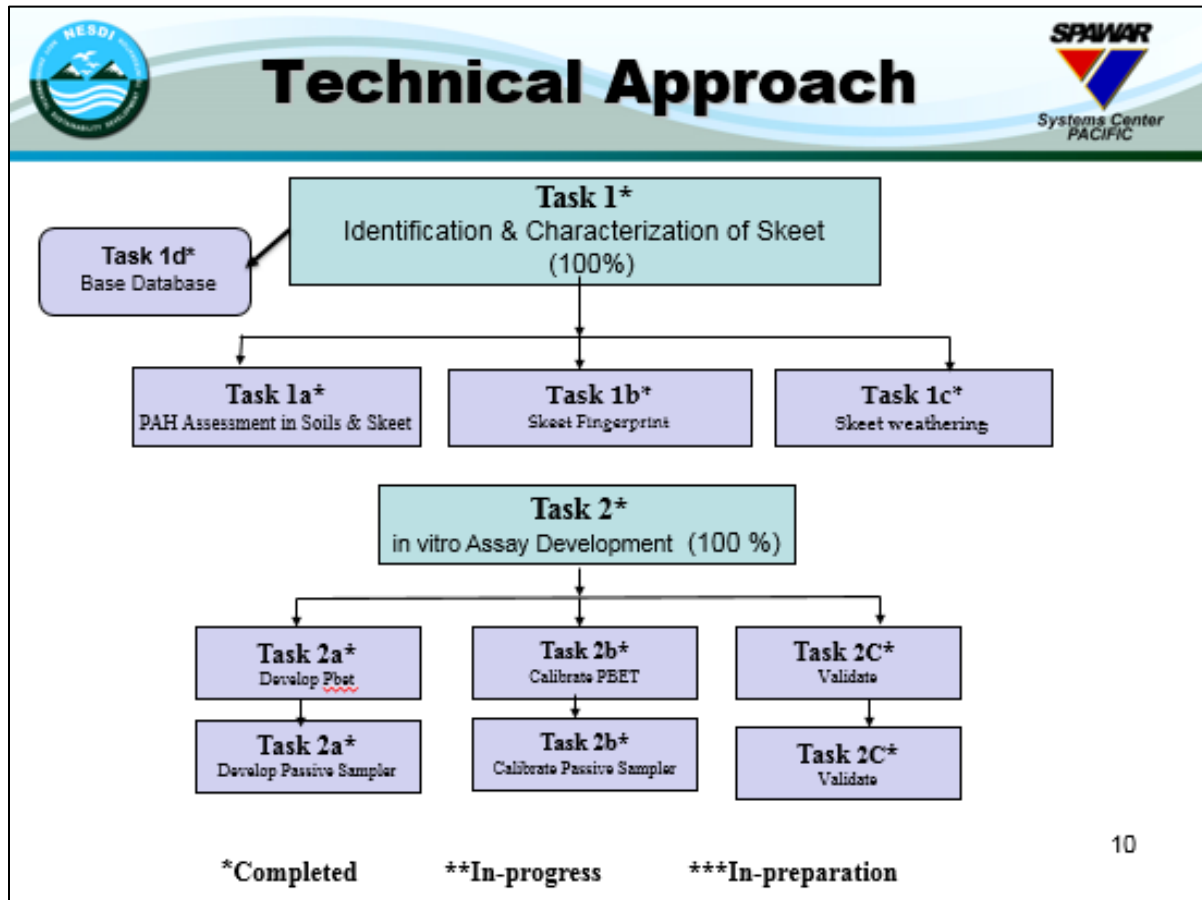
- a. development of the IVIVC model
- b. calibration of IVIVC model
- c. validation of IVIVC model.

1.5.2.2.4 Task 4: Demonstrate Model

This final task was focused on demonstrating the IVIVC model by applying the in vitro methods to a real world skeet impacted site and recalculating the relative bioavailability (RBA) for that site. Ideally this task would involve skeet impacted soils from a site run using both an in vitro and in vivo assay. However, due to limited funds, a more limited /small scale demonstration was performed on real skeet-impacted soils, using prior feeding trial soils, multiple environmental soil samples, along with soil characterization data for each site, and analysis of skeet-impacted soils by in vitro assays developed under task 2. Subtasks included under this task included

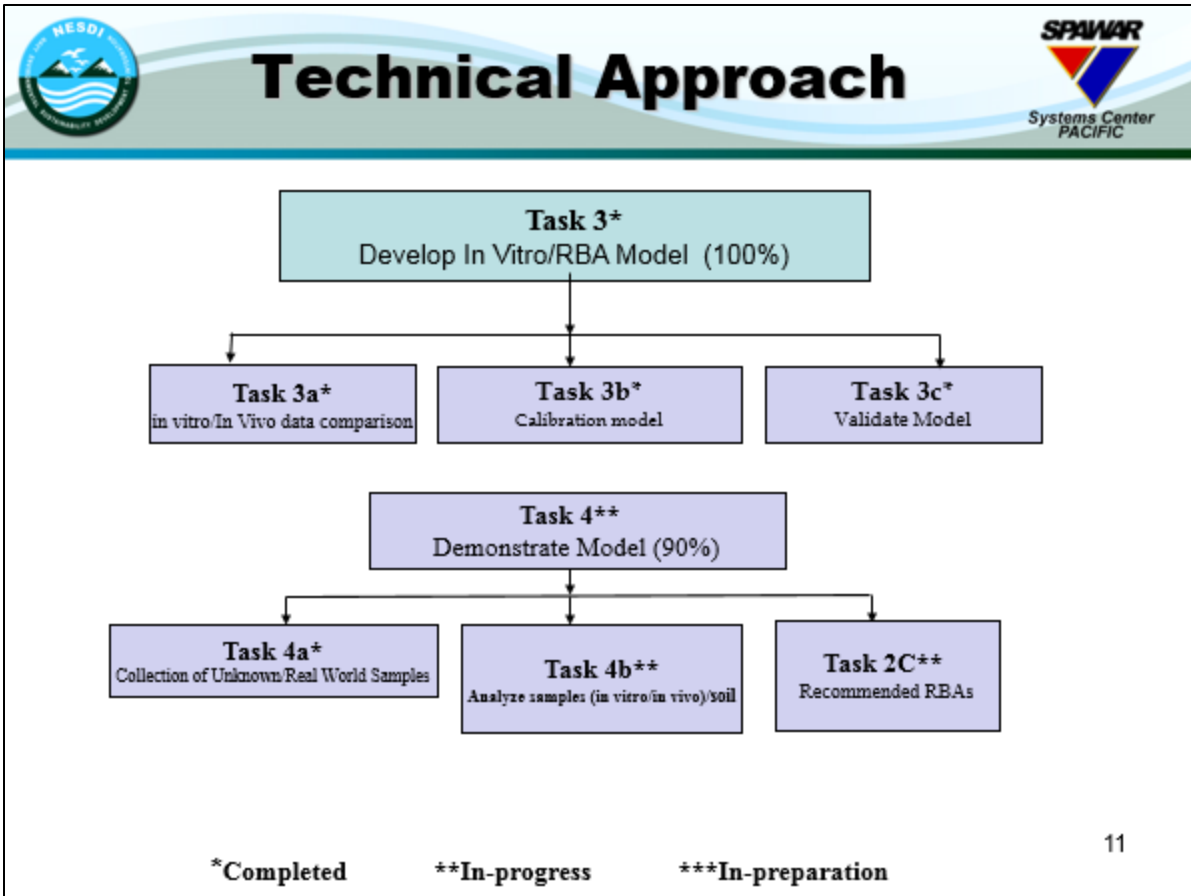
- a. collection of multiple “unknown” real world samples from multiple sites
- b. analysis of soils using soil characterization and bulk chemical extraction methods (task 1) and in vitro assays (task 2)
- c. apply the model and calculation of the RBAs for each site based on IVIVC.

Results of demonstration are described in Section 4 below. It should be noted that while a full demonstration was not feasible under this effort, results of this study are now being applied (funded separately) at a site in Florida as part of their site remediation assessment. A site specific in vivo / in vitro assay comparison is currently in progress.



- Source: NESDI Final IPR presented in March 2017

Figure 16. Technical Approach: Tasks 1 and 2.



- Source: NESDI Final IPR presented in March 2017
- Note (** In progress - at time of brief referred to transition of technology and current ongoing demonstration at site in Florida)

Figure 17 Technical Approach: Tasks 3 & 4) Note (** In progress - at time of brief referred to transition of technology and current ongoing demonstration at site in Florida)

2. BACKGROUND

2.1 SCOPE OF SKEET MATERIALS AND IMPACT ON DOD/USN FACILITIES

2.1.1 Skeet Impacted DoD Sites

Under the Munitions Response Program (MRP), the United States (U.S.) Navy is required to address and remove hazardous munitions constituents from soils under certain conditions. One such material—polycyclic aromatic hydrocarbons (PAHs)—was historically observed at high levels in clay skeet targets, which are found on skeet and target practice ranges service-wide. With at least 35 of the 60 U.S. Naval installations and at least 10 of 18 U.S. Marine installations containing skeet and target practice ranges, and an average size of 6 acres per site, PAHs within clay targets at skeet ranges are a major concern for the Department of Defense (DoD). The DoD recognizes its responsibility to protect the public from potential hazards associated with military munitions, and constituents as a result of training and testing activities conducted on past, current, and future military lands. Under the Munitions Response Program (MRP) and Resource Conservation and Recovery Act (RCRA), as well as Federal and DoD regulations (32 CFR Part 119 and 45 CFR Parts 260–266 and 270) both active DoD installations as well as Base Realignment and Closure (BRAC) installations are required to evaluate total encompassed acreage of a munitions response area (MRA) and provide a cleanup plan. Under these regulations debris from skeet and trap shootings are classified as munitions solid waste and subject evaluations and clean up. Level of clean up required is based on degree of ecologic and human health hazard, which is evaluated based on total chemical concentration rather than what would be bioavailable within a contaminated substrate. By applying these regulations and estimated potential acreage with contaminated soils, skeet and target practice ranges could feasibly represent a multi-million dollar environmental liability for the DoD. For example, at least 35 of the 60 US Naval Installations have at least one skeet range (more than one is common) and average size is 6 acres. Current cost estimates of per site cleanup within the Southeast Region of the Country are \$100/CYD. This would equate to roughly \$1M per site for the remedial manager to excavate the entire 6 acres to the required 1ft, if required.

The primary driver of remediation decisions at these sites is often human health risks due to the presence of lead from expended munitions rounds and soil-associated PAHs derived from the historical use of PAH-containing binder materials (e.g., pitch) in the clay targets. Clay targets contain approximately 30% binder (Baer et al., 1995; ITRC, 2005) and can range in concentrations of total PAHs from 3,000 to 40,000 milligrams per kilogram (mg PAHs/kg skeet). However, presence of PAHs often drive the remediation decisions at these particular skeet impacted sites as current clean up criteria are much more stringent for PAHs versus presence of lead. For example, current lead cleanup criteria in the South East (Region 4) ranges from 400 mg/kg (residential) to 1,400 mg/kg (industrial). Current posted PAH clean up criteria in the South East (Florida) (based on Benzo (a)

Pyrene equivalent value) is 0.1 mg/kg (residential) and 0.7 mg/kg (industrial) respectively (EPA, 1996; 2006).¹ Under these clean up criteria it would be very difficult to apply an average or 95% UCL to PAHs, in order to demonstrate a site meets cleanup goals without doing a complete acreage excavation.

2.2 PAHS IN SKEET

2.2.1 Bioavailability of PAHs in skeet

Site-specific cleanup levels for PAH-impacted soils are often based on risks of incidental consumption of soil and clay target fragments by humans and wildlife. PAHs associated with clay targets are presumed to be less biologically available than PAHs derived from other sources (and therefore less likely to affect humans and other organisms at similar concentrations) because the PAH molecules are tightly bound to the clay target molecules, reducing the probability of PAH molecules leaching out of the clay target material and impacting the surrounding environment. Research has shown the availability of clay target-derived PAHs is much lower than the regulatory default of 100%. For example, Xia et al. (2016) found PAHs in soils containing skeet sorbed much more strongly to soils (i.e., low availability and mobility) compared to PAHs associated with other contamination sources such as oils and solvents. Magee et al. (2014) confirmed the low bioavailability of clay target PAHs using a mammalian in vivo feeding study in which mice were fed rodent chow with (1) clay target fragments mixed with native soil and (2) pure benzo(a)pyrene (BaP)² in solvent. The known concentration in the rodent chow (consumed by the mouse) was compared to the concentrations of BaP metabolites excreted by in the mouse (as measured in mouse urine), and this was then used to calculate the relative bioavailability (RBA) of the clay target BaP compared to the solvent BaP. An RBA of 12% to 60% (relative to 100% as the pure BaP in solvent) was observed with concentrations of BaP in soil of 0.1 to 183 mg/kg. As a final example, a mammalian study of industrially-derived pitch with RBA as low as 47% as determined with excretion of parent PAH in rat feces for concentration of BaP in soil of 12 mg/kg (van Schooten et al., 1997 as cited by Ruby et al. (2016)³).

2.3 PAH-SKEET SITES

2.3.1 Incorporating Relative Bioavailability at PAH-Skeet Sites

It is clear from prior research that low PAH bioavailability for soils impacted by clay targets should be considered for purposes of avoiding overly protective risk assessments and unnecessarily stringent remediation targets. Default risk assessment models that assume 100% PAH bioavailability result in unnecessary remediation, inflating cleanup costs at DoD clay target sites, which can range from the several hundred thousand to millions of dollars per site. For example, applying the range of RBAs cited by Magee et al. (2014) of 12% to 60% to a hypothetical total BaP risk-based threshold in

¹ However, it should be noted that the EPA recently updated their oral risk factor for BaP from 0.0073 mg/kg to 1.0 mg/kg (EPA, 2017) which would presumably raise required cleanup criteria to more the 1-2 mg/kg range during the next base permitting cycle.

² Of the 16 priority pollutant PAHs evaluated in soil investigations, BaP has the highest carcinogenicity and often drives remedial goals at PAH-contaminated soil sites.

³ Note: Ruby et al. (2016) did not specifically include clay target studies.

soil of 1.1 mg/kg (1×10^{-5} , EPA 2017), would result in less stringent cleanup values of 1.8 to 9.2 mg/kg (i.e., $1.1 \div 12\%$, $1.1 \div 60\%$). Increasing the total BaP cleanup level at sites by accounting for bioavailability could result in significant cost savings for the DoD, as cleanup costs are approximately \$100 per cubic yard. Within the SouthEast Region alone the Navy has 12 sites slated for cleanup with estimated costs at \$1M or more per site. Inclusion of RBA in the risk assessments could result in savings of greater than \$500,000 to several million per site at each site (Schoolfield, 2016).

2.4 PAH RBA APPROACH

There is no default RBA value for BaP because RBA values vary on a site-specific basis. The most robust approach for quantifying mammalian digestive bioavailability is to develop RBA estimate using a mammalian feeding trial; however, such studies are expensive for contaminated sites, particularly those with multiple skeet ranges (e.g., \$50,000 to \$100,000 or more for each skeet range) and time consuming (requiring many months) to conduct. Rapid and inexpensive approaches for quantifying RBA estimates and/or BaP availability in soil are needed. Such approaches could be used as surrogate approaches for animal testing or provide useful screening information for when animal tests would potentially be useful. The objective of this tasking was an evaluation of two such surrogate bioavailable fraction measurements: 1) Physiologically Based Extraction Tests (PBET) that extract PAHs from soil using a simulated digestive matrix and 2) determination of freely-dissolved (C_{free}) concentrations of PAHs in soil as indicated by a commercially-available polyethylene passive sampling device.

One main technical objective of this research is to evaluate PBET and passive sampling approaches for assessing chemical availability for application to BaP risk assessments of PAHs in soils impacted by clay targets. The approaches were evaluated for measuring the availability of BaP using clay target-impacted soils previously used in an *in vivo* study with mice (Magee et al., 2014). This allowed PBET and passive sampling results to be directly compared with biological data and RBA estimates. Using the empirical relationships derived from the PBET and passive sampling results and the *in vitro* biological results, additional clay target-impacted soils were evaluated using PBET and passive sampling to predict BaP bioavailability/RBA estimates without the need for animal testing.

2.5 RBA EVALUATION METHODOLOGY

To establish an empirical relationship between chemical availability measures (PBET and passive sampling) and measured mammalian bioavailability in PAH-impacted soils, both *in vitro* and *in vivo* assay measurements were made on PAH contaminated soil samples (derived from clay targets). Five soils were obtained from DoD clay targets range soils (samples G1 to G5, Table 1). The *in vivo* assay was a mouse feeding study with clay target soils in food and was referenced from Magee et al. (2014). *In vitro* assays were PBET and passive sampling, as described below.

2.5.1 PBET Approach and Relationship to RBA

PBET is an *in vitro* assay to simulate ingestion, digestion (stomach), and other digestive and excretion processes (intestines) on soils. In the approach, soil is combined with a high protein matrix (mixture of glycine, pepsin, bovine serum albumin, and porcine bile and pancreatin) used to simulate saliva, gastric juice, duodenum juice, and bile. After the PBET extraction process, the matrix is centrifuged for analysis of PAHs in the supernatant, which are assumed to be available for uptake. *In vitro* assays are less expensive than mammalian feeding trail studies, which can be tens to hundreds

of thousands of dollars per site. PBET costs much less than *in vivo* tests, at approximately \$1,500 per sample, and is thousands to tens of thousands of dollars less than *in vivo* assays on a per sample basis.

2.5.2 Passive Sampler Approach and Relationship to RBA

Passive sampling is another approach for measuring availability of chemicals in soil, and passive sampling results have been shown to correlate well with dermal uptake of PAHs in soil (Xia et al., 2016). Passive samplers measure freely-dissolved concentrations in soil (C_{free}), providing a value that is analogous to a soil porewater or activity measurement in soil. Passive samplers are generally sorbents such as polyethylene (PE) sheeting that are exposed to a soil slurry, allowing the sorption of available PAHs by the PE. After the exposure process, the PE is removed from the soil and the PAHs sorbed in PE are then extracted and analyzed. Passive sampling is less expensive than *in vivo* assays such as mammalian feeding trail studies. Passive sampling measurements cost approximately \$1,000–\$2,000 per sample (including analysis cost), thousands of dollars to tens of thousands less than *in vivo* assays on a per sample basis, similar to PBET.

3. EXPERIMENTAL METHODS

3.1 OVERVIEW

As summarized above, experimental methodologies utilized under this effort enabled us to: first better understand the environment and difference between contaminant of concern vs. background; and second provide us with tools to more accurately assess area of concern. The battery of tools generated to accomplish our goals can be broken down into three subgroups: (1) tools to assess soils and skeet material (the environment); (2) assays to determine bioaccessibility or bioavailability; and (3) tools to recalculate relative bioavailability (RBA). Methods used and/or developed under each subgroup are outlined below.

3.2 STUDY SITES-SOIL COLLECTION (TASK 1)

The soils used to evaluate the bioavailability of PAHS in soil were five clay target-impacted soils previously used in both a pilot in vivo study with mice as well as a site specific feeding trial (Hoeger and Magee, 2011; Magee et al., 2014; Arcadis, 2017).

Additionally, 8 soils were analyzed using PBET and passive sampling to demonstrate the approach and highlight conclusions with regards to evaluating risks using the default method (using total BaP in soil) versus the PBET and passive sampling approaches. A brief description of each site and methods used to collect and process the soils from each site for both chemical and in vitro/ in vivo analysis are described below.

3.2.1 General Soil Sampling Method and Processing for Analysis

For all but the Laredo and Foster soil samples, surface samples were collected down to 2 feet, both at the impacted location as well as from a “reference location” outside the impacted area. For long since de-activated sites, determination of impacted and non-impacted area was based on historic photographs as well as base restoration program manager’s guidance/knowledge of the site. In addition to soil, both unspent and fragmented skeet material found present at the impacted site were collected into an unused 1 gallon zip lock bag. Soil samples were collected in unused/new glass containers (2 liter) and/or zip lock bags (1gallon) and both soil and skeet material were stored at room temperature in a temperature and light controlled room until samples could be processed. Prior to homogenizing and separating samples for analysis by methods described below, soil samples were sieved to remove any organic material, pebbles and rocks. Soil samples were then homogenized and separated into 1 liter jars and sent to both commercial (ALS Environmental) and non-commercial (University of Illinois) analytical labs for PAH and carbon analysis. In addition, a portion of the soil sample and skeet material (1 liter jar) was provided to University of Illinois to conduct soil chemistry and skeet fingerprinting analysis. The remaining sieved soil and skeet material (~150 g soil) was stored at 4°C until analyzed under Task 2 methods (in vitro assays).

For the Laredo and Foster site locations, both horizontal and vertical profile samples were collected (ITRC 2017; Arcadis 2017). For the horizontal profile, 79 surface soil samples were collected in a grid pattern to generate a composite sample, following a multi-incremental sampling (MIS) approach. For the vertical profile 3 samples were collected down to 5 ft and placed in 5 gallon buckets. A single 5 gallon bucket was collected from a nearby un-impacted area for reference soil. Soil samples from each site were cleaned (sieved), homogenized, further portioned by size for chemical analysis and use in the feeding trials, in a manner similar to other samples collected under this effort. For full details regarding processing of samples for use in feeding trials the authors refer the reader to Arcadis 2017; Magee et al 2014; Hoeger and Magee 2011.

3.2.2 Army Feeding Trial Soils

This effort leveraged data from an Army Corp of Engineers (PM: Anita Meyer) funded animal feeding trial for its in vivo in vitro comparison (Task 3 &4). As part of this comparison the contractor conducting the feeding trial for the Army Corp of Engineers, Arcadis provided this study team a total of 5 skeet impacted soil samples (250 g) with a range of PAH concentration; which was a subset of soils that had been used in the animal feeding studies; for analysis by PBET and passive sampling approach. A brief description of study sites is provided here. For full detail of sites and animal feeding trial studies the authors refer the reader to Arcadis, 2017; Magee et al 2014; Hoeger and Magee 2011; and ITRC 2017.

3.2.2.1 Site 1 Laredo

The former Laredo Air Force Base (LAFB) was an active military base between 1942 and 1947 and between the 1950s /60s until its final deactivation in 1974. It was located on the northeast side of Laredo Texas and was a little over 2,000 acres. The shotgun range (SGR) appeared to be operational from ~1942 – ~1960s when a portion of it was re developed as a golf course, however an additional pistol range had been constructed further north of the site and was operational until the early 1980s. Estimated impacted acreage based on descriptive information and area maps (<https://www.swf.usace.army.mil/Missions/Environmental/Formerly-Used-Defense-Sites/Laredo/Map/>) is 70 acres.

Figure 18 provides an approximation of both base boundaries and SGR impact area. This site was part of the pilot feeding trial study (Arcadis, 2017; Hoeger and Magee 2011) and is being evaluated under the FUDs program. The author refers the reader to Arcadis (2017) and Hoeger and Magee (2011) for additional details regarding this site. Further site investigation documentation related to this site can also be found on the USACE website.



- Source: Google Earth Maps, accessed October 2018

Figure 18. Former Laredo Air Force base. Red line approximately outlines the base. Light blue box approximates impact area of firing range.

3.2.2.2 Site 2 Foster (Animal Feeding Trial Soil)

The former Foster Air Force Base (FAFB) is located 6 miles east of Victoria TX. It was inactivated in 1959 and is now the Victoria Regional airport. This site was being investigated for remediation under the Formerly Used Defense Site program (FUDS) by the US Army Corps of Engineers (USACE). FAFB had one operational skeet shooting range used by the Army for training from 1941–1945. Figure 19 provides an aerial image of the former range as well as an outline of the half circle firing points and range span. The average concentration BAP detected at this site was 34.5 mg/kg with a maximum detected concentration of 657 mg/kg. There was one soil sample taken from the west side of the airfield (un-impacted area) with concentration < 0.12 mg/kg. Information provided here, in addition to a case study report of this site, along with data from the feeding trial used in calculating the site specific relative bioavailability, was included in the recent ITRC report titled “Bioavailability of Contaminants in Soil: Considerations for Human Health Risk Assessment. BCS-1” (ITRC 2017).



- Source: Image copied from ITRC report 2017; USACE, 2016 original cited source
- Red area - represents the half circle firing locations as well as the range fan

Figure 19. Former Foster Air Force Base skeet shooting range location.

3.2.3 Additional Demonstration Sites

At least two core soil samples (skeet impacted and non-skeet impacted soil) were collected from each of the below sites. Skeet fragments, if visible at time of collection were also collected from each of these sites. In total 6 soil samples from 4 different sites, encompassing a range of soil types, were evaluated using methods developed under Task 1 and 2 of this effort.

3.2.3.1 Marine Corp Air Station (MCAS), Miramar, CA

MCAS Miramar is located approximately 13 miles north of downtown San Diego and 4 miles east of the Pacific Ocean, encompassing a property that is about 12 miles long from east to west and about 4 miles from north to south, totaling ~23,065 acres. The eastern portion of the installation (East Miramar) is primarily undeveloped and is used for military training and operational exercises, warehousing, and supports the military need for encroachment and access control. MCAS Miramar currently has two former skeet ranges.

Figure 20 is a photo of site soil collected from MCAS Miramar for this effort. Note the insert include in this Figure shows broken up skeet fragments visible on the surface of the soil. In total, both sites are estimated at about 25 acres and are contaminated with significant concentrations of

munition constituents (MC) and PAHs. Both sites were operational for an approximate 25 year time frame. These sites are undergoing investigation to determine a remedial strategy and the final remedial action alternative will be impacted by the presence of threatened and endangered species present on site.



- Picture taken by Kara Sorensen May 2018.
- Insert and arrow show close up of broken skeet material visible throughout the site

Figure 20. MCAS Miramar, CA Site 19C.

3.2.3.2 Naval Base Guam, Guam (NAVFAC Marianas)

Located on Apra Harbor, near the Pacific Ocean. The island itself is 30 miles long with the base occupying about 38,000 square acres. In 2009 it was combined with Andersen Air Force Base to form the Joint Region Marianas. Several World War II (WWII) area skeet ranges are present on Guam. Soils from two separate former Skeet ranges (Spanish Steps and Finegayan) were collected and processed for use under this effort.

3.2.3.2.1 Site 1 Spanish Steps

The Spanish Steps Trap and Skeet Range Figure 19 site is located along the northern escarpment of Orote Point, also known as Point Udall, approximately 500 feet above mean sea level, on the southern side of Apra Harbor within Naval Base Guam. The site encompasses the firing area of three former small arms ranges, two skeet ranges and one trap range as well as an area for associated range maintenance. In total this site covers approximately 54 acres with the fringing Reef and associated

islands constituting approximately 12 acres of the site. The fire trajectory for these former ranges extends over a 140-foot escarpment and in the area below, north toward Apra Harbor, and east and west of the firing locations. Historically, the site was used as a recreational trap and skeet range from the 1940s into the 1970s, with all three ranges deactivated in the late 1980's.



Image provided by NBG Restoration manager Vincente Ada, May 2018

Figure 21. Spanish Steps Skeet Range.

3.2.3.2.2 Site 2 Finegayan

The second location, Finegayan Trap and Skeet range (Figure 22) was formerly a communications annex and contained a small arms range (rifle). The site is located in the northern limestone structural province of the island. The site itself is on the edge of a plateau with steep cliffs that drop down to a narrow coastal lowland. Total acreage for this site is ~3 acres and was operational for about 20 years.



- Yellow circle shows Finegayan sampling location
- Image created in Google earth, May 2018

Figure 22. Finegayan Skeet and Trap Range, Naval Base Guam, Guam.

3.2.3.3 Naval Air Station Whiting Field, Milton Florida

Naval Air Station Whiting Field occupies approximately 12,000 acres and is located in northwest Florida (Figure 23). It is one of two primary pilot training facilities. There are two listed historic skeet range and skeet/gunnery range sites located at Whiting which are about 12 to 18 acres respectively. The gunnery and skeet range site had 3 firing positions and was operational from ~1940s to the 1970s, whereas the Skeet firing range had 1 firing position and was operational from the 1970s and closed in 2000. At least one of the two sites is now listed as a Superfund site for high levels of lead and BaP and is currently undergoing evaluation. Estimated cleanup cost are ~2.5M. BaP concentration at this site averages 406 ppb.



- Image source from Google Earth, accessed October 2018

Figure 23. Naval Air Station Whiting Field.

3.2.4 Soil Characterization (Task1)

Representative soils from each site were analyzed for PAH concentrations and soil characteristics (including total PAH, particle size, total organic carbon, and black carbon). Analytic methods used under this tasking were as follows:

3.2.4.1 PAH Analysis

Soil samples were treated following general NOAA Status and Trends (NS&T) methodologies (Peven & Uhler, 1993). Samples were stored frozen and thawed prior to sub-sampling for extraction and moisture determination. Polycyclic Aromatic Hydrocarbons and Petroleum Biomarkers were analyzed in accordance to standardized methods. In short, sample extracts, prepared as described above, will be analyzed by gas chromatography with mass spectrometry (GC/MS), following a modified EPA 8270D (US EPA, Method 8270D - Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 1998), in which the mass spectrometer is operated in the selected ion monitoring (SIM) acquisition mode to quantify the diagnostic PAH compounds.

3.2.4.2 Particle size, total organic carbon, and black carbon

Representative soil samples from each site were separated into particle-size fractions by dry sieving in accordance with standard methods (ASTM D6913 / D6913M – 17). Clay targets were also collected from each site, and were either in their original, pristine state or larger fragments collected from shooting-range sites.

3.2.4.2.1 Elementary C, H, N analysis (CHN).

CHN analysis was performed to determine total carbon content in contaminated soil samples, as well as in pure skeet targets. The total C content was obtained using a CHN analyzer.

3.2.4.2.2 Carbon content analysis (CCA).

Because of the predominance of calcite (CaCO_3) and dolomite (MgCO_3) and organic carbon in the pure skeet material, an analysis of C content on the samples was undertaken. Because the source of C could be either organic (e.g., skeet targets) or inorganic (carbonates), the samples were acid treated with 0.67 M HCl at room temperature for 12 h to remove the carbonates, then washed with DI water, freeze dried, weighed, and analyzed for total carbon (TC) using a CNS analyzer. Organic carbon (OC), inorganic carbon (IC), and black carbon (BC) contents was then calculated for each sample.

3.2.4.2.3 Total organic content (TOC).

Subsequent to acid digestion of carbonates, a portion of organic matter in soil samples was determined gravimetrically after thermal treatment in a furnace at 440°C overnight.

3.2.4.2.4 Water content (WC).

An amount of the physically adsorbed water on the soil and skeet surfaces was determined gravimetrically after drying at 105°C overnight.

3.2.4.3 Geochemical Analysis of Soil and Skeet (Assessing Fingerprint potential)

While we did not anticipate a strong correlation of bioaccessibility/bioavailability with soil geochemistry, representative samples of skeet impacted soils from each site were analyzed to determine skeet and soil differences between sites. A more detailed description of methodologies used can be found in Appendix B (Stucki et al 2016)

3.2.4.3.1 X-Ray Diffraction (XRD).

The mineralogical characteristics of powdered and oriented patterns of the skeet and soil samples were determined using Scintag XDS2000 X-Ray Diffraction Machine (XRD) and analyzed by Jade 9 software for XRD mineral identified and quantified.

3.2.4.3.2 Infrared spectroscopy (FTIR).

Infrared (IR) spectra in the middle infrared (MIR) region (4000 cm^{-1} – 400 cm^{-1}) were collected in transmission mode using a Fourier Transform Infrared (FTIR) spectrometer from MIDAC Corp, model M2000 (Westfield, Massachusetts, USA) equipped with DTGS detector. Spectra were collected at a resolution of 2 cm^{-1} , and 128 raw data scans were collected and combined for each sample (prepared as KBr pellets using 0.5 mg of the sample powder mixed with 200 mg KBr, pressed up to 109,267 PSI, and heated overnight at 150°C to minimize water content in the sample and KBr). The raw spectra were processed using the OPERANT LLC Essential FTIR software package.

3.2.4.3.3 Mössbauer spectroscopy.

Mössbauer spectra were recorded on a Web Research, Inc. (Edina, Minnesota) spectrometer equipped with a Janis model SHI-850-5 (Janis, Inc., Woburn, Massachusetts) closed cycle low temperature cryostat, with transducer operated in a triangular waveform mode with a 50 mCi ^{57}Co source dispersed as 10 wt. % in a thin Rh foil (Ritverc, Inc. St. Petersburg, Russia). Calibration of the velocity scale is performed by measuring the magnetic hyperfine field (B_{hf}) of a 7 mm thick $\alpha\text{-Fe}$ foil at the sample temperature (Stucki et al., 2014). The data are analyzed by the WinNormos-for-

IGOR (Brand, 2008) extension software pack within IGOR Pro (WaveMetrics Inc., Lake Oswego, Oregon, USA) using Lorentzian line shapes (Murad and Cashion, 2004).

3.2.4.4 Weathering analysis

To assess weathering conditions that might occur in the field, we conducted a simulated weathering process by using both particle distribution and ASE methods to extract PAHS from two different particle sized samples (small pieces vs. fine powder) of equal weights (0.005 g). The results provided different leaching rates of particle size fractions of skeet. Differences in the leaching rates were evaluated to determine a qualitative effect of weathering (particle break down) in the soil.

3.2.4.4.1 Particle size distribution.

Samples were separated into particle-size fractions by dry sieving. Seven clay targets were received in their original, pristine state and were gently ground in an agate mortar and pestle to particle sizes that passed through a 230 mesh sieve, which gave particles of <60 μm equivalent spherical diameter (esd). The soils, both contaminated and uncontaminated, were not ground but were sieved directly into four particle sizes, namely, > 500 μm esd (+35 mesh), 125 – 500 μm esd (-35 mesh, +120 mesh), 60 – 125 μm esd (-120 mesh, + 240 mesh), and < 63 μm esd (-230 mesh). The “+” and “-” signs indicate the particles retained by (+) or passed through (-) the selected mesh-size sieve. In selected samples (WF and BF), the <2 μm fractions were removed by dispersing the sample in distilled water, then fractionating by centrifugation methods according to Stoke’s Law (Jackson, 1956). This < 2 μm fraction was then freeze dried.

3.2.4.4.2 ASE.

A Dionex ASE 200 extractor and extraction solvent mixture of acetone and dichloromethane (1:1) was used. Samples were weighed and transported to the cylindrical body of extraction cells (22mL RESTEK, Inc., City, State, USA) and sealed by diatomic mesh (200,000). The top and bottom of the cell’s body were closed by metal caps. The extraction procedure was performed at 100°C. The accuracy of the extraction, concentration and cleanup steps was determined using a volatile internal standard Terphenyl-d14 Surrogate (D-14). On the top of the extraction cell and before each concentration and cleanup steps a 25 μL portion of 50 ppm D-14 was spiked in. The final concentration of D-14 in all extracts prepared for the GC-MS measurement was 1 ppm. A calibration curve was plotted by using the 16 target PAH standards of prepared concentrations 0.5, 1, 3, 5, 7 up to 10 ppm. All solvents and chemicals (except analytical standards) were of HPLC grade and delivered by Fisher Scientific, Chicago, IL, USA.

3.2.5 PAH Contaminated Site Database (Task 1)

The primary focus of this task was to generate a project working document to guide the projects research development by having a central database of Navy and Marine Corp installation’s skeet impacted sites. The database was built in an Excel spreadsheet format. Most of the information was compiled from information found in the Naval Installation Restoration Information Solution (NIRIS) database. NIRIS was queried based on region and data was compiled to summarize information from each installation/range, which might be useful in future work. Database query efforts focused on such questions as:

- Approximately how many skeet ranges are there in the Navy/Marine Corps?
- What kind of regulatory clean-up levels are being required?
- What are typical PAH contamination levels at sites?
- How are the sites being remediated?

- Where can I find more information about a particular site?
- What sites are good candidates for us to collect soil samples?

As this work was conducted and completed by the prior project manager (Mr. William Major, NAVFAC EXWCC) who retired in December of 2013, an exact description of methods used, and the QA/QC process, is not available.

3.3 IN VITRO ASSAY DEVELOPMENT (TASK 2)

The main goal of this task was to develop and calibrate a low cost, robust, and rapid in vitro method that simulates mammalian digestion to evaluate RBA of PAHs in soil from skeet-impacted sites. The methodologies presented in this section describe the development and optimization of the two in vitro assays (i.e. Physiologically Based Extraction Test (PBET) and the PE passive sampler assay) used as extraction and sampling tools for this effort.

3.3.1 PBET Methodology and Details

As described above, PBET is an in vitro assay to simulate mammalian ingestion, digestion (stomach), and other digestive and excretion processes (intestines) to predict the bioavailability of a target chemical (PAHs) from a substrate (soil) to humans. Methods used were based on methods described previously (Xia et al 2016, Ruby et al 2016, Duan et al., 2014) but optimized for samples containing skeet impacted soils and BaP as the index chemical. The key steps of the PBET assay performed in our laboratory were: (1) gastric solution (GS) preparation; (2) PAH extraction by sample incubation in GS at 37°C; (3) stabilization of extracted PAHs in GS by solvent (acetone: dichloromethane); and (4) shipment to the analytical lab for mass spectrometry analysis of PAH mixture. All steps of this approach, starting from PBET matrix preparation to simulated gastric extraction conducted in our laboratory are described in detail below.

3.3.1.1 Supplies cleaning procedure

All items including glassware, stir bars and centrifuge cups used in the PBET assay underwent a thorough sterilization procedure prior to use. Glassware preparation procedure was as follows:

1. soaking in 1% soap solution
2. rinsing with deionized (DI) water
3. soaking in 5% HCL
4. 2nd rinse with DI water to remove any HCL.
5. Glass material such as cups and stir bars were rinsed with acetone or methanol and dried at room temperature.
6. As a final step, all glassware was baked overnight or for a minimum of 4 hours at 500°C to ensure sterilization.

3.3.1.2 Gastric solution (GS) preparation

Batch GS was prepared using DI water (17.8 mΩ-cm) filtered through a Barnstead E-pure water purification unit. The following compounds were added into the flask containing 950 mL filtered water: 30 mL HCl, (trace analysis grade, Fisher Scientific), 30.03 g glycine (Sigma-Aldrich), 1 g porcine pepsin (Sigma-Aldrich), 2.5 g porcine mucin (Sigma-Aldrich), 5 g bovine serum albumin (Fisher Scientific), and 3 mL sunflower oil (Sigma-Aldrich). Using stir bar plate, all components were mixed thoroughly until all added chemicals were completely dissolved, generally 2-6 hours.

After homogenization, additional DI water was added to bring total volume to 1 L. Lastly, the pH was adjusted to 1.5 ± 0.05 by drop-wise addition of HCl.

3.3.1.3 Sample preparation (spiked/positive control and soil samples)

- **Soil Sample:** Prior to analysis, soil samples were weighed, homogenized and stored at 4°C until added to gastric solution. A subset of soil was removed using pre-cleaned glassware, placed on an un-used weighing dish and weight adjusted (on a calibrated Mettler Toledo scale) to a final weight of 0.5 ± 0.05 g. Weighed soil sample was then placed into a 100 ml pre-cleaned glass centrifuge tube (Pyrex) to serve as the reaction vessel and 50 ml GS was added. Soil samples were prepared and analyzed in triplicate.
- **Spiking solution:** Standard solutions were prepared and analyzed in triplicate using certified PM-612-1 mixture standard 16 EPA priority polycyclic aromatic hydrocarbons (PAH) in dichloromethane as matrix (Agilent, Formerly ULTRA Scientific Inc.). The list of analytes components is presented in the Table 3. A copy of the chemical quality assurance is provided in the appendix for reference.
- Positive control/spiked samples.

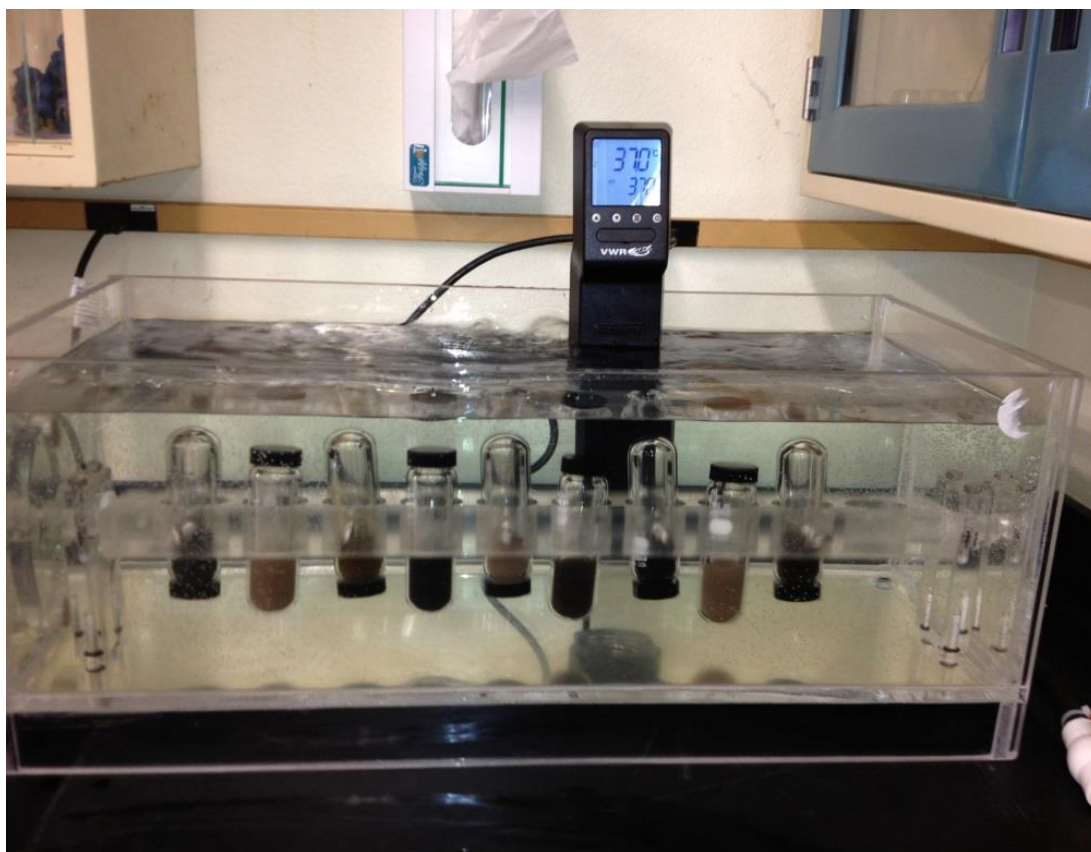
Table 4. List of PAH mixture components in the dichloromethane matrix.

Analyte	Concentration, $\mu\text{g/mL}$
naphthalene	1000
pyrene	100
fluorine	200
anthracene	100
phenanthrene	100
fluoranthene	200
acenaphthene	100
acenaphthylene	200
dibenz[a,h]anthracene	200
indeno[1, 2, 3-cd]pyrene	100
chrysene 1	100
benzo[k]fluoranthene	100
benzo[b]fluoranthene	200
benzo[a]pyrene	100
benz[a]anthracene	100
benzo[ghi]perylene	200

To prepare a 10–20 ppb spiked sample, 30 μL of the PAH control mixture was removed from the ampule and added to a flask containing 299.97 mL of GS with stirring. Solution was mixed using stir plate and stir rod.

A 1–2 ppb spiked sample was prepared by removing 15 ml of solution from the 10–20 ppb solution and immediately added to 135 mL of GS. The 1–2 ppb spiked sample was then mixed as above. Note, as the concentration of naphthalene is much higher than the other PAHs present in the analytical standard mixture (Table 4), targeted naphthalene concentration was 100 and 10 ppb in 10–20 ppb and 1–2 ppb spiked samples, respectively. Each spiked sample was then separated into 3, 50 mL volumes and placed in pyrex incubation tubes.

All samples, spikes (positive controls), blanks (GS-only negative controls), and soil samples were then sealed using a Teflon-lined screw cap (Cole Parmer Inc.) and placed in a head over tail heated tumbler (Figure 24) for a 1 hour rotation at 370C. Note the water in this device was previously equilibrated to 370C. Each soil or spiking sample was processed in triplicates and negative control tubes with GS only were duplicates.



- Test done at at NIWC Pacific, formerly SSC Pacific, SPAWAR
- The device is operated at 370C temperature control and rotation is end-over-end at 28 rpm.
- The device conception was utilized from Drexel and Brattin (Drexel and Brattin, 2007)
- Constructed was done by Oregon State University Mechanical Shop (2012).
- Photo source: SSCPAC 2016

Figure 24 Head over Tail Heated Tumbler (extraction device) for PBET procedure.

3.3.1.4 Extraction procedure

Following the initial 1 hour incubation/rotation period, all sample incubation tubes were removed and opened for pH adjustment and addition of remaining reagent as follows:

The pH for each sample vial was adjusted to 6.5 ± 0.5 using 50% w/w sodium hydroxide (NaOH) (Sigma-Aldrich) or HCL (Fisher) by dropwise addition using disposable Pasteur pipets. The pH was determined using a calibrated pH-meter (Oakton 11 series, Eutech Instruments).

Following pH adjustment 100 ± 5 mg porcine bile (Sigma-Aldrich) and 25 ± 5 mg porcine pancreatin (Sigma-Aldrich) was added to each sample vial. Vials were then re-capped and placed into heat tumbler for an additional 4 hour rotation at 37°C .

Following the 4 hour extraction period, all sample incubation tubes were removed from the tumbler and centrifuged for 10 min at 1500 rpm. An optional method was to keep tubes in vertical upright position of rack in tumbler for 10–15 minutes to allow solid particles to settle to the bottom of the incubation tube. Post centrifugation, the liquid phase of each sample was transferred into certified (based on EPA requirement) pre-cleaned glassware (I-Chem A Nalgene Company) and placed on a balance for weighing and recording.

While samples were being centrifuged, a solvent mixture containing 1:1 analytical grade acetone (Fisher Scientific) and analytical grade dichloromethane (DCM) (Sigma-Aldrich) was prepared.

Post weighing of samples, a maximum volume of 1:1 acetone/DCM solvent mixture was added to each sample bottle to avoid the presence of air head space and stabilize the samples during shipping. The total volume of supernatant with solvent mixture was recorded to calculate dilution factor. Each vial was tightly closed with Teflon screw cap and placed in horizontal shaking basket at room temperature and vortexed overnight at 350 rpm.

The following morning, all sample vials were removed from the horizontal shaker and packed into an insulated cooler or thermosafe box with blue ice and shipped overnight by FedEx to a commercial lab for chemical analysis (ALS, Kelso, WA). Results of chemical analyses were delivered back in Excel format. A summary of data is provided in Appendix A. A summary of the PBET process is provided in Figure 25.

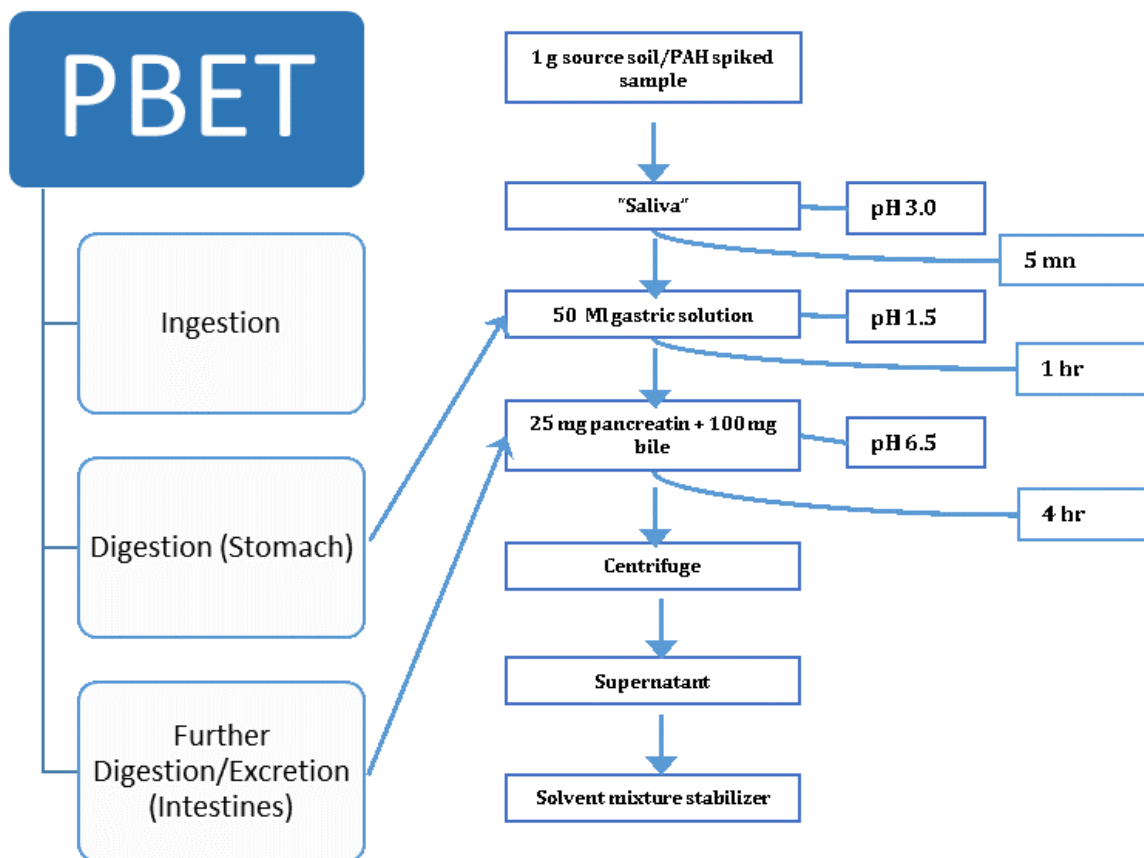
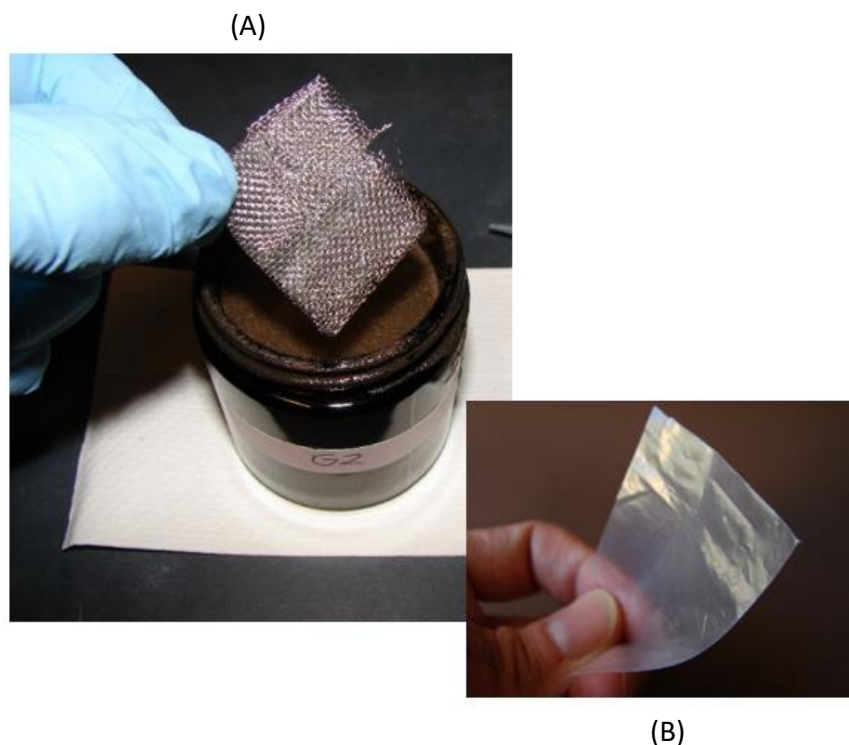


Figure 25. Physiologically Based Extraction Test (PBET) Methods Flow chart.

Passive Sampler Methodology and Details

A custom passive PE sampling device (SP3™) comprised of a 3 × 3 centimeter (cm) sheet of 17 micrometer (μm) thick low density PE housed in a stainless steel mesh envelope was used to provide a measure of concentrations of freely-dissolved (C_{free}) PAHs in soils (Figure 26). The PE was spiked with Performance Reference Compounds (PRCs) to correct for non-equilibrium conditions within deployment time and consist of rare polychlorinated biphenyl (PCB) congeners assumed to: 1) not be present in the media in which the samplers were deployed, or 2) present at concentrations so low as to be inconsequential, i.e. not affect calculations involving PRCs, and insignificant compared to the concentration of other C_{free} PCBs in the media sampled. The PRCs used for this project were PCB-14, PCB-36, PCB-78, PCB-104, PCB-121, PCB-142, PCB-155, PCB-184, PCB-192, and PCB-204. In the laboratory, 80 grams, dry weight (g, dw) of soil was exposed to SP3™ sampler in a 4-ounce amber glass jar with approximately 75 mL of deionized water (to reach a moisture content of 60-90%) containing a microbial inhibitor to inhibit breakdown of PAHs. Amber jars containing the soil slurry and PE were continuously rotated at 20 rotations per minute (rpm) at room temperature for 14 days. After exposure, the samplers were placed in opaque sample bags and shipped cool (4 degrees Celsius) to the analytical laboratory (Test America) for extraction and analysis for PRC PCBs and PAHs by modified method EPA 8270. The concentrations of PRC PCBs in PE (Appendix A, Table A2) were used to calculate the PRC elimination rate and percentages to steady state reached for each PAH analyte during deployment. The percentage of steady state was then used to calculate the C_{free} concentration of PAHs (Appendix A, Table A3).



- Passive sampler is polyethylene based) in stainless steel mesh (A)
- Source material used to construct the mesh sample shown in (A) is shown in (B)

Figure 26. Example of SP3™ Passive sampler.

3.4 PAH CHEMICAL ANALYSIS

3.4.1 Passive Samplers

After exposure, the samplers were placed in opaque sample bags and shipped cool (4 degrees Celsius) to the analytical laboratory (Test America) for extraction and analysis for PRC PCBs and PAHs by modified method EPA 8270. The concentrations of PRC PBCs in PE (Appendix A,

Table A2) were used to calculate the PRC elimination rate and percentages to steady state reached by the PAH analytes during deployment. The percentage of steady state was then used to calculate the C_{free} concentration of PAHs (Appendix A, Table A3).

3.4.2 PBET

Post overnight solvent mixing samples were removed from horizontal shaker and packed into an insulated cooler or thermosafe box and shipped overnight on ice by FedEx to a commercial lab (ALS, Kelso, WA) for extraction and analysis of PAHs using standard EPA methods. Initial extraction procedure was completed ideally within 72 hours of receipt of sample to avoid sample degradation and stabilize sample for analysis. Extraction of samples was conducted by a modified method EPA 3520C in a silica gel and analyzed for the 16 priority PAHS using EPA method 8270D SIM.

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4. RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF SKEET IMPACTED SOILS (TASK 1)

As mentioned in section 1, many factors impact bioavailability of PAHs bound to both skeet material and soils. The main driver for this task was examine some key variables through differentiating skeet & soil particles and characterizing those particulate material, as well as examining how the environment can alter key variables through normal environmental process such as weathering. This section provides a summary of our findings for the four main subtasks: (a) collect soil samples from a variety of Navy skeet ranges and analyzing concentrations of PAH in skeet material, skeet impacted soil and non-skeet impacted soil; (b) determine means of differentiating skeet material from soil and “fingerprint” the most widely used types of clay; (c) conduct a baseline analysis of skeet material under “weathered” conditions; and (d) determine manufacturers and varieties of targets used (Database) on Navy ranges. Excluding soil collection, the majority of this task was performed by either the University of Illinois or prior project manager Bill Major (EXWC). As such, only a brief overview of results and major conclusions is presented here. A more detailed discussion of results for this section can be found in the two University of Illinois Summary reports included in the appendix section (Appendix B).

4.1.1 Sample Collection and Chemical and Mineralogical Analysis

A total of 25 field/site specific soil samples (henceforth referred to as field soils) including non-contaminated site reference soil (henceforth referred to as SRS soil) and 5 feeding trial soil samples (henceforth referred to as FT soils) were collected. Eighteen of the 25 field soil samples received a full chemical and mineralogical analysis whereas the remaining 6 were analyzed only for PAH content. Of the 5 FT soil samples, 3 of the 5 samples received a full chemical and mineralogical analysis, whereas the remaining 2 samples were analyzed only for PAH and carbon content. The decision to not conduct a full suite of analysis on all 25 field samples and the 5 FT samples was driven primarily by funding limitations. Table 5 provides a summary field soil samples collected, including sample type, range/collection site, and state.

Additionally, all 5 of the FT soils and 8 of the 25 field soils were analyzed by PBET and passive sampling under tasks three and four below (section 4.3, page77), results of which will be discussed in section 4.3 of this report.

Initially 3 reference soils were also purchased (Research Technology Corp) and examined for use as positive control. Only one reference soil, CRM141 received a full mineralogical and chemical analysis. Use of reference soils as a control was later dropped due to lack of homogeneity within batch material and inconsistencies discovered early on under the SERDP effort (See Lowney et al 2017). Samples purchased are provided in Table 6. As these samples were dropped from the study results will not be discussed here but data from the U of I report can be found in Appendix B

In addition to soil samples both field site skeet fragments (henceforth referred to as field skeet) and unused, e-bay purchased skeet targets (henceforth referred to as e-bay skeet) were also collected. A total of 8 field skeet samples and 7 e-bay skeet samples were collected. All 7 e-bay skeet received a full chemical and mineralogical analysis, but due to limitations in funds only 3 field skeet samples received a mineralogical and chemical analysis. 1 of the 3 field skeet samples was also used in the weathering analysis. A summary of skeet and reference soil samples including source and location is provided in Table 6.

Table 5. Field Soil Samples.

SSC ID	Collection Date	Sample Type	Base/Range	Location
BF-SA-01	12/10/2012	Skeet Range	NAS/ Bronson Field	Florida
BF-BG-01		Ref Soil		
BF-SF-01		Skeet Fragment		
WF-SA-01	12/10/2012	Skeet Range	NAAF /Whiting Field	Florida
WF-BG-01		Ref Soil		
WF-SF-01		Skeet Fragment		
AAFB-17A-C	8/28/2014	Skeet Range	Andersen AFB / IR Site 17 (remediated?)	Guam
AAFB-17A-SF		Ref Soil		
AAFB-17A-U		Skeet Fragment		
FNG-TSF-C	8/28/2014	Skeet Range	Naval Base Guam/ Finegayan	Guam
FNG-SF		Skeet Fragment		
FNG-U		Ref Soil		
FNG-HSF-C		Skeet Range		
MCASM-19-C	12/10/2014	Skeet Range	MCAS Miramar / IR Site 19	California
MCASM-19-SF		Skeet Fragment		
MCASM-19-U		Ref Soil		
FN-NBG-SF	4/9/2014	Skeet Fragment	Naval Base Guam/ Finegayan	Guam
FN-NBG-C		Skeet Range		
FN-NBG-R		Ref Soil		
AAFB-SR-ASA	4/9/2014	Skeet Range	Andersen AFB / IR Site 17	Guam
AAFB-RS-U		Ref Soil		
AAFB-SF		Skeet Fragment		
ST-SR-NBG	4/9/2014	Skeet Range	Naval Base Guam/Spanish Steps	Guam
ST-RS-NBG		Ref Soil		
ST-NBG-SF		Skeet Fragment		

- Notes: unless otherwise specified in table, Field sample ID was in two general formats (1) Base-site ID-type material-number sample (if more then one) or (2) site ID- type material. For example: AAFB-17A-SF (Andersen Air Force Base-IR Site 17- Skeet Fragment).

Table 6. Skeet and Reference Soil Samples.

SAMPLE ID	Collection Date	Sample Type	Source	Base/Range	Location
BF-SF-01	10-Dec-12	fragment	Field	NAS Bronson Field	Florida
WF-SF-01	10-Dec-12	fragment	Field	(former) NAAF Whiting Field	Florida
AAFB-17A-SF	28-Aug-14	fragment	Field	Andersen AFB / IR Site 17	Guam
FNG-SF	28-Aug-14	fragment	Field	Finegayan Naval Base Guam	Guam
MCASM-19-SF	10-Dec-14	fragment	Field	MCAS Miramar IR Site 19	California
FN-NBG-SF	9-Apr-15	fragment	Field	Finegayan Naval Base Guam	Guam
AAFB-SF	9-Apr-15	fragment	Field	Andersen AFB IR Site 17	Guam
ST-NBG-SF	9-Apr-15	fragment	Field	Spanish Steps Naval Base Guam	Guam
Skeet1 (S1)	N/A	clay target	EBay	EBay purchased (yellow center)	N/A
Skeet2 (S2)	N/A	clay target	EBay	EBay purchased (vintage blue rock)	N/A
Skeet3 (S3)	N/A	clay target	EBay	EBay purchased (Black and white center)	N/A
Skeet4 (S4)	N/A	clay target	EBay	EBay purchased	N/A
Skeet5 (S5)	N/A	clay target	EBay	EBay purchased (white flyer 409)	N/A
Skeet6 (S6)	N/A	clay target	EBay	EBay purchase (white flyer 28)	N/A
Skeet7 (S7)	N/A	clay target	EBay	EBay purchase (blue rock)	N/A
CRM141	N/A	reference soil	commercial	research technology Corp (purchased)	N/A
HS5	N/A	reference soil	commercial	research technology Corp (purchased)	N/A
SRM	N/A	reference soil	commercial	research technology Corp (purchased)	N/A

- Notes: unless otherwise specified in table, Field sample ID was in two general formats (1) Base-site ID-type material-number sample (if more than one) or (2) site ID- type material. For example: AAFB-17A-SF (Andersen Air Force Base-IR Site 17- Skeet Fragment).

4.1.1.1 Mineralogical and Carbon content Analysis

The mineralogical and carbon content of both skeet and soil samples was determined using Mössbauer spectroscopy and x-ray diffraction. Overall there was an increase in organic C and PAH in the contaminated soils compared to the background soils and the level of skeet contamination had little impact related to particle size distribution however it did play a significant role in PAH concentration. This section will provide some general findings and examples of results. A summary of mineralogical and TOC analysis, both site (field and SRS) as well as FT soils for all samples analyzed is provided in Table 7. For a summary of mineralogical and TOC analysis in Skeet samples (field and EBay) please refer to the University of Illinois final reports included in appendices.

Table 7. Summary of Mineralogical and Chemical Analysis for Soil Samples.

Soil ID	Uofl ID	Mineralogical Composition		Total Organic Content	Total PAH Target
		main mineral	admixture	[%]	[mg/kg]
BF-BG-01	same	quartz	illite, illite/smectite, feldspar, calcite, dolomite	0.32	0.6
BF-SA-01	same	quartz	calcite, illite, illite/smectite, feldspar	0.45	101.95
WF-BG-01	same	quartz	illite, illite/smectite, feldspar, calcite, dolomite	0.39	0.45
WF-SA-01	same	quartz	dolomite, calcite	2.49	296.34
AAFB-17A-U	1	calcite	quartz, corundum, boehmite	18.6	0.15
AAFB-17A-C	2	calcite	quartz, corundum	32.9^	331.5
FNG-TSF-U	3	calcite	quartz, gibbsite	13.5	1.62
FNG-TSF-C	4	calcite	quartz	10.4	832.2
FNG-MSF-C	5	gibbsite	boehmite, hematite, goethite, dolomite, calcite	26.4*	2360.5 ^l
MCASM-19-U	6	quartz	corundum, albite, microcline	9.3	21.21
MCASM-19-C	7	quartz	muscovite/illite, corundum, albite	4	168.8
AAFB-RS-U	8	calcite	quartz, corundum, muscovite/illite, kaolinite, pyrite	15.4	12.7
AAFB-SR-ASA	9	calcite	quartz, corundum, lead	9.3	151.35
FN-NBG-R	10	calcite	quartz, corundum, lead, gibbsite	12.6	4.89
FN-NBG-C	11	calcite, dolomite	quartz, corundum, lead, gibbsite	22.5	7828.45*
ST-SR-NBG	12	calcite	dolomite, quartz, corundum, aragonite	15.1	12081.23^
ST-RS-NBG	13	calcite	dolomite, quartz, corundum, aragonite	26.7 ^l	64.57
G1	same	quartz	no data	6	0.6
G2	same	quartz	dolomite, calcite, illite	11.5	101.95
G3	same	quartz	smectite, mica	6.15	0.45

- Note: highlighted cells indicate 3 highest concentrations of TOC and Total PAH concentration. Darkness of color from darker to lighter shows highest to lowest or (^) high, (*) medium, and (l) low.

SKEET

Carbon analysis of the clay targets (“skeets”) revealed a significant amount of carbon in the samples, as would be expected. The inorganic carbon (dolomite MgCO_3 and/or calcite CaCO_3) content averaged ~ 28 wt. % and the organic content ~ 16 wt. % (Figure 27). Figure 28 and Figure 29 show the Mössbauer spectral analysis for all 7 Ebay skeets. With the exception of Skeets 4, 5 and 6, which contains a quartz signature not seen in other EBay Skeets, the 7 EBay skeet compositions were generally similar.

The presence of skeet had little effect on the particle-size distributions (PSD) in the soils. WF for example contained a larger amount of the finest fraction of $< 66 \mu\text{m}$ at 11 wt. %, whereas the BF was at 5 wt. % (Figure 30).

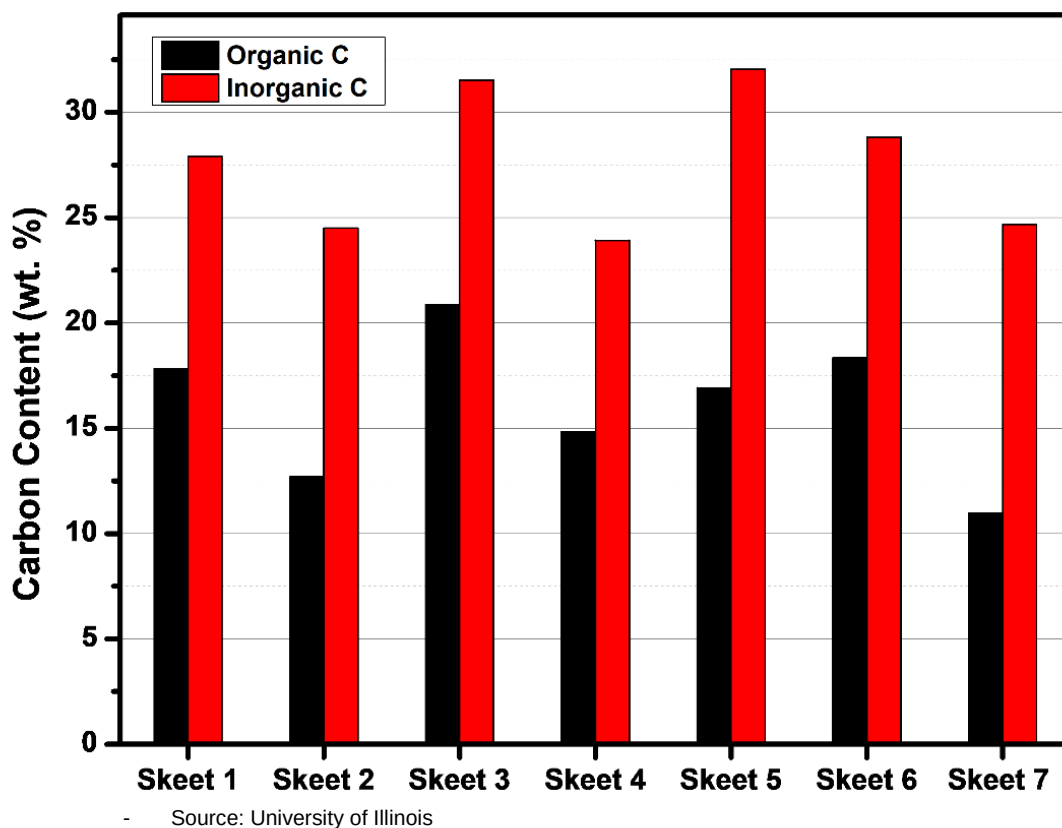
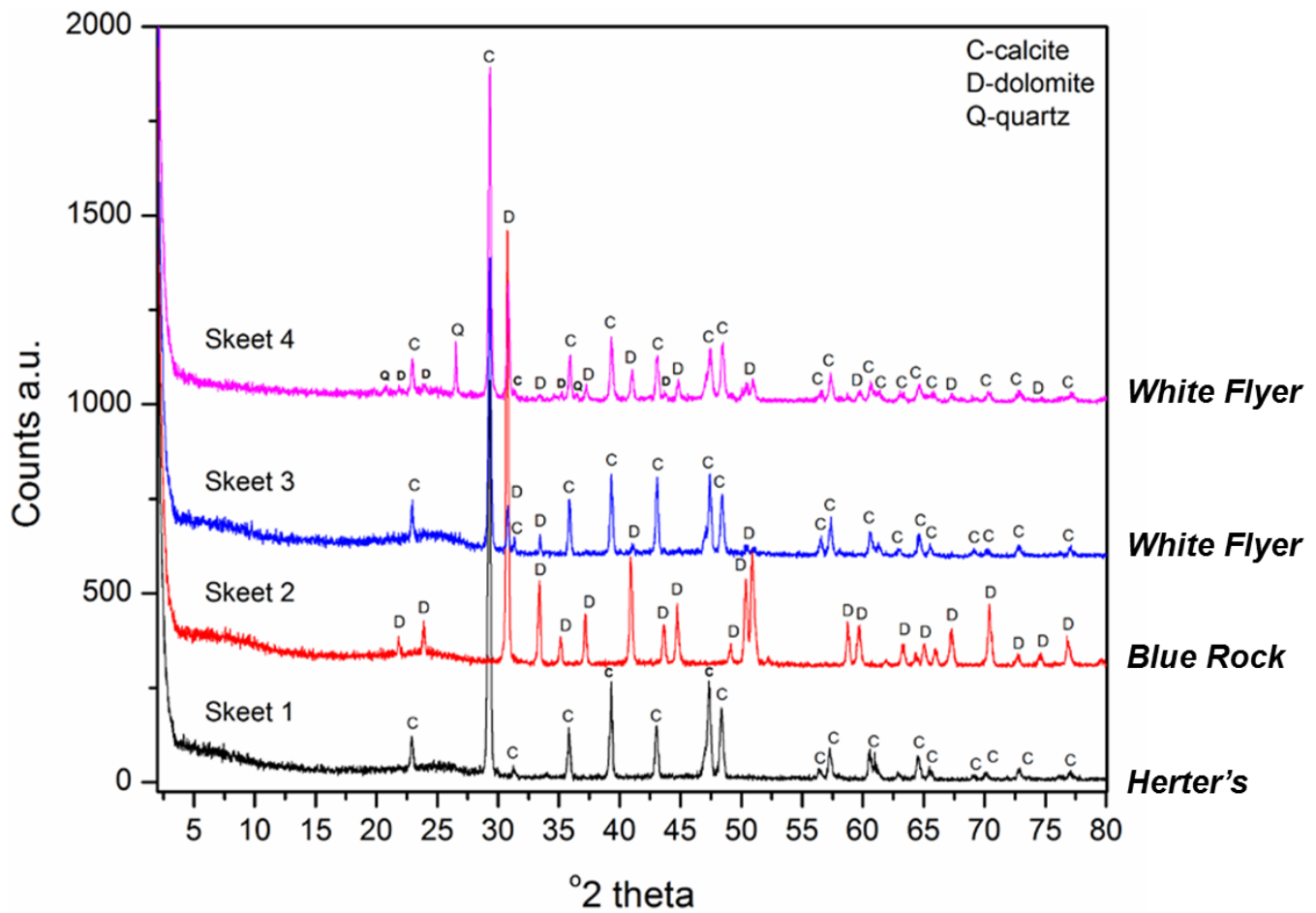
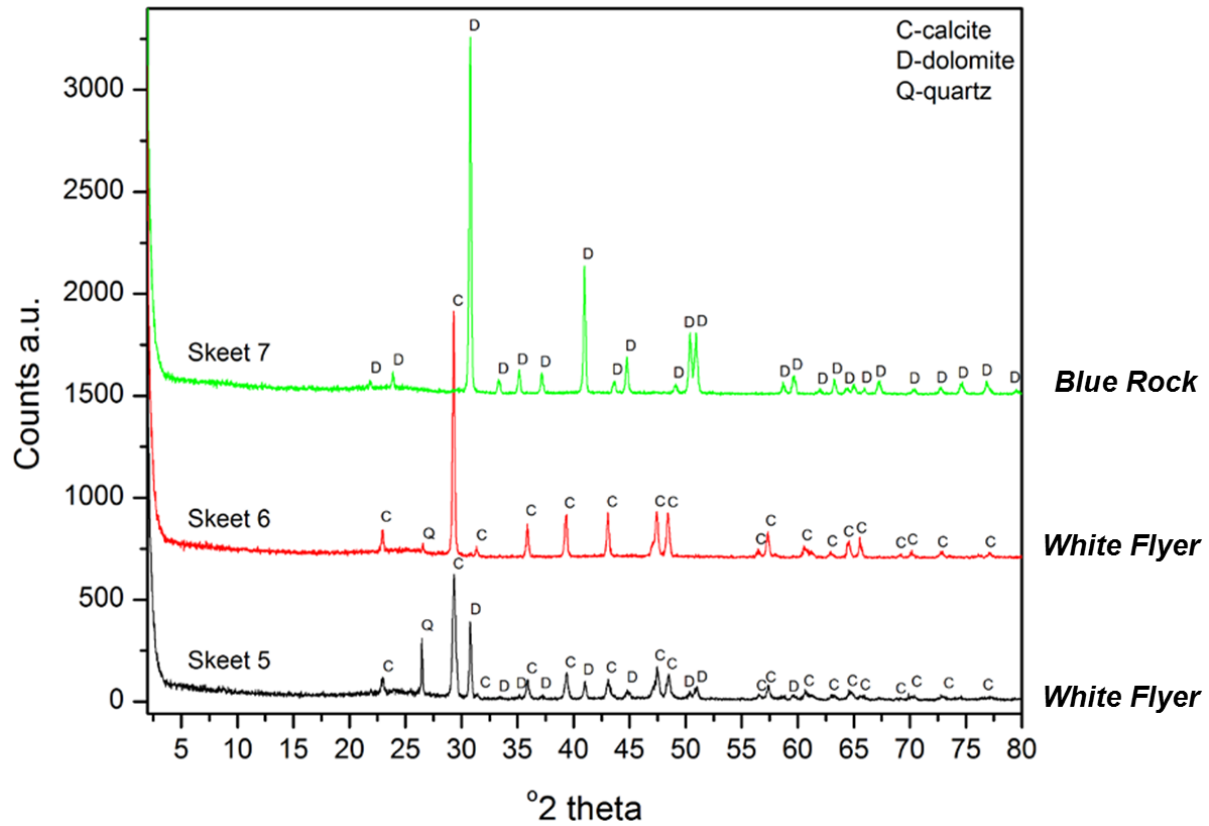


Figure 27. Summary of Total Carbon Content (TOC) for 7 EBay Skeet Samples.



- Image source: University of Illinois
- Brand of skeet target is provided to right of spectra for reference
- Note the presence of quartzite peak near $2\theta = 26.6^\circ$ (marked by Q) in Skeet 4 which was not present in the other skeets. Skeet 4 was also the only skeet sample that exhibited a significant mixture of all 3 mineralogical signatures (C, D, Q)

Figure 28. Mössbauer spectroscopy Carbon/Mineral Analysis of EBay Skeets 1–4.



- Image source: University of Illinois
- Brand of skeet target is provided to right of spectra for reference.
- Note the presence of quartzite peak near $2\theta = 26^\circ$ (marked by Q) in Skeets 5 and 6 (much smaller intensity), which was not present in the other skeets.

Figure 29. Mössbauer spectroscopy Carbon/Mineral Analysis of EBay Skeets 5–7.

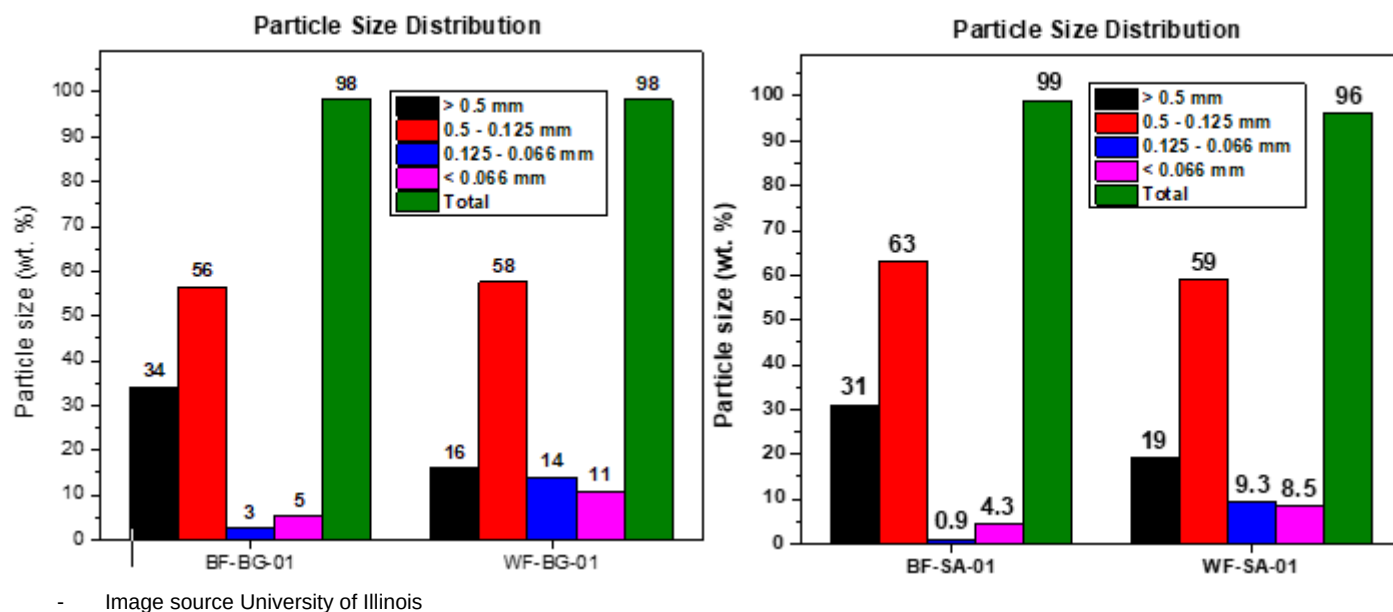
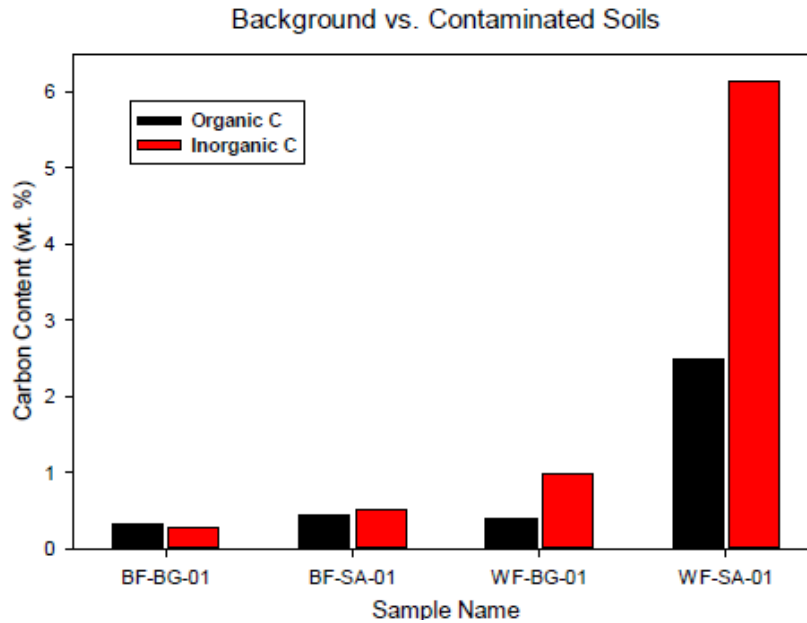


Figure 30. Soil Particle Distribution from two sites in both background soil (BG) and skeet impacted soil (SA).

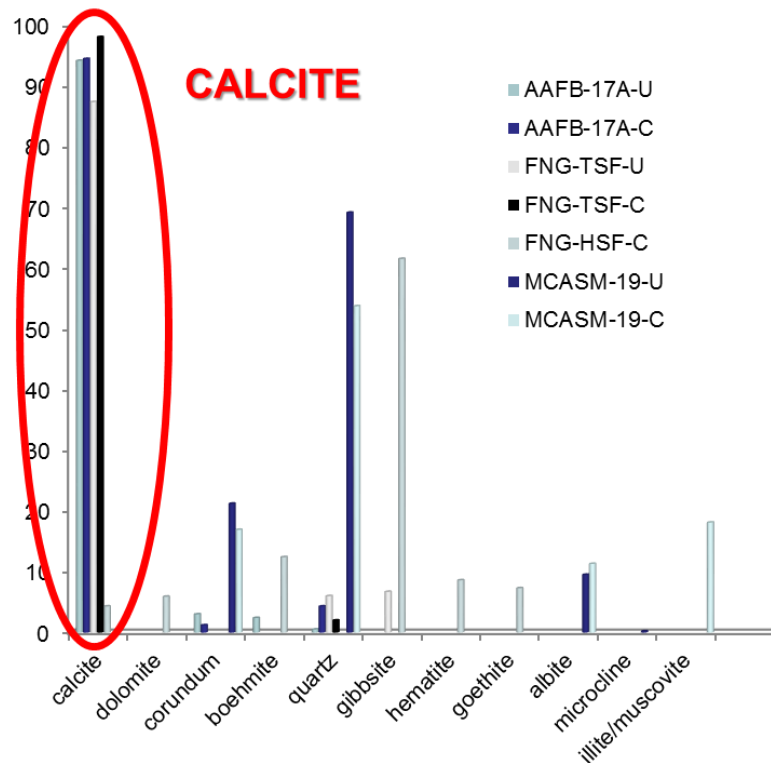
SOIL

In general, carbon content between site field soils in similar locations (Florida) was similar, yet carbon content in uncontaminated soil (SRS soils) vs. contaminated soils typically was higher (Table 7). For example, carbon analysis showed that the organic and inorganic carbon contents of the uncontaminated (background) soils were similar at both the Whiting Field (WF) and Bronson Field (BF) sites. The C content of the contaminated BF soil was rather similar to the background soil (~ 1 wt. %), but in the contaminated WF soil the C content approaches 9 wt. % (Figure 31). Mineralogical difference were not associated with contaminated vs. uncontaminated soils but rather were dependent upon location (region) from which soil was collected and the skeet material present (Table 7). For example, Soils from AAFB-17A and FNG-TSF shooting area ranges, located in Guam, provided similar mineralogical compositions, while soil from MCASM (California) contains different mineral phases. One interesting finding is the presence of Calcite in samples collected from Guam. This mineral was not found present in samples collected in California and Florida (Figure 32). In addition, carbon content also varied by region. California samples had lower level of carbon content than what was measured in samples collected from Guam (Figure 33).



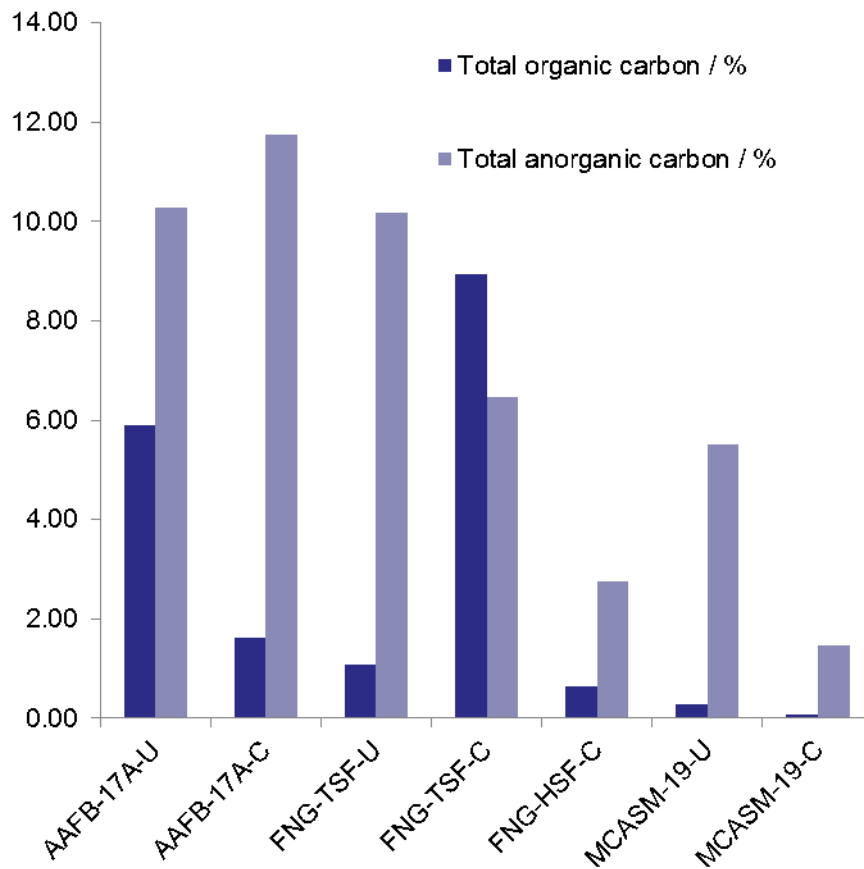
- Image source: University of Illinois

Figure 31. A Comparison of Total Carbon Content (TOC) for 2 Field samples and SRS Soil samples. BG indicates SRS or background soils while SA indicates field soils.



- Note, presence of calcite in Guam samples (red circle) that was not found present in soil samples from California –University of Illinois

Figure 32. Mineralogical Analysis of Field Soils.



- Image source University of Illinois

Figure 33. Organic Carbon Analysis of Field Soils.

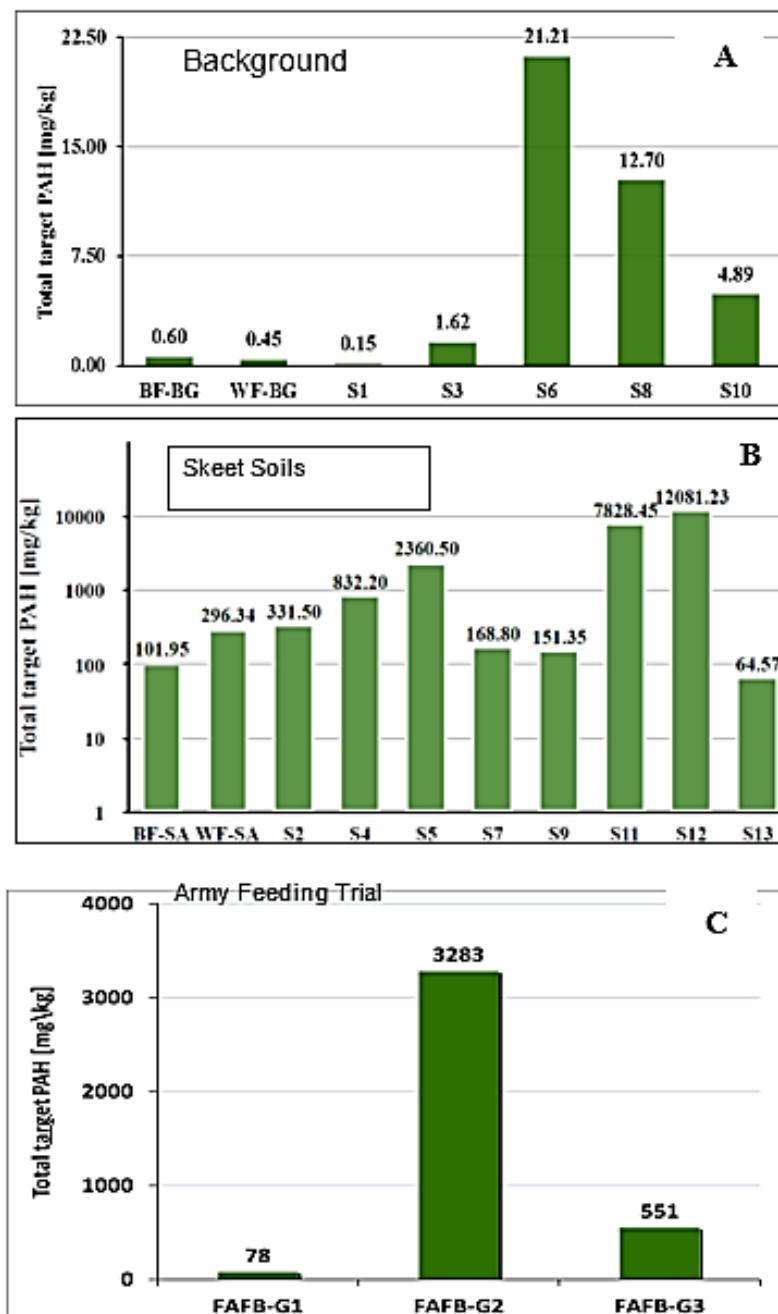
4.1.1.2 Chemical Analysis

Total of 28 soils (contaminated vs. uncontaminated, including 3 FT soils) from 9 skeet ranges on several bases were analyzed. It was observed that PAH content was significantly different in skeet soils vs. background soils and that the majority of PAH material occurs in <66 micron particle fraction of soils. A summary of Total PAH analyzed from each soil is provided in Table 7. A breakdown of individual PAH concentrations measured by soil sample and site can be found in the appendices. Overall general findings, including a few examples will be presented here.

SOILS

The PAH contamination by the skeet was clearly evident from comparing background with contaminated soils (in both the raw soil and the < 66 μm fraction), Figure 34 and 35.

The PAH content of the contaminated WF was greater than that of the BF in the raw soil (296 and 102 mg/Kg soil, respectively), but was slightly less in the < 66 μm fraction (351 and 462 mg/Kg soil, respectively)



- Source: University of Illinois

Figure 34. Total PAH Concentration of Base Soils including reference soils.

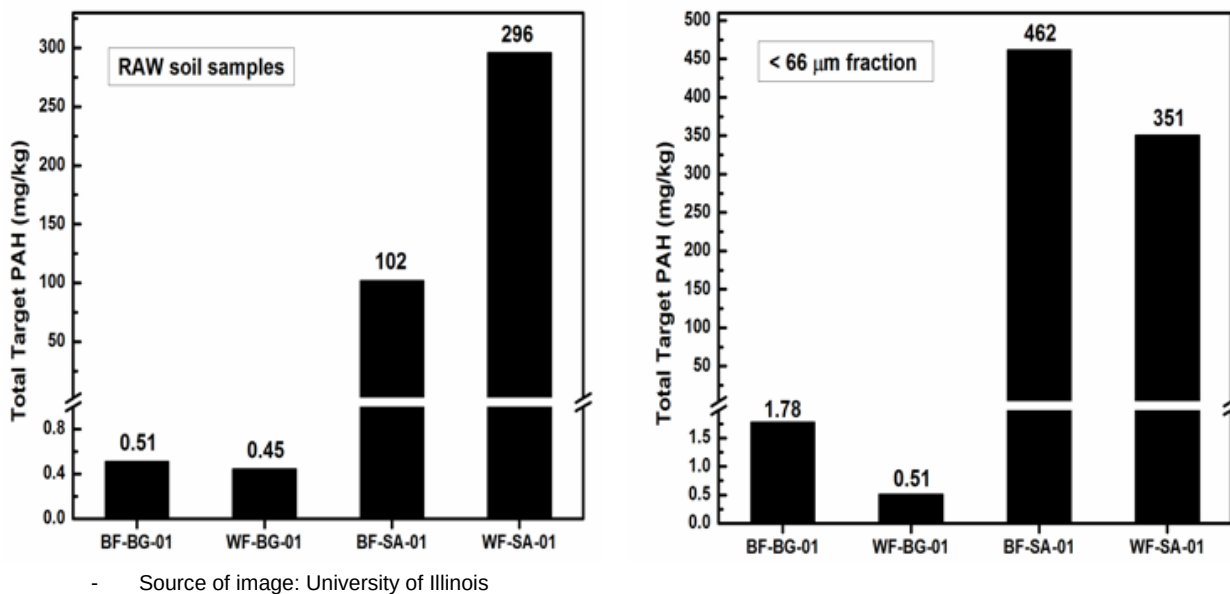
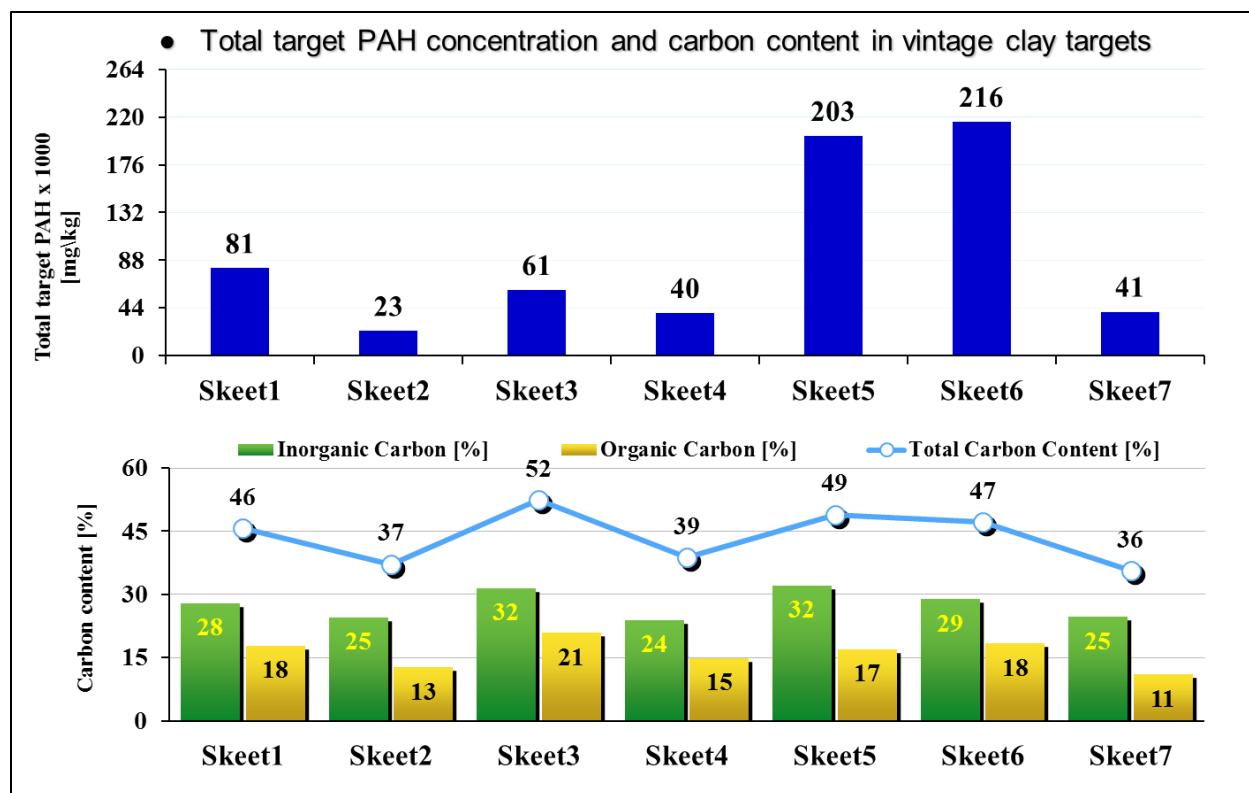


Figure 35. Comparison of Total PAH concentration from two sites.

SKEET

All 7 eBay skeet targets were analyzed for PAHs. All 7 samples showed high concentrations PAH. While TOC content was similar amongst the 7 historic skeet targets analyzed samples 5 and 6 had the highest concentrations of Total PAH (203 mg/kg and 216 mg/kg respectively), while sample 2 had the lowest concentration of Total PAH (23 mg/kg) in Figure 36. As mentioned previously, higher levels of PAH were also evident in skeet impacted field soils (Figure 35). Figure 35 clearly shows that presence of skeet is the driver in higher PAH concentrations measured in field soils. This is also evident when comparing organic carbon, and PAH contents of background (labeled with –BG or –U) with skeet-impacted (labeled with –SA or –C) soils. Notice the sharp increase in organic C and PAH in the contaminated soils compared to the background soils.



- Source of image: University of Illinois

Figure 36. Historic Skeet (EBay Skeet) Total PAH and Carbon Analysis.

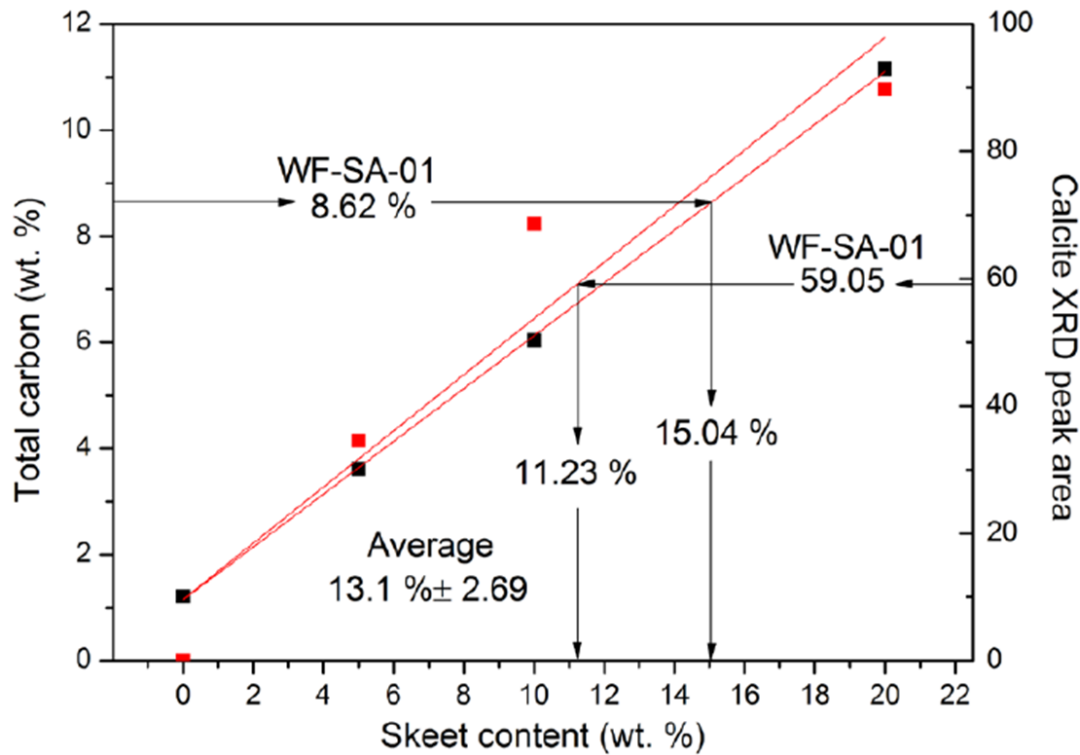
4.1.2 Skeet Fingerprint evaluation

The main focus of this subtask was to determine if it was feasible to identify markers specific to skeet targets to (a) determine presence of skeet as compared to other sources of PAH and (b) determine if it was feasible to distinguish between different manufactures of skeet targets. Overall, with the possible exception of skeet 4, we found that skeet materials are fairly similar in composition and there are significant differences between skeet impacted soil vs. non skeet impacted soil making it feasible to identify signature. However, mineralogical difference, found in the soils, from different bases in different regions of the country vary, thus additional regional analysis would be beneficial to better understand concentration gradients as well as calibrate the analysis tool. A few examples of analysis is presented in this section. A more detailed description of findings and analysis tools can be found in the University of Illinois final reports, included in the appendices.

In order to determine difference and identify potential “unique” signature a complete mineralogical analysis including: chemical, Scanning Electron Microscopy (SEM); X-ray Powder Diffraction (XRD); Fourier Transform Infrared Spectroscopy (FTIR); Differential Thermal (DTA) & Thermal Gravimetric Analysis (TGA); and Mossbauer Spectroscopy was performed on all 7 vintage clay (EBay). This information was then compared to data collected from field soils, reference soils (SRS) and field skeet fragments.

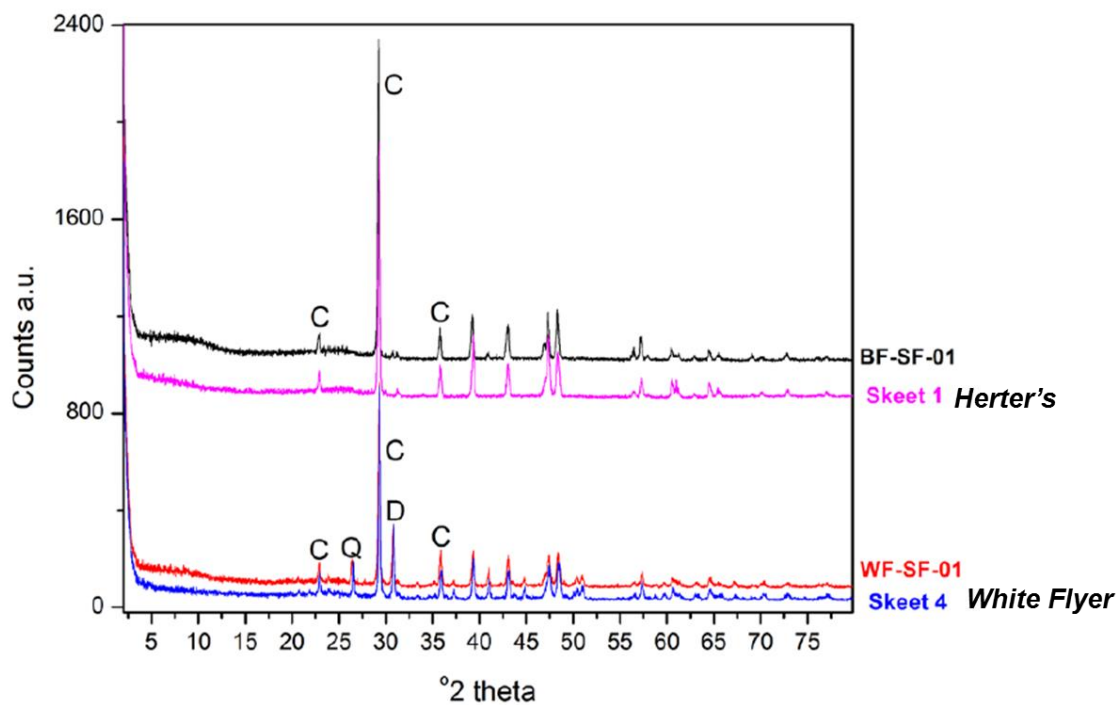
Initial data did indicate it was feasible to differentiate between different skeet types and that PAH content is significantly different in skeet soils/background soils. Spectroscopic signatures for EBay skeet fragments was present above (Figure 27–Figure 29). The most distinguishable difference is between Skeet 4 (presence of quartz, calcite, and dolomite), a white flyer, and the other 6 vintage skeet samples. The high levels of

Calcite found present in all 7 skeet samples appeared to be the one strong linking variable (Appendix B). Based on this the overall mineralogical signature, % of Skeet content, and Total Carbon found in field soil samples was calibrated against a Calcite XRD peak (Figure 37) and known skeet samples (EBay skeet). Figure 38 and Figure 39 shows that skeet material present at Whiting fields most likely is a white flyer, whereas the skeet material found present at Bronson Fields most like is a Herter's.



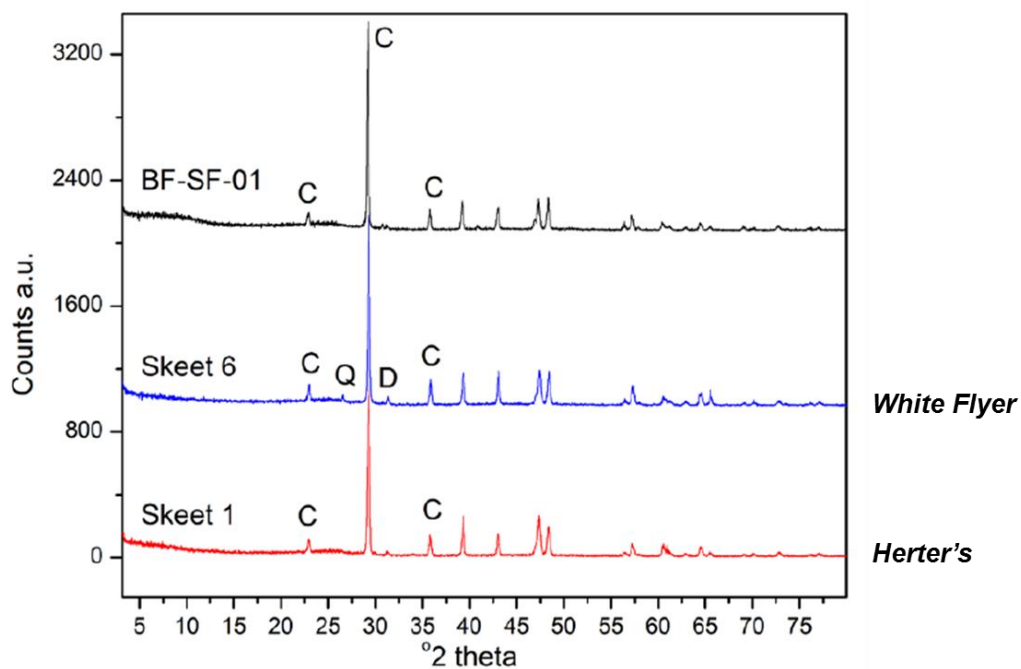
Source of image: University of Illinois

Figure 37. Xray Diffraction Carbon Analysis, calibrated to Calcite comparison of Whitening Field.



- Source of image: University of Illinois
- Brand of skeet target as well Field soil ID is provided to right of spectra for reference

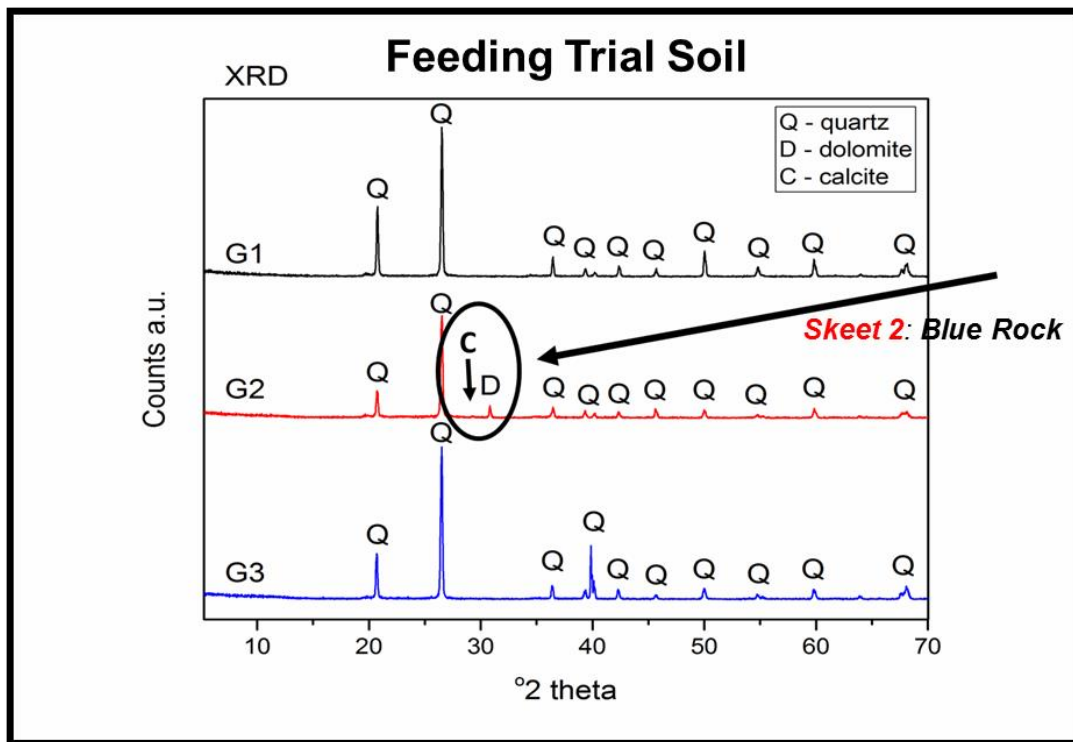
Figure 38. Mössbauer spectroscopy Carbon/Mineral Analysis compared to 2 Field soil samples.



- Source of image: University of Illinois
- Brand of skeet target as well Field soil ID is provided to right of spectra for reference

Figure 39. Mössbauer spectroscopy Carbon/Mineral Analysis compared to 1 Field soil samples.

The need for further regional and concentration gradient calibration became evident when analyzing field samples collected in Guam vs. field samples collected in California, and Texas. As stated above, Skeet material have high levels of Calcite present, Calcite concentrations were either much lower or not present in background soil from California, Texas, and Florida. However, background soils collected in Guam were found to have much higher concentrations of Calcite making calibration of skeet fingerprinting analysis against Calcite not possible for field samples collected in Guam (Figure 32). Further, concentration of skeet material present in sample also impacts reliability of identification/analysis potential. Identification of skeet signature in field soil samples collected from Foster Air Force Base (FT Soil-G1, G2, and G3) FAFB proved difficult to identify due to the overall lower levels of contamination (Total PAHs < 1 mg/kg for G1 and G3 Table 7). Some signature was detected Table in G2 (~100 mg/kg). The results revealed that 33.6 % of dolomite (calibration via Skeet 2), 4.9 % of calcite (calibration via Skeet 1), and 4.0 % of calcite (calibration via Skeet 3) making Skeet 2 (Blue Rock) the more likely candidate as type of Skeet used at this site (Figure 40).



- Source of image: University of Illinois

Figure 40. Identification of Skeet Signature in FT Soils.

4.1.3 Skeet weathering analysis

The main focus of this task was to ascertain if certain environmental processes (such as weathering) would impact the amount of PAH that could become available in the soil. Due to limitation of funds a mechanical weathering analysis was only conducted using one vintage skeet (Skeet3) and two field soils. A PAH weathering comparison was performed by breaking skeet fragments (both intact (vintage clay target #3) and non-intact (weathered fragments collected in field) into smaller particle sizes and comparing PAH

content measured at two skeet ranges (Whiting Field and Bronson Field). A brief summary of findings is provided here. Additional details can be found in the appendices (Appendix B).

Figure 41 shows that by mechanically “weathering” skeet material to a fine powder (smaller particle size) a higher concentration of PAHs is observed. A similar pattern was observed when applied to a specific field soil (separation of soils into smaller fraction) the same trend is observed.

Figure 42 shows the effect of particle size (weathering) on PAH extractability (logarithmic scale) from vintage clay target #3 (Skeet) and from contaminated Whiting Field soil (WF-SA). A higher concentration of Total PAH is observed in the <0.066 mm fraction of WF-SA field soil. This simulated weathering process was equivalent to increasing the surface area to increase extraction efficiency, something that while theoretically expected, was shown empirically here. How this is best interpreted is in terms of how much could be extracted out of the sample with larger particle size vs a smaller particle size that presumably results from the long term weathering processes, which has similar implications with respect to bioaccessibility and ease of release to organisms during ingestion/digestion. While this analysis is limited, this data indicates that particle size does impact release of PAH from skeet material. PAHs are more likely to be released from smaller particle fractions.

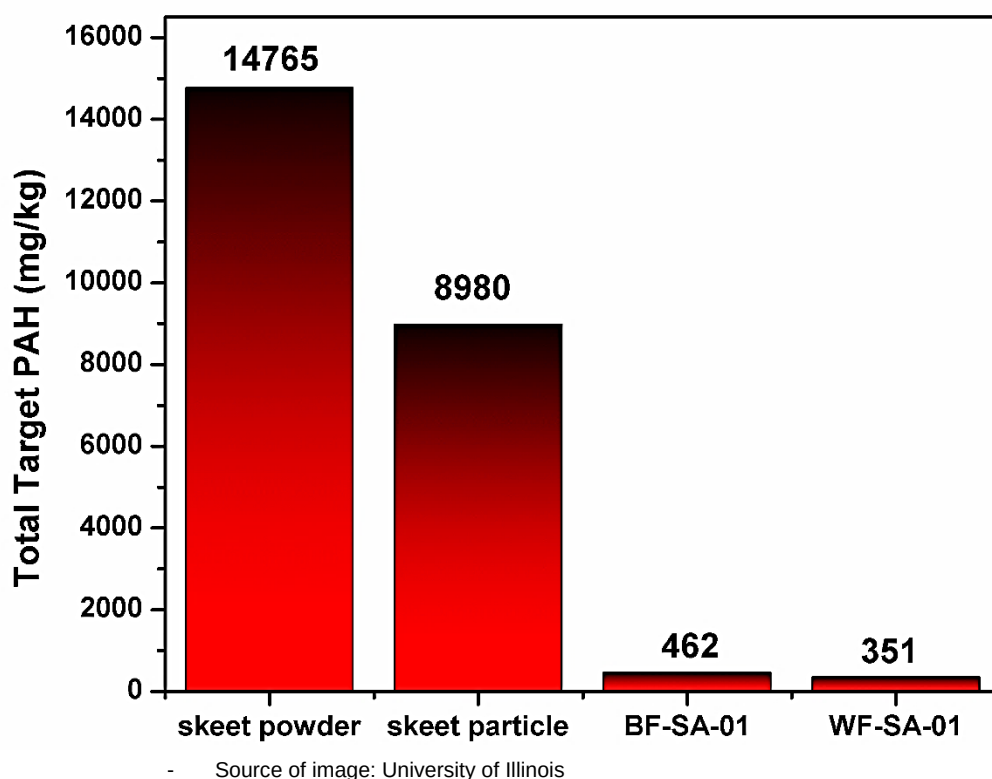
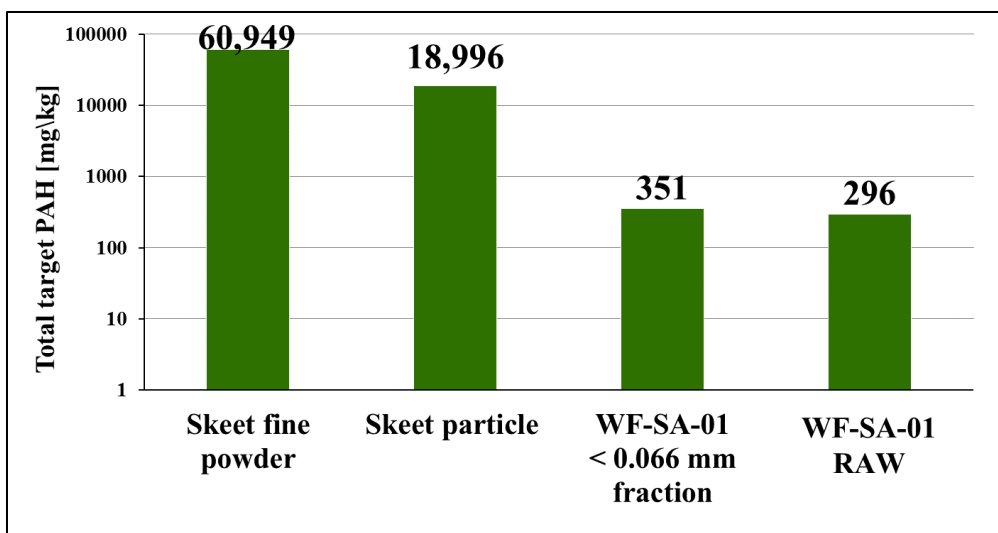


Figure 41. Mechanical Weathering of Vintage Skeet3 (EBay) as compared to skeet from two field soils.



- Source of image: University of Illinois

Figure 42. Mechanical Weathering of Vintage Skeet3 (EBay) as compared to mechanical weathering of skeet fragments at Whiting Field (WF-SA).

4.1.4 PAH contaminated skeet range database

The last subtask under this tasking was compilation of a USN and USMC skeet range database. The Excel spreadsheet database captures ~ 70% of the Navy's skeet ranges with emphasis on closed skeet ranges requiring remediation. Information was collected predominantly from NIRIS database, which represents USN skeet ranges better, meaning the relative information collected from Marine Corps skeet ranges much less. The database was generated by prior project Manager (Bill Major-EXWC) who was unable to complete the database prior to his retirement. Due to limited funding and the costs associated with in vitro assay development, no additional data was added to this file subsequent to Bill Majors departure. Overall, the current format of this database document would make it difficult to use in a quantitative manner, however it does compile useful historic information and potential resources available for many of the Navy historic skeet ranges. General findings were used early on in the development of analytical tools used in this effort, and are described below. A summary spreadsheet of all information compiled/collected is provided in the appendices.

General findings/information compiled and included in the database.

- At least 35 of the 60 US Naval Installations evaluated have skeet ranges
- At least 10 of 18 US Marine Installations evaluated have skeet ranges
- Multiple ranges are common; some have up to 7 ranges per base
- 25 Navy skeet ranges are currently entering RI/FS phase
- Typical skeet range PAH contamination is 10 – 80,000 ug/Kg
- Primary skeet weathering data collected:
 - Annual/seasonal rain data
 - Avg/Hi/Low seasonal temperatures
 - Wind exposure (transport)
- General soil type for each site evaluated only for a few ranges
- USPTO search of clay target manufacturing patents – partially completed

One of the biggest contributions was identification of potential manufacturers of Skeet targets in the US, from which the DOD might have procured their skeet targets. There were two primary clay target manufacturers in the USA in the 1940's: "Blue Rock" made by Remington/DuPont and "White Flyer" made by Winchester/Olin Industries. Other lower volume and discontinued clay targets were Herter's Shamrock, Boston Target Co., True Flight; Black Diamond, Federal, Champion; and Duncan Miller Glass Co. (special Army WWII order). Based on this, EXWC was able to procure unused samples of these clay targets on EBay which paved the way for the fingerprint analysis conducted by the University of Illinois. Figure 43 shows photographs of intact procured clay targets.



Figure 43. Example of Vintage Clay Targets (Skeet) Purchased from EBay.

Additionally, some manufacturer listed composition information was also identified (Figure 44). A typical skeet target composition at the time consisted primarily of dolomitic limestone and pitch. Current skeet targets are typically polymeric.

MATERIAL	CAS NUMBER	%
AROMATIC PETROLEUM PITCHES	68334-31-6 / 68187-58-6	32
DOLOMITIC LIMESTONE	16389-88-1	67
FLUORESCENT AQUEOUS PAINT, or		1
LATEX PAINT - WHITE		1
POLYNUCLEAR AROMATIC HYDROCARBONS (0.1% OF TOTAL WEIGHT)		

- Image source: EXWC 2013

Figure 44. Sample Manufacturer Label.

4.2 IN VITRO ASSAY DEVELOPMENT AND OPTIMIZATION (TASK 2)

The main goal of this task was to develop, evaluate, and calibrate a low cost, robust, and rapid *in vitro* method as an alternative to *in vivo* mammalian approaches. The *in vitro* approach simulates mammalian ingestion and digestion processes to evaluate RBA of PAHs in soil from skeet-impacted sites. The initial concept was to optimize a method developed under the SERDP effort (Lowney et al 2017), a Physiologically Based Extraction Test (PBET), to be used on skeet impacted soils. Early in the assay set up and evaluation, it became apparent that a much greater methods development and optimization effort was required to achieve an assay with maximum accuracy and reproducibility. Most of this section is focused on the development and optimization of the PBET assay, as Geosyntec's PE passive sampler assay was far more mature and required less optimization.

4.2.1 Optimization of PBET Method Using Standard PAH Mixture Solution

Before using the PBET assay to analyze field soil samples, we tested this assay to verify accuracy, stability and reproducibility using standard reference material for PAH spiking (PAH mixture PM-612). The assay was calibrated on the basis of BaP recovery. Ideal recovery for this type of assay is > 70% (Ruby et al., 2016). A total of 200 samples including replicates and controls were analyzed over the course of several months until an accurate, optimal, reproducible protocol was achieved. The final modifications to our standard operation procedure (SOP) are summarized below (Section 4.2.1.4). Some of the key variables that led to these modifications were: (1) early in the analysis process we observed large recovery variation between replicates; (2) data results were not reproducible, i.e. we observed significant differences in percent recovery from one experiment to the next in our positive controls; (3) amount of time between shipping of samples and initial extraction of samples drastically impacted recovery; and (4) use of solvent as well as type of solvent mixture significantly impacted recovery results. A brief summary of each of these findings is discussed below.

4.2.1.1 Stabilization Solvent Implementation

The first issue was related to the inability to extract the PAHs from the matrices in a reliable and reproducible way. Figure 45 demonstrates issues with extraction of the PAH from the bio-matrix. The red and blue bars show PAH spiked matrices as measured using GS/MS subsequent to solvent extraction. The sample labeled PBET went through the entire assay process, whereas the sample labeled no PBET did not. The sample labeled 13-4 refers to DI water spiked with PAH control.

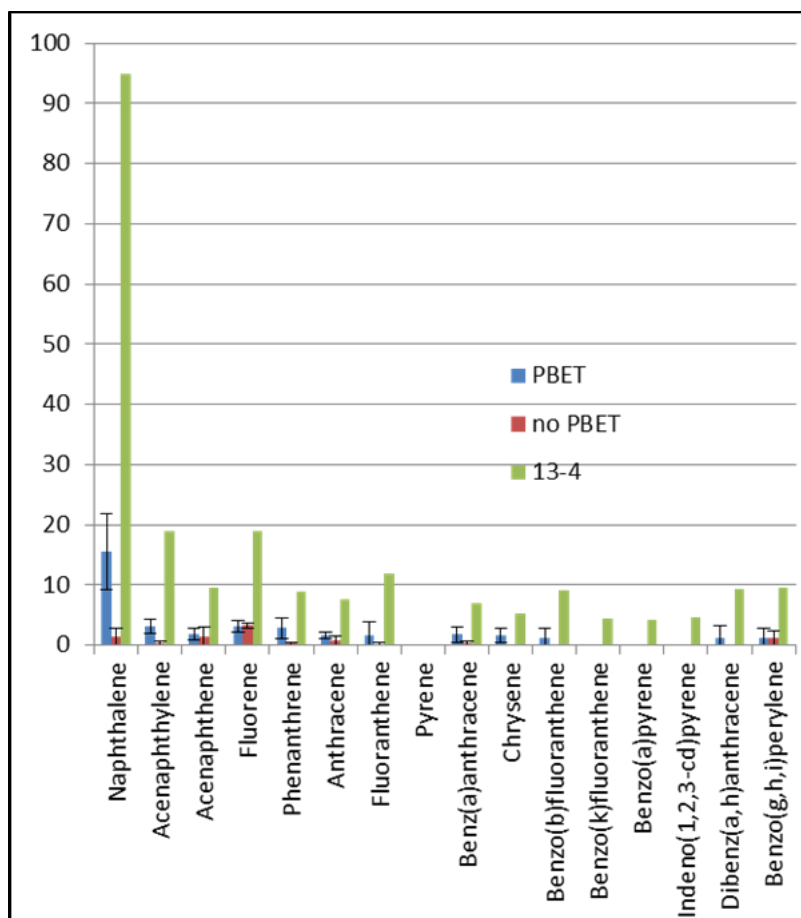
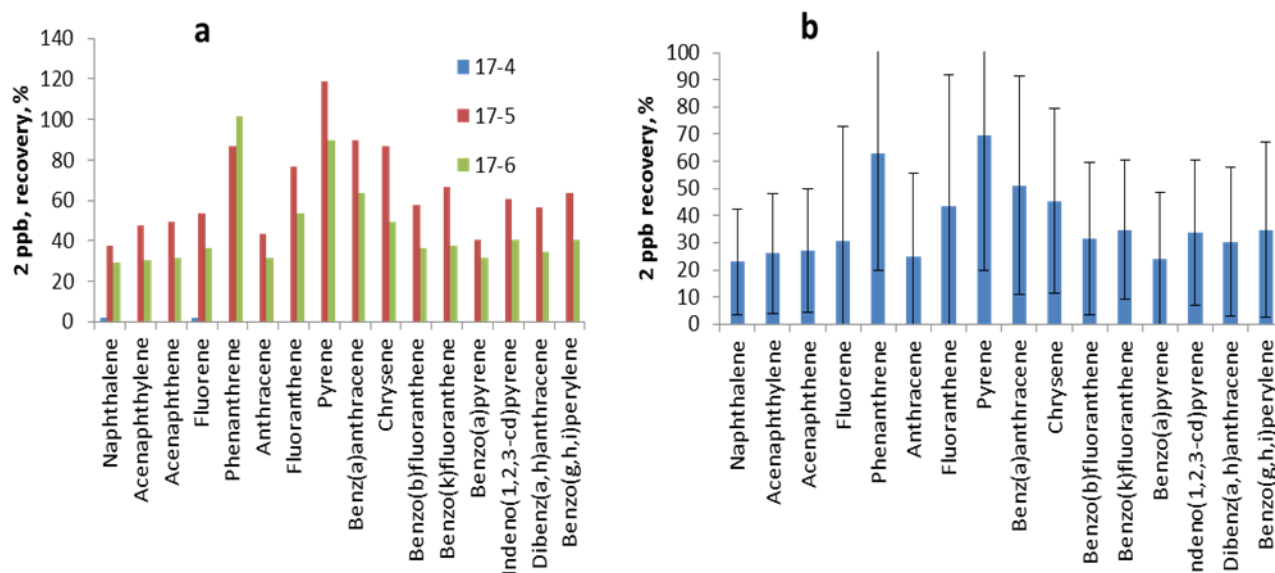


Figure 45. PBET Assay extraction from matrix issue (* y axis (ppb, recovery %) while X axis is polycyclic aromatic hydrocarbon constitute (PAH).

The second issue concerned consistency between replicates. Figure 46 is an example of very poor reproducibility between replicates, specifically at low concentrations (1–2 ppb). In this example there are three replicates. Two of the three show fairly similar % recovery for all PAHs however, the third replicate showed very low recovery, leading to poor average recovery using all data for all replicates. Note the extremely poor % recovery for BaP (<30% with a SD $\pm$ 40%). While not as extreme, similar poor recoveries were observed in a 10–20 ppb spiked sample (data are not shown). This observed behavior significantly impacted our confidence in future correlations with *in vivo* approaches and with using PBET as a valid surrogate.



- (a) 3 PBET replicates present, note blue bar is not visible.
- (b) Replicate average including standard deviation.

Figure 46. Example of PBET Replicate inconsistency.

It is important to note that the PBET assay uses a high protein Bio-based matrix to simulate the ingestion and digestion process. It is a mixture of glycine, pepsin, BSA (bovine serum albumin), porcine bile and pancreatin. What we believed to be occurring was binding of the heavier PAHs to the matrices making the sample difficult to extract, causing extreme variability in % recovery between replicates. As mentioned, this posed a problem for future correlation to the *in vivo* assay, which need to be addressed.

The plan to address this issue was as follows:

- Working with the commercial lab, SERDP team, and Chemist at NIWC Pacific to work out the details of the USEPA extraction process, and increase reliability of controls and percentage of recovery.
- Evaluating additional extraction solvents
- Evaluating a combination of extraction solvents and preservation/stabilization solvents
- Changing of pH upon sample arrival
- Changing from bio based matrix to simple solvent based

Recovery of matrix controls improved some after some extraction process changes at the commercial lab but not significantly enough to allow for any meaningful correlation with the *in vivo* assay (data not shown).

Through empirical trial and error (e.g. control preparation/extraction/analysis at NIWC Pacific prior to sending samples to the commercial lab), we began to suspect that the availability of PAHs in the PBET matrix to analytical extraction was dynamically changing with time. Ascertaining the potential mechanism of this instability could be time/cost prohibitive and was thus out of scope of this effort, so we began exploring ways to preserve or stabilize the samples after the final step in the PBET assay. Stabilizing/preserving in DCM or methanol solvent did not work (data not shown). But stabilizing/preserving in mixture of acetone and dichloromethane (DCM) showed promise. Despite this, the lower concentration (1-2 ppb) spiked samples, especially our index chemical, BAP, still had high variability. Figure 47 is an example of sufficient percentage recovery (~70% BAP) when a solvent was

added for stabilization. Small error bars indicate high reproducibility between replicates. It is important to note that the low recovery of naphthalene shown here and elsewhere was common and is probably due to naphthalene's high volatility however as naphthalene was not the focus of this effort this outcome is considered acceptable. Figure 48 is an example of a 1-2 ppb spiked sample. Excluding BAP, results are similar to those observed for the 10-20 ppb spiked sample. As a 1-2 ppb concentration is one of the more environmentally relevant concentrations we might observe at sites, the low % recovery and low reproducibility result of BAP at this concentration required us to conduct additional optimization experiments.

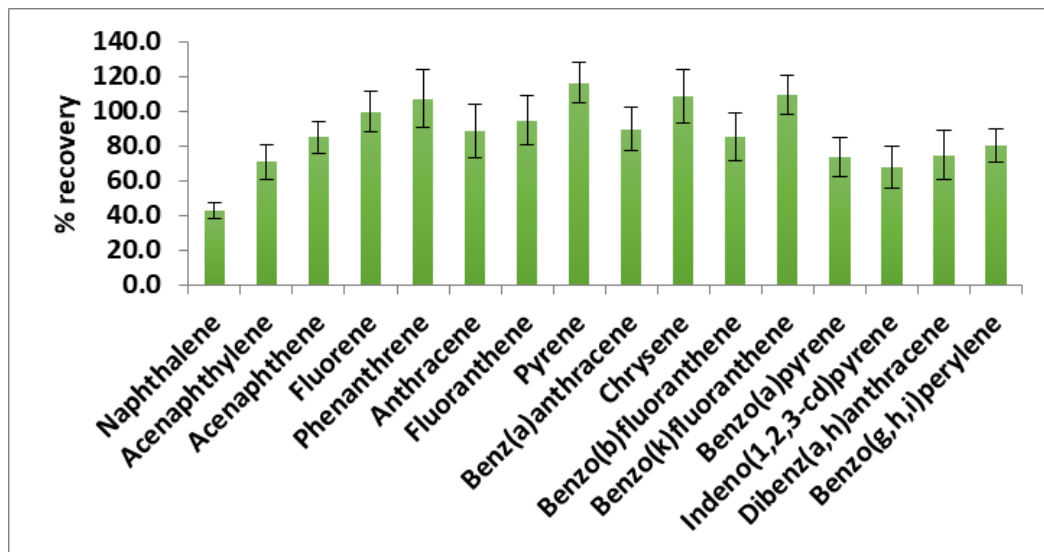


Figure 47 Example of Addition of Solvent. 10-20 ppb spiked solution w/addition of solvent for stabilization.

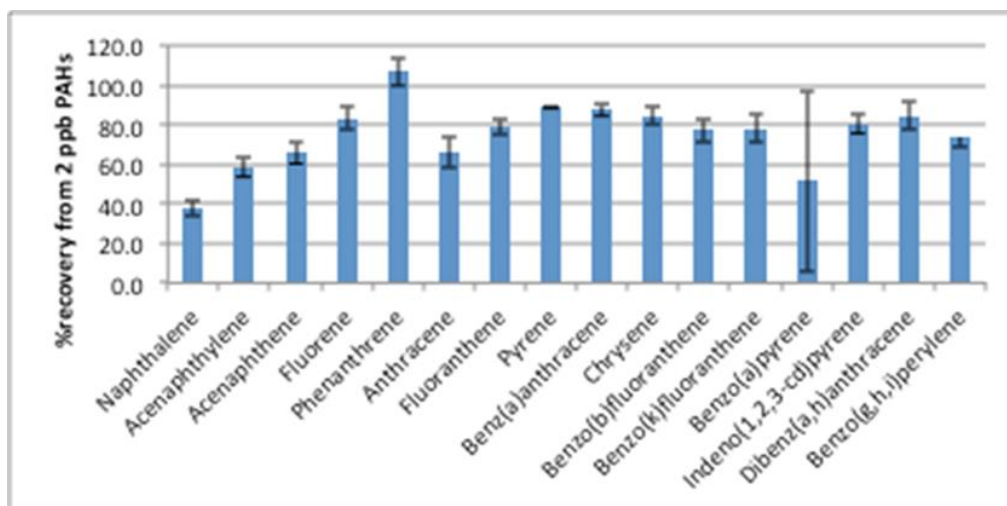


Figure 48 Example of Addition of Solvent. 1-2 ppb spiked solution w/addition of solvent for stabilization.

Based on these results our next experiments focused on:

- Evaluating process methodology
- Evaluating further solvent requirements and stoichiometry
- Establishing reproducibility and statistical confidence (QA/QC)
- Optimizing solvent system parameters

4.2.1.2 Extraction Time-frame Post Analysis

An additional key variable that was discovered to play a significant role in % recovery and reproducibility was the amount of time that passed from when the analytical lab received the sample from our lab at SSC Pacific, combined with the time that the analytical lab completed their initial extraction of sample, prior to GC/MS analysis. More specifically, if analytical lab pre extraction took place greater than 7 days post sample arrival, a significant decline was observed in % recovery and replicate reproducibility.

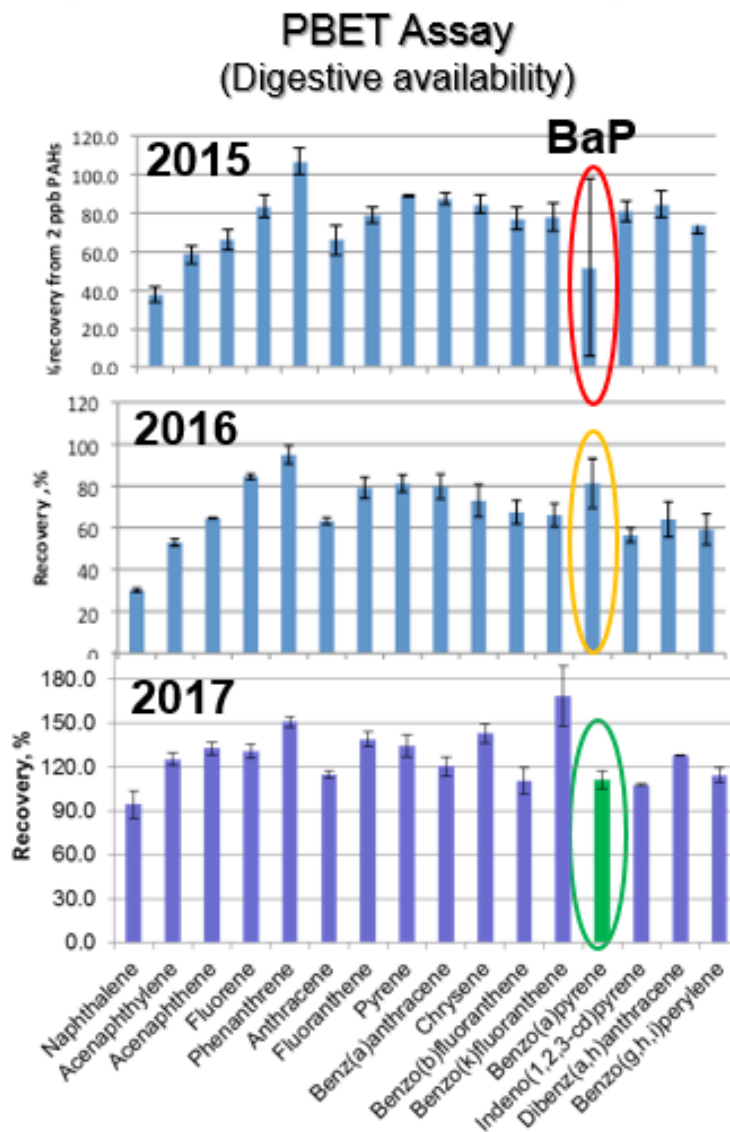
4.2.1.3 Optimization of PBET Assay Achieved

Following a systematic evaluation and optimization of the PBET assay method process, sample treatment, extraction, and logistical details, consistent, reproducible recovery results (typically 80%) for BAP was achieved. The final adjustments to the methodology included: adjustment to the analytical lab extraction process to increase reliability of controls and % recovery, additional solvent adjustments including use of extraction and preservation solvent mixtures, change of pH upon sample arrival, modifications to extraction cleanup, improvements to assay timing and post-processing, and minimization of the time to initial extraction and analysis. Figure 49 shows improvement in recovery and reproducibility of >80% BAP recovery in positive controls from 2015 to 2017.

4.2.1.4 Summary of PBET SOP Changes

To achieve reproducible and stable results, numerous PBET runs (200 extractions) were conducted using spiking material. The original SOP provided by Lowney et al (2017) was modified and adapted specifically for analysis of PAH bioavailability from skeet-impacted soils. Overall changes made to the methodology over the course of our studies included: (1) replacing a multi-step stabilization process of extraction of PAHs with hexane as solvent by using a mixture of acetone:DCM, which allowed for a reduction in labor time, stabilization of PAHs during shipment, and defensible reproducible data, especially at low concentrations. (2) Implementing stirring and swirling when spiking SRM into the matrix, which improved reproducibility between replicates and increased confidence in data interpretation. Finally, the strong time-frame compliance to process samples within 5–7 days after delivery to the analytical lab was a critical factor, with a direct impact on data quality and accuracy.

Successful PBet Matrix Stabilization and Process Optimization



- Source: NESDI IPR, 2017

Figure 49 Optimized PBET Assay.

4.2.1.5 Field Soil sample analysis results

A total of 6 field soil samples and 7 FT soil samples were analyzed by PBET to determine the bioavailability of BaP in skeet-impacted soils. Each sample was run in triplicate. Each experiment was repeated at least once and included both a positive control (1–2 ppb PAH SRM spike) and negative control (gastric solution matrix alone). A summary of measured BAP bioavailability by PBET for all samples is provided in Table 8. Examples of typical experimental concentration recoveries as well as experimental controls is provided in Figure 50 and Figure 51.

Table 8. Bioavailable concentration of Benzo(a) Pyrene (BaP) in skeet impacted soil as measured by PBET.

Soil ID	Bioavailable BaP (mg/kg. dw)
L	0.092
F	0.11
S4	0.86
S5	1.2
WF-SA	5
S11	17
S12	0.54
S13	0.23
G1	1.037
G2	18.81
G3	5.21
G4	0.21
G5	0.1

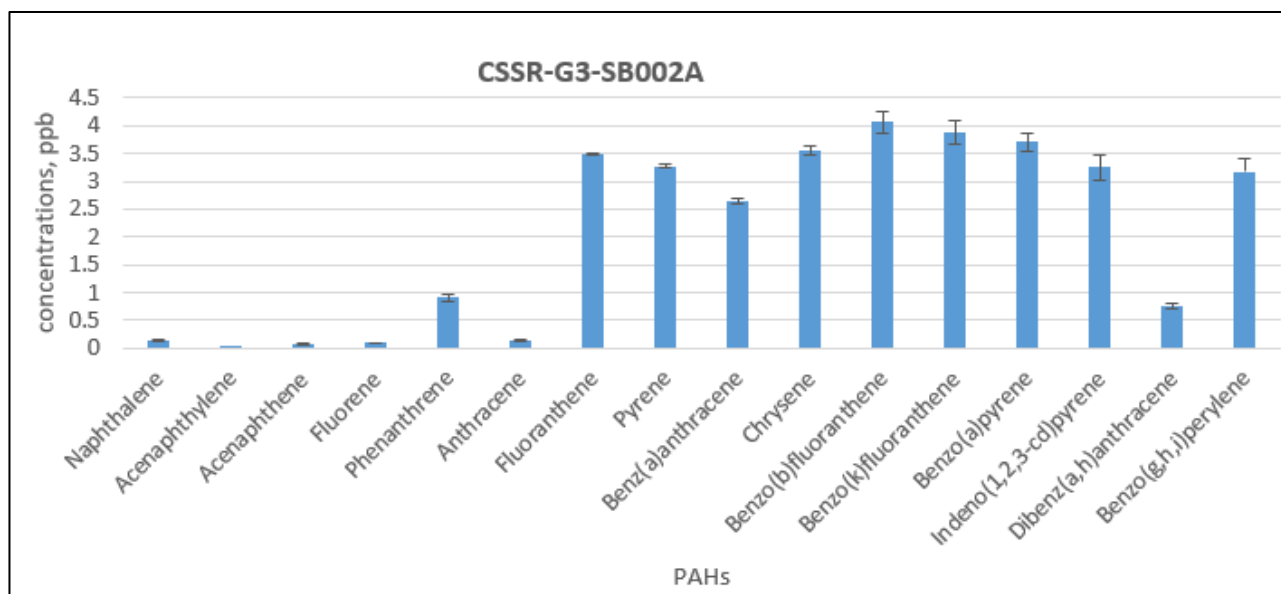


Figure 50 PBET analysis of FT soil (G3).

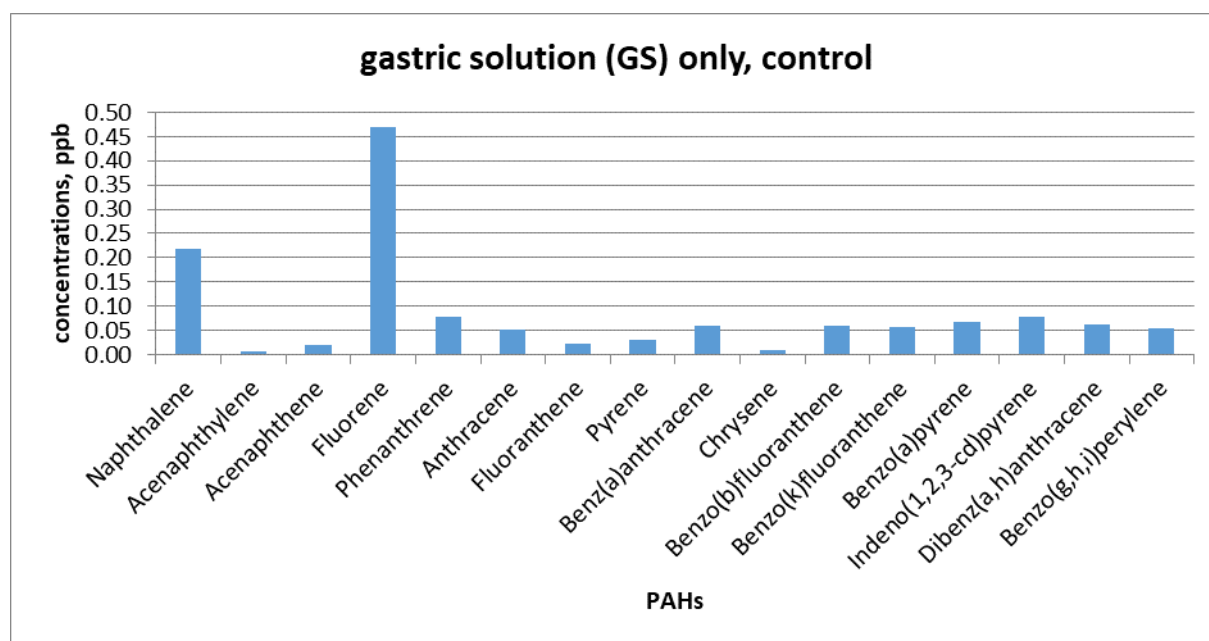


Image Source: NESDI IPR, 201

Figure 51 PBET analysis of ST Soil (G3) Negative control (gastric solution alone) results.

4.3 DEVELOPMENT OF *IN VITRO* RBA MODEL AND DEMONSTRATION OF MODEL (TASK 3 AND 4)

As mentioned previously, the main goal of this task was to develop an *in vitro* *in vivo* comparative (IVIVC) model. The purpose of the model is to develop a means of predicting the bioavailable concentration of an index chemical representing PAHs (BaP) in soil using *in vitro* measurements (passive sampling) and (PBET) and show that these measurements are predictive of RBA estimates developed from an animal feeding trial (show numerical relationship between *in vivo* and *in vitro* measurements). In order to establish the empirical relationship between chemical availability measures (PBET and passive sampling) and measured mammalian bioavailability in PAH-impacted soils, soil characterization studies were undertaken, and both *in vitro* and *in vivo* assay measurements were made on the same PAH contaminated soil samples (derived from clay targets). Five soils were obtained from DoD skeet-impacted range soils (samples G1 to G5, Table 1, Arcadis, 2017). This section describes general results of model development. A schematic of the RBA model components is summarized in Figure 52. Table 9 provides a summary of field soil samples and FT soil samples analyzed, in addition to type of analysis performed on each.

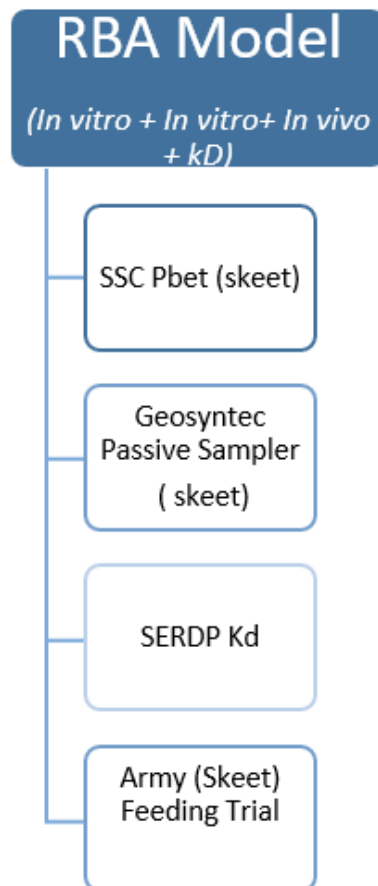


Figure 52 Schematic of RBA Model Components.

Table 9. Summary of field soil samples collected and type of analysis performed on each.

	Soil ID	Bioavailability Assay (In vivo & In Vitro)			Spectral Analysis			
		In vivo	PBET	Passive	XRD	FTIR	NIR	Mossbauer
1	G1	✓	✓	✓	✓	✓	✓	✓
2	G2	✓	✓	✓	✓	✓	✓	✓
3	G3	✓	✓	✓	✓	✓	✓	✓
4	G4	✓	✓	✓	n/a	n/a	n/a	n/a
5	G5	✓	✓	✓	n/a	n/a	n/a	n/a
6	L	✓	✓	✓	n/a	n/a	n/a	n/a
7	F	✓	n/a	✓	n/a	n/a	n/a	n/a
8	BF-SA	n/a	n/a	n/a	✓	✓	✓	✓
9	WF-SA	n/a	✓	✓	✓	✓	✓	✓
10	S1	n/a	n/a	n/a	✓	✓	✓	✓
11	S2	n/a	n/a	n/a	✓	✓	✓	✓
12	S3	n/a	n/a	n/a	✓	✓	✓	✓
13	S4	n/a	✓	✓	✓	✓	✓	✓
14	S5	n/a	n/a	n/a	✓	✓	✓	✓
15	S6	n/a	n/a	n/a	✓	✓	✓	✓
16	S7	n/a	✓	✓	✓	✓	✓	✓
17	S8	n/a	n/a	n/a	✓	✓	✓	✓
18	S9	n/a	n/a	n/a	✓	✓	✓	✓
19	S10	n/a	n/a	n/a	✓	✓	✓	✓
20	S11	n/a	✓	✓	✓	✓	✓	✓
21	S12	n/a	✓	✓	✓	✓	✓	✓
22	S13	n/a	✓	✓	✓	✓	✓	✓

Notes: Lines 1–7 correspond to feeding trial soils; Lines 8 and 9 two Florida samples; lines 10–22 other skeet ranges

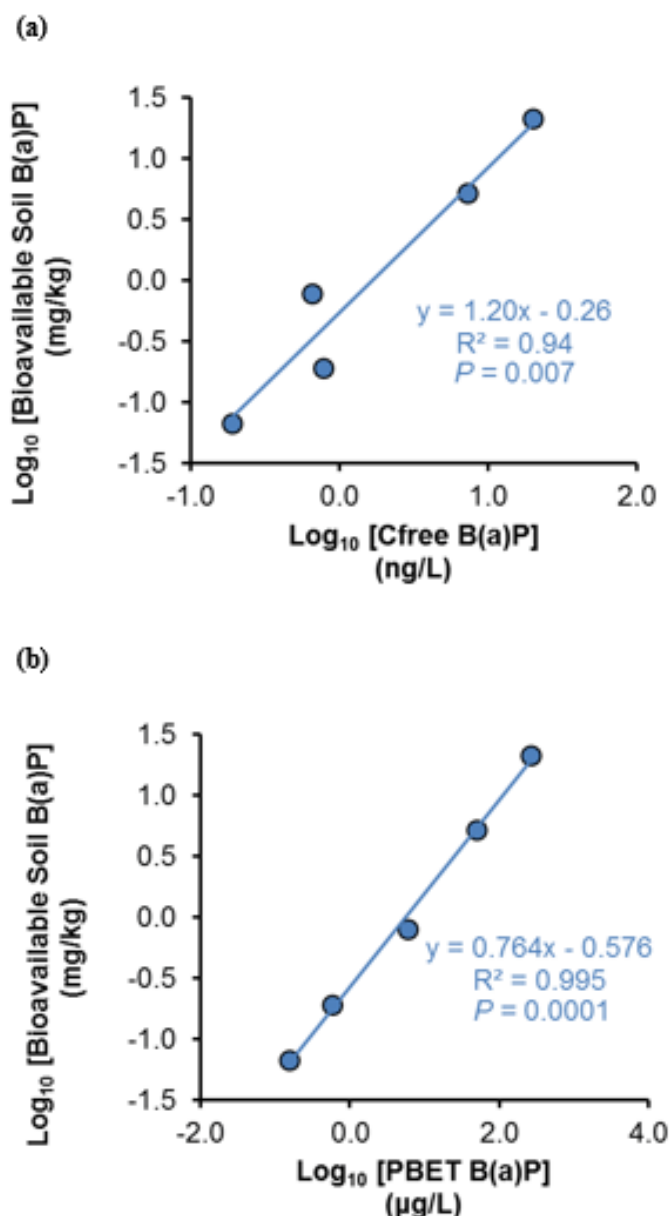
4.3.1 Ability of PBET and Passive Sampling to Predict Mammalian Digestive Bioavailability of BaP in Soils Impacted by Clay Targets

Bioavailable concentrations of BaP as predicted by in vivo testing (Table 10, Magee et al., 2014) were positively correlated with both measures of chemical availability (PBET and C_{free}, Figure 53) based on samples that were measured by these three approaches. Both C_{free} and PBET were positively correlated with the concentration of bioavailable PAHs in soil, calculated by RBA × the concentration of BaP in soil. The regression models for C_{free} and PBET regression relationships were very precise, with r² values of 0.94 and 0.96, respectively (Figure 53), indicating empirical models can be developed to relate chemical BaP availability measures to RBA estimates.

Table 10. Concentration of BaP, RBA, concentration of bioavailable BaP (RBA × concentration of BaP), and total organic carbon content (TOC) of the five test soils used in the mammalian feeding experiment.

Analyte	G1	G2	G3	G4	G5
Concentration of Benzo(a)pyrene in Soil (mg/kg, dw)	4.5	183	28	0.54	0.11
RBA	18%	12%	18%	35%	60%
Bioavailable Concentration of Benzo(a)pyrene in Soil (mg/kg, dw)	0.8	21.4	5.2	0.2	0.1
TOC content	1.7%	23%	12%	4.7%	0.19%

- Notes: RBA: relative bioavailability; TOC: total organic carbon; Bioavailable Concentration calculated as the concentration in soil multiplied by the RBA.



- (a), the concentration of total BaP in soil, based on average RBA versus the concentration of BaP in PBET extract (b).

Figure 53. Concentration of bioavailable BaP in soil versus the concentration of Cfree BaP in soil.

4.4 DEMONSTRATION OF THE USE OF PBET AND PASSIVE SAMPLING TO EVALUATE THE RISK OF BAP IN SOILS IMPACTED BY CLAY TARGETS

As a demonstration of how the PBET and passive sampling chemical measures can be used in a risk assessment, the above regression models were used to predict the concentration of bioavailable BaP in soils impacted by clay targets. Based on the relationship between bioavailable concentrations and chemical availability (Figure 53), the bioavailable concentration or RBA can be predicted based on either PBET or Cfree and directly used in a risk assessment. In the demonstration described here, DoD soils from areas not impacted by PAHs (sample IDs L and F, Table 11) and areas with PAH soil contamination from skeet-impacted sites (sample IDs Finegayan 2, Finegayan T+S, Whiting Field, ST-SR-NBG, ST-RS-NBG, and

MCASM-19-C; Table 11) were analyzed by traditional bulk chemical analysis, PBET, and passive sampling methods. PBET and passive sampling approaches were used with each of the 8 soils, and passive sampling and PBET results were input into the models to predict the bioavailable concentration of BaP in the 8 soils, shown in Figure 53 a and 53b, respectively. As shown in Table 11, bulk concentrations of BaP in soil ranged from 0.03 to 2581 mg/kg, dw. Seven of the 8 soils could indicate levels of potentially unaccep

Table residential cancer risks. Two of the 8 soils could be indicative of residential cancer risk for BaP⁴ in the 1×10^{-5} to $< 1 \times 10^{-4}$ range (yellow shading), and five of the 8 soils could be indicative of a 1×10^{-4} residential cancer risk for BaP (red shading). In contrast, the approach with PBET and Cfree suggests risks based on bulk concentrations could be greatly overestimated due to the overly conservative assumption that 100% of the bulk BaP is bioavailable. For example, PBET indicated two soils were in the 1×10^{-5} to $< 1 \times 10^{-4}$ range, and one additional soil exceeded the 1×10^{-4} risk threshold. Passive sampling identified more soils with potential risk compared to PBET. Agreement was found in one sample (ST-SR-NBG) that exceeded the 1×10^{-5} risk threshold. Passive sampling found greater risk in two soils (Finegayan 2 and MCASM-19-C) that exceeded the 1×10^{-5} to $< 1 \times 10^{-4}$ range, whereas no risk was observed as measured by PBET in these two soils. Also, two soils exceeded the 1×10^{-4} risk threshold (Finegayan T+S and Whiting Field) via passive sampling, whereas PBET indicated risk for these two soils were noted to be within the 1×10^{-5} to $< 1 \times 10^{-4}$ range. For the additional 5 soils evaluated in the *in vivo* study, the PBET and passive sampling approaches were in disagreement for only 2 of the 13 soils (15%) in terms of exceeding the 1×10^{-5} risk threshold.

In general, PBET and passive sampling approaches both indicate that the assumption that 100% of the bulk total PAH concentration for 12 soils are overprotective with regards to BaP risk by an average factor of approximately 75 and 11, respectively. Predicted RBA estimates (bioavailable BaP ÷ bulk total BaP) based on PBET were in the 0.2 to 56% range (average 14%), whereas RBA estimates based on passive sampling were in the 3 to 76% range (average 25%).

⁴ This approach only incorporates an evaluation of cancer risks from BaP. Additional carcinogenic risks would be present from other PAHs in soil that are not accounted for in this example. However, evaluation of the BaP equivalency in the five soils used in the *in vivo* study indicate that this approach likely accounts for approximately 70% of the hypothetical cancer risk.

Table 11 Estimation of potential BaP risk in 8 example soils (using example BaP/kg soil risk-based criteria) using total bulk analysis of BaP in soil, analysis of BaP via PBET, and analysis of freely-dissolved BaP via passive sampling.

Approach	Analyte	L	F	FINEGAYAN 2	FINEGAYAN T+S	WHITING FIELD	ST-SR- NBG	ST-RS- NBG	MCASM- 19-C
Bulk "Total" Analysis	Concentration of Benzo(a)pyrene in Soil (mg/kg, dw)	1.6	0.03	350	147	75	2581	6.8	32
PBET	Available Concentration of Benzo(a)pyrene (µg/L)	0.25	0.32	4.6	7.0	47	231	2.5	0.82
	Bioavailable Concentration of Benzo(a)pyrene in Soil Based on Availability as Predicted by PBET (mg/kg, dw) ¹	0.092	0.11	0.86	1.2	5.0	17	0.54	0.23
Passive Sampling	Freely-Dissolved Concentration of Benzo(a)pyrene in Soil Porewater (ng/L)	0.15	< 0.12	12	72	17	150	0.63	6.3
	Bioavailable Concentration of Benzo(a)pyrene in Soil Based on Availability as Predicted by C _{free} (mg/kg, dw)	0.056	< 0.043	11	93	16	225	0.32	5.0

Notes

- 1 PBET: $y = 10^{(0.764 \cdot \log_{10}(x) - 0.576)}$
- 2 C_{free}: $y = 10^{(1.20 \cdot \log_{10}(x) - 0.26)}$
- Yellow shading indicates a hypothetical residential risk of 1×10^{-5} (criterion of 1.1 mg/kg) to $< 1 \times 10^{-4}$, whereas red shading indicates exceedance of a 1×10^{-4} risk (criterion of 11 mg/kg), based on EPA (2017)
- ng/L: nanogram per liter; mg/kg, dw: milligram per kilogram, dry weight basis; µg/L: microgram per liter

4.4.1 Site Specific Results

4.4.1.1 MCAS

An initial in vitro analysis of one soil sample was analyzed as part of this effort. Results demonstrated significant potential reduction in in vitro bulk analysis from traditional bulk analysis (MCASM 19C, Table 11). In short, initial total PAH bulk analysis indicated concentrations at 32 mg BaP/kg soil, dw, indicating that it would likely generate concern for potential human health risks using most risk-based criteria. PBET analysis and subsequent application of our PBET-based BaP relationship (Table 11) indicated that the concentration of bioavailable BaP in soil is 0.23 mg bioavailable BaP/kg soil, which would likely not trigger risk concerns. Given the ranges of total and bioavailable BaP, and high degree of unavailable BaP, this site would make an optimal site for future characterization work. This improvement in understanding the relative bioavailability and associated risk would lead to a more accurate remediation. Remedial project managers from this location have conducted an initial investigation at both locations and can provide PAH data.

4.4.1.2 Guam

An initial in vitro analysis was conducted on two of the three locations sampled from at NBG (Spanish Steps and Finegayan). Results from this effort show analysis of total PAHs in bulk soils from NAVFAC Marianas (

Table 11, Finegayan samples) indicated approximate concentrations of BaP in soil of 150 to 350 mg BaP/kg soil, dw, indicating that these soils would likely generate concern for potential human health risks under most state risk-based criteria. PBET analysis and subsequent application of our draft PBET-to-bioavailable BaP relationship model indicated that the concentration of bioavailable BaP in the soils is 0.9 to 1.2 mg bioavailable BaP/kg soil, which may represent minimal or borderline risk concerns. The passive sampling analysis indicated higher levels of bioavailable BaP (10 to 90 mg bioavailable BaP/kg soil), which may indicate risk concerns.

Results from the ST-SR-NBG, and ST-RS-NBG soil samples (Spanish step) showed much more dramatic consequence potential. PAH bulk analysis from these two soils for BaP was 2581 and 6.8 mg BaP/kg soil, dw, respectively. PBET analysis and subsequent application of our draft PBET-to-bioavailable BaP relationship model indicated that the concentration of bioavailable BaP in the soils 17 to 0.54 mg bioavailable BaP/kg soil, which would represent minimal risk for the ST-SR-NBG but remove the risk for the ST-RS-NBG soil. The passive sampling analysis indicated higher levels of bioavailable BaP (225 and 0.32 mg bioavailable BaP/kg soil), which would indicate risk concerns for ST-SR-NBG but unlikely risk concerns for ST-RS-NBG. Given the ranges of total and bioavailable BaP, this site would be an optimal site for further evaluation and could greatly benefit from a re-evaluation of RBA values.

4.4.1.3 Whiting Field

An initial in vitro analysis of one soil sample was analyzed as part of this effort. Results demonstrated significant potential reduction in in vitro bulk analysis from traditional bulk analysis (Whiting Field Table 11). In short, initial total PAH bulk analysis indicated concentrations at 75 mg BaP/kg soil, dw, indicating that it would likely generate concern for potential human health risks using most risk-based criteria. PBET analysis and subsequent application of our draft PBET-to-bioavailable BaP relationship (Table 11) indicated that the concentration of bioavailable BaP in soil is 5 mg bioavailable BaP/kg soil, which would likely trigger minimal risk concerns. Given the ranges

of total and bioavailable BaP, this site would make an optimal site for future characterization work. This improvement in understanding risk would lead to a more accurate, less over-protective remediation. Remedial project managers from this location have conducted an initial investigation at this location.

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5. SUMMARY AND CONCLUSIONS

5.1 CONCLUSIONS

Both PBET and Cfree *in vitro* measurements, obtained using inexpensive and rapid benchtop animal free *in vitro* approaches, can be used to predict bioavailable concentrations of BaP in soil and used directly in human health risk assessment, as discussed in the example above. Both PBET and Cfree approaches correlate well with bioavailable BaP as measured in *in vivo* feeding trials with rodents, which is the default, much more time and resource intensive approach for evaluating PAH RBA for soils at PAH contaminated site sites. Using PBET and passive sampling data would result in more accurate and less overly conservative risk assessments and remediation approaches at sites impacted with clay targets. .

Although there is minor disagreement between the *in vitro* approaches regarding indication of potential BaP risk predictions (for 15% of the soils studied), both indicated low availability of BaP in clay target-impacted soils. Relying on traditional bulk chemistry measurements would overestimate risks by greater than a factor of 10 or more on average. Compared to animal testing, both PBET and passive sampling measurements are cost- and time- efficient for predicting mammalian digestive PAH bioavailability and improving the accuracy of site-specific PAH risk assessments.

There are several advantages and disadvantages to PBET compared to passive sampling as noted below:

- Less sample mass is required for PBET (5 g for PBET compared to 80 g for passive sampling).
- Less time is required for PBET (12 hours for PBET compared to 14 days for passive sampling).
- The holding time for PBET samples is critical and requires careful coordination with the analytical laboratory and extraction upon receipt of the samples, whereas for passive sampling, extraction by laboratory is less time sensitive (i.e., sample processing within two weeks).
- More hands on experimental/technician time is needed for PBET (5 hours per sample for PBET compared to 1 hour per sample for passive sampling).
- PBET requires assay-specific and up front capital equipment investment (multi-sample digester costs approximately \$2,500) and supplies (PBET matrix costs \$50 per sample). Passive sampling materials (sampler, microbial inhibitor, containers) are approximately \$50-100 per sample, but only require equipment commonly present in laboratories such as rollers for agitation of passive samplers.
- Passive sampling services are available commercially, and standardized methods are currently under development by USEPA and others.
- Finally, the analytical and data reporting costs of PBET analysis are approximately \$1,500 per sample compared to \$1,000 per sample for passive sampling.

Further research would add confidence in the ability of PBET and passive sampling approaches to accurately predict bioavailable concentrations, particularly since the relationship between *in vitro* BaP availability data and animal BaP availability data is based on a limited (5-sample) dataset, as described in this report. In contrast, the correlation between a chemical availability method and animal availability measurements, as approved by California EPA (DTSC, 2016) was based on

approximately 20 soils. To that end, the ability to increase sample size through direct comparison of soil samples analyzed via PBET, Passive Sampler, correlated to RBA values determined by animal feeding trials is warranted to further refine the relationships between PBET and passive sampling results and bioavailability. Additional data would also allow a better understanding of which measure is most predictive, reliable, and cost effective.

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APPENDIX A
PBET AND PASSIVE SAMPLER DATA

OVERVIEW

This section contains three tables which provide the raw PAH analytic laboratory data for each soil and skeet sample analyzed and summarized in report.

Table A-1. Concentrations of PAHs in PBET matrix, as applied to soil.

Analyte	PBET Result (µg/L)														
	G1	G2	G3	G4	G5	L	F	Finegayan 2 (Non-homogenized)	Finegayan 2 (Weathered)	Finegayan 2 (Homogenized)	Finegayan T+S Trap and Skeet	Whiting Field Skeet Area WF-SA-01	ST-SR-NBG	ST-RS-NBG	MCASM-19-C
Acenaphthene	0.25	8.19	1.41	ND	ND	ND	ND	0.31	0.48	0.54	0.38	0.73	15.0	0.22	ND
Acenaphthylene	0.04	0.11	0.04	ND	ND	0.07	ND	ND	ND	ND	0.05	0.16	0.19	ND	ND
Anthracene	0.42	25.6	4.48	0.05	ND	0.06	ND	0.32	0.50	0.51	0.51	1.01	13.8	0.10	ND
Benzo(a)anthracene	4.28	204	42.33	0.64	0.50	0.35	0.22	2.81	5.64	5.31	4.95	29.1	148	1.72	0.54
Benzo(a)pyrene	5.95	264	49.18	0.58	0.15	0.25	0.32	4.64	9.22	8.85	7.04	47.2	231	2.53	0.82
Benzo(b)fluoranthene	7.96	359	72.83	0.96	0.59	0.46	0.29	4.22	8.36	7.79	6.27	26.5	276	3.02	0.59
Benzo(ghi)perylene	4.88	172	32.38	0.39	0.18	0.70	0.23	3.85	7.43	6.82	4.74	36.2	169	2.13	0.63
Benzo(k)fluoranthene	3.12	131	26.77	0.41	0.23	0.15	0.12	1.68	3.12	3.27	3.83	7.76	170	1.44	0.19
Chrysene	5.47	292	54.17	0.78	0.74	0.31	0.16	3.85	8.10	7.54	5.99	56.9	186	2.25	1.00
Dibenz(a,h)anthracene	1.20	46.9	8.72	0.09	0.06	0.08	0.12	0.99	1.70	1.64	3.23	8.99	42.6	0.37	0.15
Fluoranthene	6.83	444	79.68	1.01	1.72	0.24	0.27	3.3	6.04	5.82	4.53	11.4	188	2.06	0.28
Fluorene	0.40	3.29	1.07	0.17	0.27	0.08	0.32	0.24	0.31	0.34	0.52	0.38	3.10	0.27	0.40
Indeno(1,2,3-cd)pyrene	5.07	207	37.98	0.42	0.22	0.39	0.17	2.99	5.37	5.04	4.39	14.4	201	2.01	0.25
Naphthalene	0.30	1.82	0.75	0.04	0.09	0.23	0.18	0.17	0.13	0.15	0.21	0.39	1.24	0.17	0.16
Phenanthrene	2.28	137	24.27	0.50	0.78	0.10	0.16	1.68	2.79	2.73	1.71	10.3	73.7	0.83	0.30
Pyrene	5.95	306	61.00	0.84	1.25	0.36	0.18	4.03	7.50	7.21	4.35	40.7	215	2.51	0.87

Notes

- µg/L: microgram per liter
- PBET: Physiologically Based Extraction Test

ND: non-detect

Table A-2. Concentration of analytes in polyethylene (PE).

Compound	PAH Group	PRC	G1		G2		G3		G5	
			[PAH or PCB PE] Result	[PAH or PCB PE] MDL	[PAH or PCB PE] Result	[PAH or PCB PE] MDL	[PAH or PCB PE] Result	[PAH or PCB PE] MDL	[PAH or PCB PE] Result	[PAH or PCB PE] MDL
			(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Acenaphthene	PPAH		ND	110	770	110	420	120	ND	130
Acenaphthylene	PPAH		ND	33	ND	33	ND	37	ND	39
Anthracene	PPAH		ND	100	1200	100	790	110	ND	120
Benzo(a)anthracene	PPAH		580	150	16000	150	9200	170	ND	180
Benzo(a)pyrene	PPAH		1000	100	30000	100	11000	110	230	120
Benzo(b)fluoranthene	PPAH		2200	130	45000	130	24000	150	400	160
Benzo(ghi)perylene	PPAH		1400	79	34000	79	13000	88	170	94
Benzo(k)fluoranthene	PPAH		1000	120	23000	120	12000	130	190	140
Chrysene	PPAH		980	110	27000	110	18000	120	240	120
Dibenz(a,h)anthracene	PPAH		290	37	7000	37	3300	41	ND	44
Fluoranthene	PPAH		850	190	28000	190	18000	210	280	220
Fluorene	PPAH		ND	250	ND	250	280	280	ND	290
Indeno(1,2,3-cd)pyrene	PPAH		1300	89	33000	89	15000	100	160	110
Naphthalene	PPAH		ND	2800	ND	2800	ND	3100	ND	3300
Phenanthrene	PPAH		ND	840	6800	840	6100	940	ND	1000
Pyrene	PPAH		950	580	30000	580	18000	650	ND	690
1-Methylnaphthalene	AlkPAH		ND	680	ND	680	ND	760	ND	810
2-Methylnaphthalene	AlkPAH		ND	1500	ND	1500	ND	1700	ND	1800
PCB-14		PRC	ND	5.3	ND	5.3	ND	5.9	10	6.2
PCB-36		PRC	ND	5.3	ND	5.3	ND	5.9	17	6.2
PCB-78		PRC	ND	5.3	ND	5.3	10	5.9	32	6.2
PCB-104		PRC	ND	5.3	ND	5.3	6	5.9	15	6.2
PCB-121		PRC	38	5.3	55	5.3	42	5.9	110	6.2
PCB-142		PRC	30	5.3	40	5.3	29	5.9	76	6.2
PCB-155		PRC	81	5.3	110	5.3	76	5.9	150	6.2
PCB-184		PRC	300	5.3	330	5.3	260	5.9	380	6.2
PCB-192		PRC	380	5.3	410	5.3	300	5.9	440	6.2
PCB-204		PRC	770	5.3	750	5.3	680	5.9	810	6.2

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second MDL column for each sample.
- PPAH: Priority Pollutant PAH ; AlkPAH: Alkylated PAH; PRC: Performance Reference Compound

Table A-2. Concentration of analytes in polyethylene (PE). (Continued)

Compound	PAH Group	PRC	L		F		FB1		FB2	
			[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]
			Result	MDL	Result	MDL	Result	MDL	Result	MDL
			(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Acenaphthene	PPAH		ND	120	ND	150	ND	130	ND	120
Acenaphthylene	PPAH		ND	37	ND	45	ND	39	ND	37
Anthracene	PPAH		ND	110	ND	140	ND	120	ND	110
Benzo(a)anthracene	PPAH		ND	170	ND	210	ND	180	ND	170
Benzo(a)pyrene	PPAH		230	110	ND	140	ND	120	ND	110
Benzo(b)fluoranthene	PPAH		820	150	380	180	ND	160	ND	150
Benzo(ghi)perylene	PPAH		480	88	190	110	ND	94	ND	88
Benzo(k)fluoranthene	PPAH		350	130	ND	160	ND	140	ND	130
Chrysene	PPAH		340	120	210	140	ND	120	ND	120
Dibenz(a,h)anthracene	PPAH		91	41	ND	50	ND	44	ND	41
Fluoranthene	PPAH		ND	210	ND	260	ND	220	ND	210
Fluorene	PPAH		ND	280	ND	340	ND	290	ND	280
Indeno(1,2,3-cd)pyrene	PPAH		370	100	120	120	ND	110	ND	100
Naphthalene	PPAH		ND	3100	ND	3800	ND	3300	ND	3100
Phenanthrene	PPAH		ND	940	ND	1100	ND	1000	ND	940
Pyrene	PPAH		ND	650	ND	790	ND	690	ND	650
1-Methylnaphthalene	AlkPAH		ND	760	ND	930	ND	810	ND	760
2-Methylnaphthalene	AlkPAH		ND	1700	ND	2100	ND	1800	ND	1700
PCB-14		PRC	ND	5.9	17	7.1	160	6.2	140	5.9
PCB-36		PRC	ND	5.9	18	7.1	240	6.2	230	5.9
PCB-78		PRC	ND	5.9	31	7.1	400	6.2	370	5.9
PCB-104		PRC	ND	5.9	17	7.1	130	6.2	120	5.9
PCB-121		PRC	32	5.9	120	7.1	460	6.2	450	5.9
PCB-142		PRC	33	5.9	99	7.1	350	6.2	320	5.9
PCB-155		PRC	89	5.9	180	7.1	390	6.2	360	5.9
PCB-184		PRC	320	5.9	440	7.1	590	6.2	580	5.9
PCB-192		PRC	390	5.9	510	7.1	710	6.2	650	5.9
PCB-204		PRC	760	5.9	790	7.1	920	6.2	870	5.9

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second MDL column for each sample.
- PPAH: Priority Pollutant PAH ; AlkPAH: Alkylated PAH; PRC: Performance Reference Compound

Table A-2. Concentration of analytes in polyethylene (PE). (Continued)

Compound	PAH Group	PRC	G4		FB4		FINEGAYAN 2		FINEGAYAN T+S	
			[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]	[PAH or PCB PE]
			Result	MDL	Result	MDL	Result	MDL	Result	MDL
			(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Acenaphthene	PPAH		ND	96	ND	96	460	230	1600	230
Acenaphthylene	PPAH		ND	29	ND	29	ND	70	ND	70
Anthracene	PPAH		ND	86	ND	86	730	210	6400	210
Benzo(a)anthracene	PPAH		540	130	ND	130	4500	320	72000	320
Benzo(a)pyrene	PPAH		890	86	ND	86	5800	210	100000	210
Benzo(b)fluoranthene	PPAH		1200	110	ND	110	6000	280	110000	280
Benzo(ghi)perylene	PPAH		380	68	ND	68	2600	170	40000	170
Benzo(k)fluoranthene	PPAH		720	100	ND	100	2000	240	50000	240
Chrysene	PPAH		830	91	ND	91	8000	220	90000	220
Dibenz(a,h)anthracene	PPAH		110	32	ND	32	490	78	10000	78
Fluoranthene	PPAH		720	160	ND	160	6600	400	120000	400
Fluorene	PPAH		ND	210	ND	210	ND	520	710	520
Indeno(1,2,3-cd)pyrene	PPAH		460	77	ND	77	1200	190	40000	190
Naphthalene	PPAH		ND	2400	ND	2400	ND	5900	ND	5900
Phenanthrene	PPAH		ND	730	ND	730	3900	1800	23000	1800
Pyrene	PPAH		820	500	ND	500	11000	1200	140000	1200
1-Methylnaphthalene	AlkPAH		ND	590	ND	590	ND	1400	ND	1400
2-Methylnaphthalene	AlkPAH		ND	1300	ND	1300	ND	3200	ND	3200
PCB-14		PRC	ND	4.6	5.7	4.6	ND	11	ND	11
PCB-36		PRC	6.5	4.6	55	4.6	87	11	46	11
PCB-78		PRC	83	4.6	230	4.6	140	11	ND	11
PCB-104		PRC	ND	4.6	20	4.6	43	11	ND	11
PCB-121		PRC	62	4.6	290	4.6	340	11	20	11
PCB-142		PRC	1900	4.6	2200	4.6	350	11	12	11
PCB-155		PRC	80	4.6	230	4.6	610	11	64	11
PCB-184		PRC	260	4.6	470	4.6	1100	11	270	11
PCB-192		PRC	340	4.6	570	4.6	1100	11	380	11
PCB-204		PRC	590	4.6	720	4.6	840	11	510	11

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second MDL column for each sample.
- PPAH: Priority Pollutant PAH ; AlkPAH: Alkylated PAH; PRC: Performance Reference Compound

Table A-2. Concentration of analytes in polyethylene (PE). (Continued)

Compound	PAH Group	PRC	WHITING FIELD		FB1		FB2		ST-SR-NBG	
			[PAH of PCB PE]	[PAH or PCB PE]	[PAH of PCB PE]	[PAH or PCB PE]	[PAH of PCB PE]	[PAH or PCB PE]	[PAH of PCB PE]	[PAH or PCB PE]
			Result	MDL	Result	MDL	Result	MDL	Result	MDL
			(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)
Acenaphthene	PPAH		330	210	150	150	190	170	4000	100
Acenaphthylene	PPAH		ND	63	ND	45	ND	52	44	32
Anthracene	PPAH		370	190	ND	140	ND	160	12000	95
Benzo(a)anthracene	PPAH		11000	290	ND	210	ND	240	210000	720
Benzo(a)pyrene	PPAH		19000	190	ND	140	ND	160	240000	480
Benzo(b)fluoranthene	PPAH		11000	250	ND	180	ND	210	240000	620
Benzo(ghi)perylene	PPAH		13000	150	ND	110	ND	120	84000	75
Benzo(k)fluoranthene	PPAH		3700	220	ND	160	ND	180	120000	550
Chrysene	PPAH		22000	200	ND	140	ND	170	250000	500
Dibenz(a,h)anthracene	PPAH		2200	70	ND	50	ND	58	20000	35
Fluoranthene	PPAH		4300	360	ND	260	ND	300	270000	900
Fluorene	PPAH		ND	470	ND	340	ND	390	740	240
Indeno(1,2,3-cd)pyrene	PPAH		4200	170	ND	120	ND	140	81000	85
Naphthalene	PPAH		ND	5300	ND	3800	ND	4400	ND	2600
Phenanthrene	PPAH		3200	1600	ND	1100	ND	1300	48000	800
Pyrene	PPAH		21000	1100	ND	790	ND	920	370000	2800
1-Methylnaphthalene	AlkPAH		ND	1300	ND	930	ND	1100	ND	650
2-Methylnaphthalene	AlkPAH		ND	2900	ND	2100	ND	2400	ND	1400
PCB-14		PRC	ND	10	ND	7.1	ND	8.3	ND	5
PCB-36		PRC	65	10	160	7.1	160	8.3	ND	5
PCB-78		PRC	25	10	500	7.1	420	8.3	ND	5
PCB-104		PRC	ND	10	57	7.1	40	8.3	ND	5
PCB-121		PRC	100	10	460	7.1	420	8.3	15	5
PCB-142		PRC	120	10	540	7.1	450	8.3	30	5
PCB-155		PRC	270	10	560	7.1	500	8.3	83	5
PCB-184		PRC	640	10	980	7.1	890	8.3	500	5
PCB-192		PRC	710	10	1100	7.1	1100	8.3	600	5
PCB-204		PRC	660	10	720	7.1	730	8.3	740	5

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second MDL column for each sample.
- PPAH: Priority Pollutant PAH ; AlkPAH: Alkylated PAH; PRC: Performance Reference Compound

Table A-2. Concentration of analytes in polyethylene (PE). (Continued)

Compound	PAH Group	PRC	ST-RS-NBG		MCASM-19-C	
			[PAH of PCB PE]	[PAH or PCB PE]	[PAH of PCB PE]	[PAH or PCB PE]
			Result	MDL	Result	MDL
			(ng/g)	(ng/g)	(ng/g)	(ng/g)
Acenaphthene	PPAH		ND	140	ND	100
Acenaphthylene	PPAH		ND	42	ND	30
Anthracene	PPAH		ND	130	340	90
Benzo(a)anthracene	PPAH		500	190	6800	140
Benzo(a)pyrene	PPAH		960	130	8800	90
Benzo(b)fluoranthene	PPAH		1200	170	6700	120
Benzo(ghi)perylene	PPAH		440	100	3400	71
Benzo(k)fluoranthene	PPAH		650	150	2800	100
Chrysene	PPAH		800	130	12000	95
Dibenz(a,h)anthracene	PPAH		90	47	690	33
Fluoranthene	PPAH		730	240	5800	170
Fluorene	PPAH		ND	310	ND	220
Indeno(1,2,3-cd)pyrene	PPAH		400	110	2000	81
Naphthalene	PPAH		ND	3500	ND	2500
Phenanthrene	PPAH		ND	1100	2400	760
Pyrene	PPAH		960	730	12000	520
1-Methylnaphthalene	AlkPAH		ND	870	ND	620
2-Methylnaphthalene	AlkPAH		ND	1900	ND	1400
PCB-14		PRC	ND	6.7	ND	4.8
PCB-36		PRC	ND	6.7	ND	4.8
PCB-78		PRC	ND	6.7	23	4.8
PCB-104		PRC	ND	6.7	9.4	4.8
PCB-121		PRC	64	6.7	1000	4.8
PCB-142		PRC	78	6.7	2000	4.8
PCB-155		PRC	87	6.7	230	4.8
PCB-184		PRC	390	6.7	600	4.8
PCB-192		PRC	490	6.7	1500	4.8
PCB-204		PRC	630	6.7	610	4.8

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second MDL column for each sample.
- PPAH: Priority Pollutant PAH ; AlkPAH: Alkylated PAH ; PRC: Performance Reference Compound

Table A-3. Concentrations of freely-dissolved (Cfree) PAHs in soil, as measured by passive sampling.

PAH	PAH Group	G1		G2		G3		G5		L	
		[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL
		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Acenaphthene	PPAH	ND	28	190	28	110	30	ND	33	ND	30
Acenaphthylene	PPAH	ND	10	ND	10	ND	12	ND	12	ND	12
Anthracene	PPAH	ND	6.3	76	6.3	50	6.9	ND	7.6	ND	6.9
Benzo(a)anthracene	PPAH	1.5	0.38	40	0.38	23	0.43	ND	0.48	ND	0.43
Benzo(a)pyrene	PPAH	0.65	0.065	20	0.067	7.3	0.073	0.19	0.1	0.15	0.072
Benzo(b)fluoranthene	PPAH	1.4	0.084	30	0.087	16	0.1	0.33	0.13	0.53	0.098
Benzo(ghi)perylene	PPAH	0.19	0.011	4.7	0.011	1.4	0.0093	0.028	0.016	0.065	0.012
Benzo(k)fluoranthene	PPAH	0.65	0.078	15	0.081	8	0.087	0.16	0.12	0.23	0.085
Chrysene	PPAH	2.5	0.28	68	0.28	45	0.3	0.64	0.32	0.85	0.3
Dibenz(a,h)anthracene	PPAH	0.15	0.02	3.9	0.02	1.8	0.022	ND	0.031	0.048	0.022
Fluoranthene	PPAH	11	2.4	350	2.4	230	2.6	3.5	2.8	ND	2.6
Fluorene	PPAH	ND	31	ND	31	35	35	ND	37	ND	35
Indeno(1,2,3-cd)pyrene	PPAH	0.47	0.032	13	0.034	5.5	0.037	0.081	0.056	0.13	0.036
Naphthalene	PPAH	ND	3500	ND	3500	ND	3900	ND	4200	ND	3900
Phenanthrene	PPAH	ND	53	430	53	380	59	ND	63	ND	59
Pyrene	PPAH	12	7.3	380	7.3	230	8.2	ND	8.7	ND	8.2
1-Methylnaphthalene	AlkPAH	ND	360	ND	360	ND	400	ND	430	ND	400
2-Methylnaphthalene	AlkPAH	ND	730	ND	730	ND	830	ND	880	ND	830
Total Detected PAHs		31	--	1621	--	1143	--	5	--	2	--

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second (MDL) column for each sample.
- PPAH: Priority Pollutant PAH
- AlkPAH: Alkylated PAH

Table A-3. Concentrations of freely-dissolved (Cfree) PAHs in soil, as measured by passive sampling. (Continued)

PAH	PAH Group	F		G4		FINEGAYAN 2		FINEGAYAN T+S		WHITING FIELD	
		[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL
		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Acenaphthene	PPAH	ND	38	ND	24	136	74	402	58	83	53
Acenaphthylene	PPAH	ND	14	ND	9.2	ND	28	ND	22	ND	20
Anthracene	PPAH	ND	8.8	ND	5.4	69	20	404	13	23	12
Benzo(a)anthracene	PPAH	ND	0.57	1.5	0.36	29	2.04	189	0.84	30	0.79
Benzo(a)pyrene	PPAH	ND	0.12	0.78	0.075	12	0.44	72	0.15	17	0.17
Benzo(b)fluoranthene	PPAH	0.34	0.16	1	0.096	13	0.59	79	0.20	9.77	0.22
Benzo(ghi)perylene	PPAH	0.036	0.021	0.055	0.0099	0.78	0.05	3.31	0.01	2.39	0.03
Benzo(k)fluoranthene	PPAH	ND	0.14	0.63	0.087	4.18	0.50	36	0.17	3.29	0.20
Chrysene	PPAH	0.57	0.38	2.3	0.25	51	1.40	237	0.58	60	0.55
Dibenz(a,h)anthracene	PPAH	ND	0.038	0.08	0.023	0.85	0.14	5.82	0.05	1.65	0.05
Fluoranthene	PPAH	ND	3.3	9.2	2	159	9.63	1522	5.07	54	4.54
Fluorene	PPAH	ND	43	ND	26	ND	90	89	65	ND	59
Indeno(1,2,3-cd)pyrene	PPAH	0.066	0.066	0.24	0.039	1.45	0.23	15	0.07	2.29	0.09
Naphthalene	PPAH	ND	4800	ND	3000	ND	8303	ND	7428	ND	6672
Phenanthrene	PPAH	ND	69	ND	46	370	171	1452	114	202	101
Pyrene	PPAH	ND	10	10	6.4	265	29	1776	15	265	14
1-Methylnaphthalene	AlkPAH	ND	490	ND	310	ND	877	ND	735	ND	682
2-Methylnaphthalene	AlkPAH	ND	1000	ND	640	ND	1881	ND	1567	ND	1420
Total Detected PAHs		1	--	26	--	1111	--	6282	--	754	--

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second (MDL) column for each sample.
- PPAH: Priority Pollutant PAH
- AlkPAH: Alkylated PAH

Table A-3. Concentrations of freely-dissolved (Cfree) PAHs in soil, as measured by passive sampling. (Continued)

PAH	PAH Group	ST-SR-NBG		ST-RS-NBG		MCASM-19-C	
		[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL	[PAH Cfree] Result	[PAH Cfree] MDL
		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Acenaphthene	PPAH	1000	25	ND	35	ND	25
Acenaphthylene	PPAH	14	10	ND	13	ND	10
Anthracene	PPAH	760	6.0	ND	8.2	21	5.7
Benzo(a)anthracene	PPAH	530	1.8	1.3	0.48	17	0.35
Benzo(a)pyrene	PPAH	150	0.30	0.63	0.09	6.3	0.06
Benzo(b)fluoranthene	PPAH	150	0.39	0.79	0.11	4.8	0.09
Benzo(ghi)perylene	PPAH	13	0.01	0.05	0.011	0.48	0.01
Benzo(k)fluoranthene	PPAH	76	0.35	0.43	0.10	2.0	0.07
Chrysene	PPAH	630	1.3	2.0	0.33	30	0.24
Dibenz(a,h)anthracene	PPAH	10	0.02	0.048	0.025	0.41	0.020
Fluoranthene	PPAH	3400	11	9.2	3.0	73	2.1
Fluorene	PPAH	93	30	ND	39	ND	28
Indeno(1,2,3-cd)pyrene	PPAH	27	0.03	0.15	0.040	0.84	0.034
Naphthalene	PPAH	ND	3300	ND	4400	ND	3100
Phenanthrene	PPAH	3000	50	ND	69	150	48
Pyrene	PPAH	4700	35	12	9	150	7
1-Methylnaphthalene	AlkPAH	ND	340	ND	460	ND	330
2-Methylnaphthalene	AlkPAH	ND	690	ND	930	ND	690
Total Detected PAHs		14553	--	27	--	456	--

Notes

- ND: Not detected at the Method Detection Limit (MDL) shown in the second (MDL) column for each sample.
- PPAH: Priority Pollutant PAH
- AlkPAH: Alkylated PAH

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APPENDIX B

UNIVERSITY OF ILLINOIS REPORTS

OVERVIEW

This section contains two sample analysis reports and two summary reports referenced and summarized above which were provided to us as contract deliverables from the University of Illinois.

The Certified Reference Material, CRM 141

Description:

CRM 141 (loamy clay 1) was collected from the fields near Pellegrino (Italy) as a reference material for the trace element analysis in soils by European Commission BCR.

This material consist of a homogeneous powder, with particles smaller than 90 μm . Additional information is available on aqua soluble concentrations.

Certified concentrations ($\mu\text{g/g}$ dry weight):

Element	Value	Uncertainty ($\pm$)
Cu	32.6	1.4
Zn	81.3	3.7
Cd	0.36	0.10
Hg	0.0568	0.0043
Pb	29.4	2.6

Component	Value	Std. Deviation
Na ₂ O	0.43	
MgO	1.19	
Al ₂ O ₃	10.5	
P ₂ O ₅	0.16	
SiO ₂	42.58	
K ₂ O	1.56	
CaO	17.98	
TiO ₂	0.47	
Fe ₂ O ₃	3.74	
Cr ($\mu\text{g/g}$)	75.0	10.4
Mn ($\mu\text{g/g}$)	547	32
Co ($\mu\text{g/g}$)	9.2	1.1
Ni ($\mu\text{g/g}$)	30.9	3.2
Se ($\mu\text{g/g}$)	0.160	0.025

Our analysis for polycyclic aromatic hydrocarbons (PAH) in CRM 141 is given below. We performed triplicate measurements with Terphenyl-d-14 (D14) as an internal standard and based the results on the dry weight at 105°C. Results were corrected for the D14 internal standard recovery.

Sample Units Compound Group	CRM141 #1 mg/kg	CRM141 #2 mg/kg	CRM141 #3 mg/kg	Mean mg/kg	Uncertainty ±
Naphthalene	1.34	1.21	0.56	1.04	0.42
Acenaphthylene	0.85	0.77	0.33	0.65	0.28
Acenaphthene	0.96	0.88	1.09	0.97	0.11
Fluorene	0.92	0.88	0.47	0.76	0.25
Phenanthrene	1.07	1.02	0.64	0.91	0.24
Anthracene	1.10	1.01	0.43	0.84	0.36
Fluoranthene	1.28	1.19	0.58	1.02	0.38
Pyrene	0.42	0.39	0.26	0.36	0.08
Terphenyl-d14 (Internal Standard)	20.13	20.03	20.19	20.12	0.08
Benzo (a) anthracene	< 0.5	< 0.5	0.73	0.73	
Chrysene	< 0.5	< 0.5	< 0.5	< 0.5	
Benzo(b)fluoranthene	< 0.5	< 0.5	< 0.5	< 0.5	
Benzo(k)fluoranthene	2.62	2.43	1.09	2.05	0.83
Benzo (a) pyrene	< 0.5	< 0.5	< 0.5	< 0.5	
Indeno(1,2,3,c,d)pyrene	< 0.5	< 0.5	0.96	0.96	
Dibenz(a,h)anthracene	< 0.5	< 0.5	0.82	0.82	
Benzo (g,h,i) perylene	< 0.5	< 0.5	0.94	0.94	
Total Target PAH	10.57	9.76	8.17	9.50	1.22

Standard Reference Material, HS5 Marine Sediment

Description:

HS5 was collected from a harbor in Nova Scotia, Canada. According to the certificate of analysis, this material was freeze-dried, sieved to pass a 125 µm sieve, homogenized in a cement mixer, and then subsampled into 200 g portions.

Our analysis for polycyclic aromatic hydrocarbons (PAH) in HS5 is given below. We performed triplicate measurements with Terphenyl-d-14 (D14) as an internal standard and based the results on the dry weight at 105°C. Results were corrected for the D14 internal standard recovery.

Sample Units	HS5 #1 mg/kg	HS5 #2 mg/kg	HS5 #3 mg/kg	Mean mg/kg	Uncertainty ±
Compound Group					
Naphthalene	1.02	0.75	1.29	1.02	0.27
Acenaphthylene	0.66	0.49	0.86	0.67	0.19
Acenaphthene	0.82	0.60	1.07	0.24	
Fluorene	0.74	0.62	0.94	0.77	0.16
Phenanthrene	2.04	2.00	2.46	2.17	0.26
Anthracene	0.90	0.67	1.18	0.92	0.26
Fluoranthene	6.33	6.68	7.35	6.79	0.52
Pyrene	1.67	1.57	1.94	1.73	0.19
Terphenyl-d14 (Internal Standard)	20.49	19.61	19.08	19.73	0.71
Benzo (a) anthracene	1.58	1.19	2.05	1.61	0.43
Chrysene	<0.5	1.01	<0.5	1.01	
Benzo (b) fluoroanthene	<0.5	<0.5	<0.5	<0.5	
Benzo (k) fluoranthene	2.48	1.75	2.99	2.41	0.62
Benzo (a) pyrene	<0.5	<0.5	<0.5	<0.5	
Indeno (1,2,3,c,d) pyrene	1.94	1.59	2.16	1.90	0.29
Dibenz (a,h) anthracene	<0.5	<0.5	<0.5	<0.5	
Benzo (g,h,i) perylene	<0.5	<0.5	<0.5	<0.5	
Total Target PAH	20.20	18.91	24.31	21.14	2.82

Contamination of Navy Skeet Ranges

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TECHNICAL APPROACH

Goals and Objectives

The Department of the Navy desires to remediate shooting-range lands which have been contaminated with polycyclic aromatic hydrocarbons (PAH). The source of the PAH is the clay discs used as targets, fragments of which now litter the soil of the ranges. They desire characterization of the clay targets and a strategy for predicting the fate of the PAH in the associated soils.

We hypothesize that the potential for PAH leaching from clay-target contaminated soils can be estimated by comparing the characteristics and behavior of pure target materials, uncontaminated adjacent soils, and various particle-size fractions of the contaminated soils. Using a mutually agreed upon number of bulk samples representative of Navy shooting-range lands, which were supplied by Navy personnel to the University of Illinois, a battery of physical, chemical, and spectroscopic techniques were applied to make measurements and comparisons. The objective was to provide estimates of PAH leaching from various particle-size fractions of clay-target contaminated soils. In order to test this hypothesis and accomplish the overall objective, we pursued the following four specific aims.

Aim #1: Separate uncontaminated soils, pure clay targets, and corresponding clay-target contaminated soils into several particle-size fractions using physical methods.

Aim #2: Identify the mineralogical and chemical characteristics and PAH content, and the base-line rate of PAH leaching of clay targets.

Aim #3: Determine the clay mineralogy and PAH content of uncontaminated adjacent soils.

Aim #4: Characterize the mineralogy, total PAH content, and rate of PAH leaching of each particle-size fraction of clay-target contaminated soils.

Report 04-10-2016

MATERIALS AND METHODS

Soil samples origin. Soil samples investigated in this work were sampled and delivered by the Department of the Navy from several military skeet ranges located across the US. A total of 17 soil samples were studied in this project. Samples were divided into two sets. The first set of four samples (BF-BG, BF-SA, WF-BG, and WF-SA) was delivered at the beginning of the project and the second sample set (S1 - S13) was delivered during or at the end of the project due to difficulties occurred during obtaining samples from the shooting ranges and fields. Appropriate labeling of samples is included in Table 1.

Table 1. Labeling and types of studied soil samples.

#	Soil Sample	Label	Contamination
1	BF-BG-01	BF-BG	background
2	BF-SA-01	BF-SA	contaminated
3	WF-BG-01	WF-BG	background
4	WF-SA-01	WF-SA	contaminated
5	AAFB-17A-U	S1	background
6	AAFB-17A-C	S2	contaminated
7	FNG-TSF-U	S3	background
8	FNG-TSF-C	S4	contaminated
9	FNG-MSF-C	S5	contaminated
10	MCASM-19-U	S6	background
11	MCASM-19-C	S7	contaminated
12	AAFB-RS-U	S8	background
13	AAFB-SR-ASA	S9	contaminated
14	FN-NBG-R	S10	background
15	FN-NBG-C	S11	contaminated
16	ST-SR-NBG	S12	contaminated

Skeet samples. Seven types of skeets frequently used for military shooting trainings were investigated in this work. All seven were delivered directly from the manufacturers (Table 2). Broken weathered skeet fragments were collected and delivered from each skeet shooting range as well.

Table 2. Labeling of seven skeet targets investigated in this work.

#	Skeet	Label	Brand
1	Skeet 01	SK01	Herter's
2	Skeet 02	SK02	Blue Rock
3	Skeet 03	SK03	White Flyer
4	Skeet 04	SK04	White Flyer
5	Skeet 05	SK05	White Flyer
6	Skeet 06	SK06	White Flyer
7	Skeet 07	SK07	Blue Rock

Particle size distribution. Samples were separated into particle-size fractions by dry sieving. Seven clay targets were received in their original, pristine state and were gently ground in an agate mortar and pestle to particle sizes that passed through a 230 mesh sieve, which gave particles of <60 μm equivalent spherical diameter (esd). The soils, both contaminated and uncontaminated, were not ground but were sieved directly into four particle sizes, namely, >500 μm esd (+35 mesh), 125 – 500 μm esd (-35 mesh, +120 mesh), 60 – 125 μm esd (-120 mesh + 240 mesh), and <63 μm esd (-230 mesh). The “+” and “-” signs indicate the particles retained by (+) or passed through (-) the selected mesh-size sieve. In selected samples (WF and BF), the <2 μm fractions were removed by dispersing the sample in distilled water, then fractionating by centrifugation methods according to Stoke's Law (Jackson, 1956). This <2 μm fraction was then freeze dried (Table 4).

Mineralogy

X-Ray Diffraction (XRD). The mineralogical characteristics of powdered and oriented patterns of the skeet and soil samples were determined using a Scintag XDS2000 X-Ray Diffractometer (XRD) and analyzed by the *Jade 9* software for XRD mineral identification and quantification at the mineral and clay mineral lab at the Illinois State Geological Survey (ISGS).

Infrared spectroscopy (FTIR). The FTIR spectra in the middle infrared (MIR) region (4000 cm^{-1} - 400 cm^{-1}) were collected in transmission mode using a MIDAC M2000 FTIR spectrometer from MIDAC Corp. (Westfield, Massachusetts, USA) equipped with a DTGS detector. A resolution of 2 cm^{-1} and 128 scans were used to analyze samples prepared as KBr pellets (0.5 mg of the sample powder mixed with 200 mg KBr) pressed up to 109,267 PSI and heated overnight at 150°C to minimize water content in the sample and KBr. The raw spectra were processed using the OPERANT LLC Essential FTIR software package.

Near infrared spectroscopy (NIR). NIR spectra were collected on a Varian 5E UV-Vis-NIR spectrometer in reflection mode using solid phase samples. All spectra were recorded in the NIR region from 8000 cm^{-1} to 4000 cm^{-1} and manipulated by the Essential FTIR software package.

Mössbauer spectroscopy. Mössbauer spectra were recorded on a Web Research, Inc. (Edina, Minnesota) spectrometer equipped with a Janis model SHI-850-5 (Janis, Inc., Woburn, Massachusetts) closed cycle low temperature cryostat. The transducer operated in the triangular waveform mode with a $50\text{ mCi }^{57}\text{Co}$ source dispersed as 10 wt.% in a thin Rh foil (Ritverc, Inc. St. Petersburg, Russia). Calibration of the velocity scale was performed by measuring the magnetic hyperfine field (B_{hf}) of a 7 mm thick α -Fe foil at the sample temperature (Stucki *et al.*, 2014). The data were analyzed by the WinNormos-for-IGOR (Brand, 2008) extension software pack within IGOR Pro (WaveMetrics Inc., Lake Oswego, Oregon, USA) using Lorentzian lineshapes (Murad and Cashion, 2004).

Chemical analysis.

Elementary C, H, N analysis (CHN). CHN analysis was performed to determine total carbon content in both uncontaminated (background) and contaminated soil samples, as well as in pure

skeet targets. The total C content was obtained using a CHN analyzer in the University of Illinois microanalysis laboratory in the School of Chemical Sciences.

Carbon content analysis (CCA). Because of the predominance of calcite (CaCO_3) and dolomite (MgCO_3) and organic carbon in the pure skeet material, an analysis of C content on the samples was undertaken. Because the source of C could be either organic (e.g., skeet targets) or inorganic (carbonates), the samples were acid treated with 0.67 M HCl at room temperature for 12 h to remove the carbonates by the reaction then washed with DI water and freeze dried, weighed, and analyzed for total carbon (TC) content using a CNS analyzer in the University of Illinois microanalysis laboratory in the School of Chemical Sciences. Organic carbon (OC) and inorganic carbon (IC) contents were then calculated for each sample, beside those which contained other acid soluble components (for example: hematite, boehmite, goethite, etc.) by equation (1).

$$\text{IC} = \text{TC} - \text{OC} \quad (1)$$

Total organic content (TOC). The proportion of organic matter in the soil samples was also determined by weighing the sample before and after heating them in a muffle furnace at 440°C overnight.

Water content (WC). The amount of the physically adsorbed water on the soil and skeet surfaces was determined by weighing the sample before and after drying at 105°C overnight.

PAH analysis. The polyaromatic hydrocarbon contents in skeets and soils were determined following the 8001 standard PBET analytical method. The PAH analysis includes stages (1) extraction, (2) purification, and (3) GC-MS analysis.

(1) Extraction

The extraction of 16 target PAHs was performed by the accelerated solvent extraction (ASE) technique.

ASE. A Dionex ASE 200 extractor and extraction solvent, consisting of a mixture of acetone and dichloromethane (1:1), were used. Samples were weighed and transported to the cylindrical body of the extraction cells (22mL RESTEK, Inc.) and sealed by diatomic mesh (200,000). The top

and bottom of the cell's body were closed by metal caps. The extraction procedure was performed at 100°C. The accuracy of the extraction, concentration, and cleanup steps was determined using a volatile internal standard Terphenyl d14 Surrogate (D-14). On the top of the extraction cell and before each concentration and cleanup steps a 25 µL portion of 50 ppm D-14 was spiked in. The final concentration of D-14 in all extracts prepared for the GC-MS measurement was 1 ppm. The calibration curve was plotted by using the 16 target PAH standards of prepared concentrations 0.5, 1, 3, 5, 7, and up to 10 ppm. All solvents and chemicals used besides the standards were of HPLC grade and delivered by Fisher Scientific, Chicago, Illinois, USA.

(2) Purification

The purification stage included a set of three operations (concentration after extraction, clean up, and concentration after clean up), which were required for the liquid sample preparation suitable for GC-MS measurement.

Concentration after extraction (CAE). All extracted supernatants were concentrated in a water bath at 25°C in a crystallization beaker, placed on a heater that was set at low heat and controlled by a thermostat. Above each solution to be concentrated, a conical bottom vial (CCBV) (5 mL) and a stream of gaseous nitrogen were installed. The extracted solution was transferred to the CCBV using 2-mL glass tips attached to a N₂-purged syringe above the liquid surface. If the meniscus approached 1.5 mL, more extracted solution was added. Once all amounts of the extracted solution were dried, 4 mL of cyclohexane was used for the rinse of the extraction cell. Rinsed cyclohexane was then transferred from the extraction vial to the CCBV and purged by N₂. When volume of ~1.2 mL was approached, the concentrated solution was transferred to the 4 mL amber CCBV. All vials were correctly labeled (solution, concentration, date, and user) and stored in refrigerator for future analysis.

CleanUP (CU). The CU step was designed to purify the extracted supernatants by removing moisture, dissolved organic dies, and other impurities which could affect the gas chromatography measurement. The CU apparatus consists of a glass column or a 100 mL glass syringe with a stainless steel stopcock. At the column bottom, glass wool was added and wet by 10 mL of DCM. Then 5 g of activated (for 16 h at 130°C) silica-gel was added and column walls were

rinsed with 1 mL of DCM. Then 2 g of activated (for 4 h at 400°C) sodium sulphate was added on the silica gel layer and sealed by glass wool on the top. 15 mL of pentane was poured onto the top of the cylinder while the cock was open to release the DCM from the syringe by gravity. When a 10 mL volume was reached, 2 mL of sample was added and another 2 mL of cyclohexane was used to rinse the vial. When 13 mL volume level was reached the cock was stopped and a new, clean collecting vial was placed under the cock. To the syringe, 20 mL of the DCM and pentane (2:3 v/v) mixture was added and all solution passed through the column to the vial.

Concentration after clean up (CACU). The CACU procedure step is identical to the CAE step except at the end the solution is concentrated to 1 mL and then transferred to a 2 mL vial closed by a crimp cap, ready for GC-MS measurement.

Table 3. Abbreviations, ion mass, and retention times of 16 target PAH standards.

PAH compound	PAH abbrev.	Ion [m/z]	Rt [s]
1 Naphthalene	Nap	128	5.71
2 Acenaphthylene	Aty	152	7.42
3 Acenaphthene	Ath	154	7.66
4 Fluorene	Flu	166	8.52
5 Phenanthrene	Phe	178	10.94
6 Anthracene	Anth	178	11.11
7 Fluoranthene	Fla	202	15.55
8 Pyrene	Py	202	16.56
9 Benzene (a) anthracene	BA	228	22.84
10 Chrysene	Chr	228	23.00
11 Benzo (b) fluoroanthene	BbF	252	28.59
12 Benzo (k) fluoranthene	BkF	252	28.77
13 Benzo (a) pyrene	BaP	252	30.40
14 Indeno (1,2,3,c,d) perylene	IP	276	36.13
15 Dibenzo (a,h) anthracene	DBahA	278	36.37
16 Benzo (g,h,i) perylene	BghiP	276	37.28

GC-MS analysis. Concentration profiles of 16 PAHs in all soil and skeet samples were obtained using an Agilent 5975 Series GC/MSD system equipped with a diffusion pump and turbomolecular (turbo) pumps with ultra-pure He as a carrying gas. Instrument calibration was performed by a set of 16 PAH standards (Table 3) of nominal concentrations: 0.5, 1, 3, 5, 7, and 10 ppm.

Calibration of the carbon content in the soil samples.

The XRD calibration method for determination of the contamination extent in contaminated soils was obtained by preparation mixtures of SK3 and the background soil WF-BG of several skeet concentrations in WF-BG (5, 10, and 20%). In all skeet/soil mixtures a TC content was determined and correlation between the total carbon content *vs.* the calcite XRD peak area plotted. For the normalization, the most intense quartz peak at $26.5^{\circ}2\theta$ was used. The calibration curves were prepared by mixing SK1, SK2, and SK7, due to dolomite presence in SK2 and SK7.

RESULTS AND DISCUSSION

Separation of uncontaminated soils, pure clay targets, and corresponding clay-target contaminated soils into several particle-size fractions using physical methods (CLIN 0001).

Separation of soil samples by dry sieving provided a particle size distribution of all studied samples (Table 4).

Table 4. Particle size distribution of 17 soil samples.

Soil	> 500 μm [%]	500 - 125 μm [%]	125 - 63 μm [%]	< 63 μm [%]	Total [%]
BF-BG	34.69	57.14	3.06	5.05	100
BF-SA	31.31	63.64	0.91	4.34	100
WF-BG	16.16	58.59	14.14	11.11	100
WF-SA	19.79	61.46	9.69	8.85	100
S1	83.91	12.50	2.40	1.20	100
S2	85.94	12.65	1.08	0.33	100
S3	90.41	7.50	1.36	0.74	100
S4	87.20	9.90	1.76	1.14	100
S5	80.22	17.16	1.72	0.91	100
S6	45.09	34.81	8.54	11.56	100
S7	34.79	55.34	6.26	3.61	100
S8	84.50	11.22	1.95	2.33	100
S9	82.80	9.22	2.68	5.31	100
S10	78.51	17.37	1.80	2.31	100
S11	84.52	11.95	1.58	1.95	100
S12	77.52	16.82	2.62	3.04	100
S13	89.68	7.00	1.95	1.37	100

A different morphology of background soils was observed. BF-BG and WF-BG contained particles distributed mostly in the 500 - 125 μm size fraction (57.14 and 58.59%) and relatively high content of <63 μm size fraction 5.05% (BF-BG) and 11.11% (WF-BG). S1 background soil contained 83.91% of >500 μm size fraction and 12.50% of 500 - 125 μm size fractions. The finer fractions, 125 - 63 μm and <63 μm , were present in the minority 2.40% and 1.20%, respectively. Similarly, S3 background soil was distributed mostly in the larger fractions, where 90.41% of all particles were included in the >500 μm size fraction and just 7.50% of them in the 500 - 125 μm size fraction. The finer fractions of S3 were very poorly present; 1.36% for 125 - 63 μm fraction and only 0.74% for <63 μm particle size fraction. A particle size distribution of S6 background soil contains 45.09% of all particles sized in >500 μm fraction and 34.81% in 500 - 125 μm fraction. Surprisingly, the finer particles were of the higher content; 8.4% for 125 - 63 μm and even 11.4% for <0.063 mm particle size fraction. Particle size

distributions of contaminated soils followed the trends of coupled backgrounds beside sample S7 where the <63 μm fraction decreased to 3.61% (Table 4).

Identification of the mineralogical and chemical characteristics, PAH content, and base-line rate of PAH leaching of clay targets soil standards (CLIN 0002).

Mineralogy of skeet targets

XRD. The mineralogical characteristics of the skeet samples were determined by XRD, MIR, and NIR. The XRD patterns for seven skeet samples (Figures 1A and 1B) revealed that the dominant crystalline phases are dolomite (MgCO_3) and calcite (CaCO_3) in the clay targets. All targets except SK2 and SK7 contained calcite, but targets SK1, SK3, and SK6 contained no or very little discernible dolomite. Targets SK2 and SK7 contained only dolomite. This may, therefore, be a way to narrow the identification of which skeet was used at which site, i.e., if no dolomite is detected, the skeet used may have been SK1, SK3, and/or SK6.

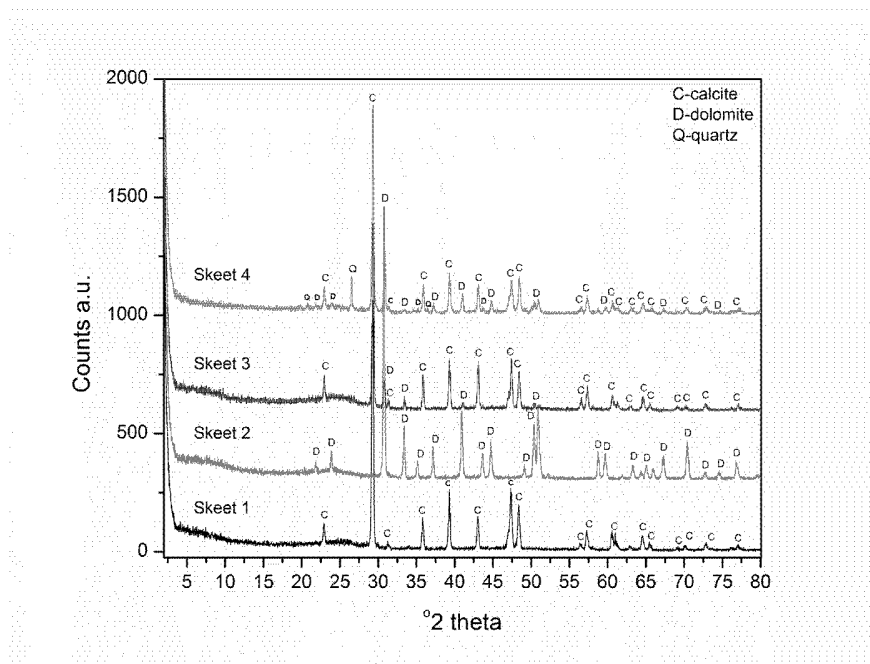


Figure 1A. X-ray diffraction patterns of SK1 thru SK4. The main crystalline phases in all skeet samples are dolomite (D) and calcite (C). The minor phase is Quartz (Q). A slight undulation in the 2 to 30 °2θ range is an evidence that a small amorphous phase is also present.

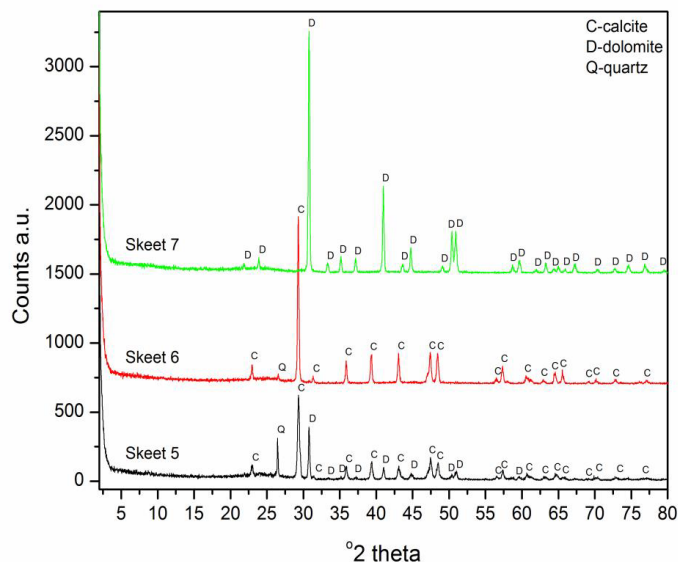


Figure 1B. X-ray diffraction patterns of SK5, SK6, and SK7 samples. The main crystalline phases in all skeet samples are dolomite (D) and calcite (C). The minor phase is quartz (Q). A slight undulation in the 2 to 30 °2θ range is an evidence that a small amorphous phase is also present.

NIR. The NIR spectra (Figure 2) of the skeet samples (SK2 and SK7) revealed that besides the combination vibration of AlAlOH at 4535 cm^{-1} , the first overtone $2\nu(\text{OH})$ at 7075 cm^{-1} and 7172 cm^{-1} (kaolinite band). These results are consistent with the XRD patterns of the <0.063 and 2 μm size fractions of these samples. The very intense water band ($\nu+\delta$)H₂O near 5190 cm^{-1} also clearly distinguished a set of C-H combination vibrations near 4302 cm^{-1} , 4387, and 4420 cm^{-1} . The skeet spectra included further C-H group vibrations, such as the vibrations at 4059 cm^{-1} and 4616 cm^{-1} , which are attributed to combination vibrations of ($\nu_{\text{CH}}+\delta_{\text{CC}}$)aromatic and ($\nu_{\text{CH}}+\nu_{\text{CC}}$)aromatic, respectively. The first overtones of C-H groups were found near 5925 cm^{-1}

and 6000 cm^{-1} , and were attributed to $2\nu\text{CH}_3$ and $2\nu\text{CH}(\text{aromatic})$, respectively (Madejová et al., 2011). These bands are visible in the spectrum of the WF-SA soil, whereas in the BF-SA spectrum they were absent due to lower carbon contamination. The absence of the combination vibration band of water OH groups perhaps also provides further evidence of the hydrophobicity of the skeet material, due to high organic C content ($\sim 35\%$).

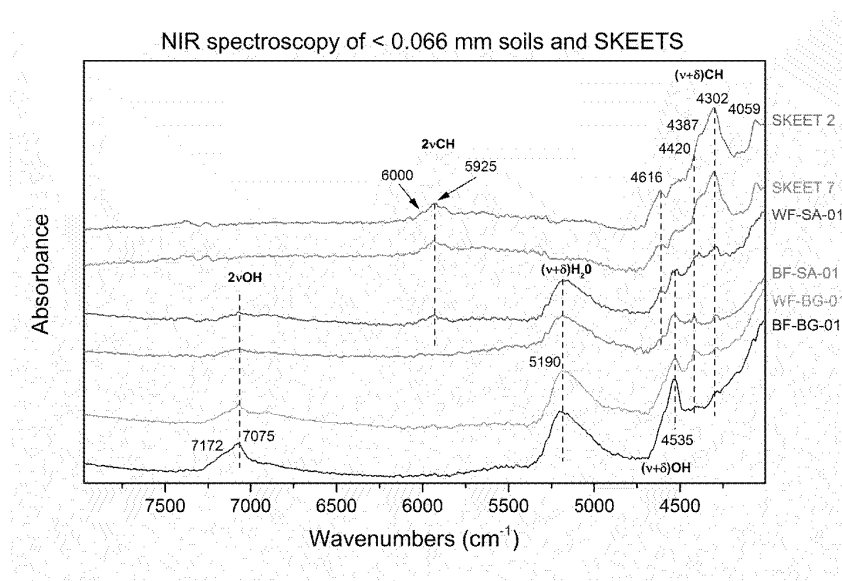


Figure 3. Near-infrared (NIR) spectra of the soils and two skeet samples

Chemical analysis of skeet targets

Carbon content. The amounts of OC and IC are summarized in Figure 3, and show that the skeet samples were similar in their C profiles, having about twice as much carbonate as organic carbon.

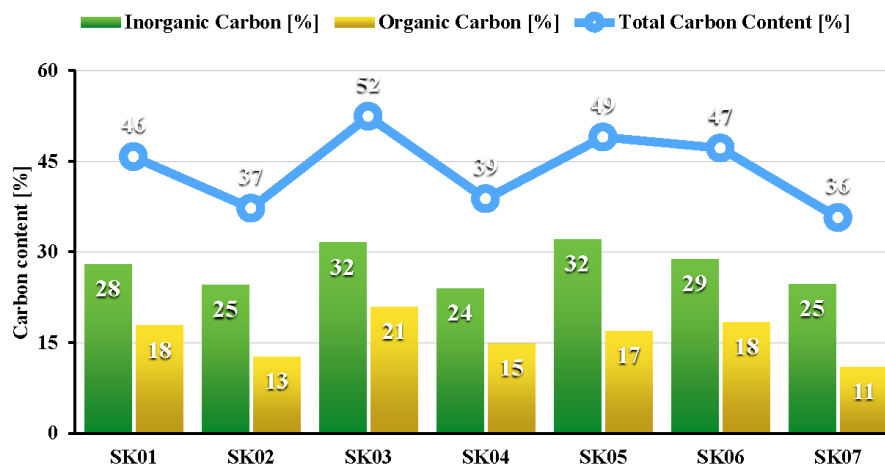


Figure 3. The total, organic, and inorganic carbon contents of seven skeet samples.

PAH analysis. The polycyclic aromatic hydrocarbon contents were determined in all seven skeet samples. For all samples a triplicate analysis was performed and 16 target PAHs were calculated on dry powder sample dried at 105°C (Table 5, Figure 4).

Table 5. Concentration of the 16 target PAHs determined in all seven flying skeet targets.

Sample		SK1	SK2	SK3	SK4	SK5	SK6	SK7
PAH		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	Nap	28.982	3.820	573.676	15.937	26.519	16.067	14.201
2	Aty	2.807	3.392	456.546	<0.001	5.514	1.503	5.372
3	Ath	20.692	0.727	454.639	6.331	307.095	149.200	<0.001
4	Flu	4.115	1.046	385.548	2.987	161.376	53.139	<0.001
5	Phe	171.949	10.815	1816.643	191.325	1798.417	1486.007	23.435
6	Anth	26.491	3.378	708.873	29.360	533.748	190.450	1.506
7	Fla	1502.669	18.196	4756.879	213.532	3449.628	4719.735	51.545
8	Py	1579.625	114.001	4766.040	1012.748	3611.449	4748.757	158.870
9	BA	3468.714	1618.373	4616.831	3981.060	7956.242	8837.675	2361.150
10	Chr	1807.500	1025.267	3198.838	1831.886	2626.273	5005.939	1215.579
11	BbF	14927.336	3368.760	11278.346	3924.514	29924.205	36658.803	6632.872
12	BkF	1320.480	590.936	2685.027	823.736	5426.398	5779.387	679.676
13	BaP	12150.194	3712.024	6504.459	12254.175	41947.034	44138.263	10619.335
14	IP	33543.001	6236.364	14493.675	3897.950	66326.466	64705.238	4097.107
15	DBah A	3944.358	4064.488	1351.698	6302.499	11777.840	11369.540	8728.211
16	BghiP	6543.128	2474.821	2901.024	5247.819	27068.520	28171.384	6427.415
Total Target PAH		81042.041	23246.408	60948.742	39735.860	202946.724	216031.086	41016.273
MDL* [ppm]		0.001	0.001	0.001	0.001	0.001	0.001	0.001

* Minimal Detection Limit

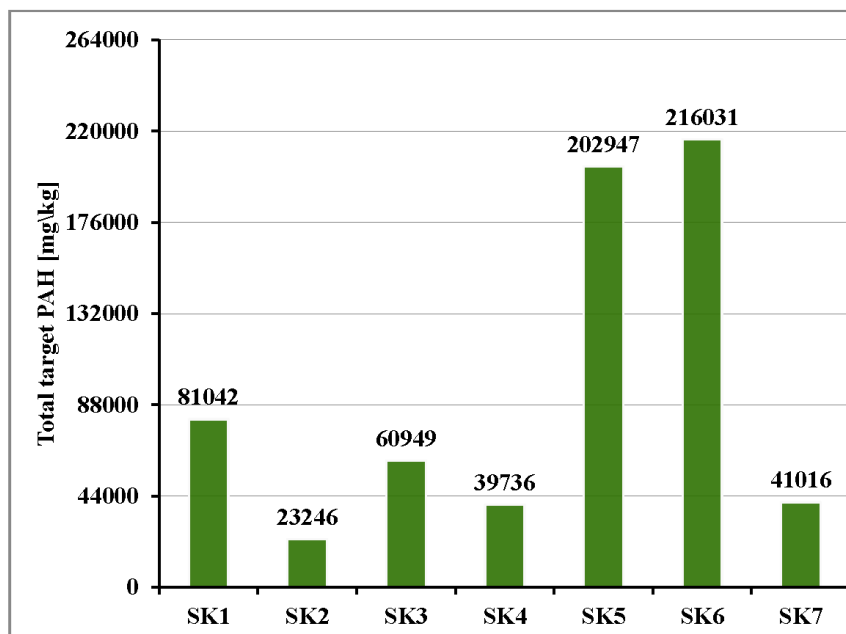


Figure 4. Total target PAHs determined in seven skeet flaying targets.

The weathering conditions on the field has been established by the ASE of different sized skeet particles: a fine powder vs. compact particles. The results provided different leaching rates of particle size fractions of skeet. Differences in the leaching rates revealed a qualitative effect of weathering (particle break down) in the soil. The weathering process was simulated by the extraction of PAHs from SK3 of two different sized samples (small piece vs. fine powder) of equal weight (0.005 g). An enormous amount of PAH was released from both differently sized samples during the leaching process: 60,949 mg/kg (ppm) for powder and 18,996 mg/kg (ppm) for one small piece, respectively. Results clearly demonstrated that the weathering process of the fine powder was >3 times faster compared with the compact small piece due to a larger surface area of powder particles (Figure 5).

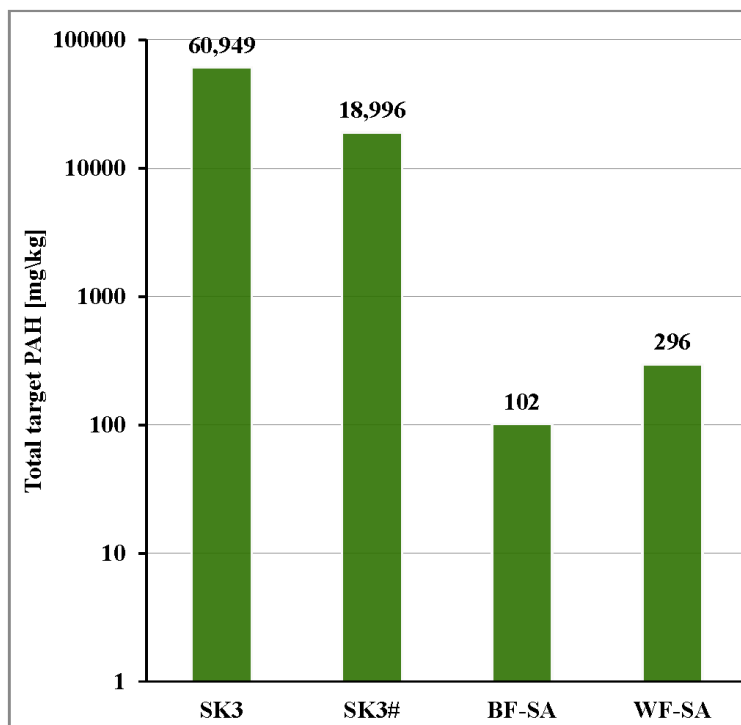


Figure 5. A comparison of PAH leaching from SK3 (powder), SK3# (a compact piece), and two contaminated soils.

Mineralogy of CRM 171 and HS5

XRD. A semi-quantitative mineralogical analysis of two reference materials, CRM 171 loamy sand and HS5 submarine sediment standard, was performed by XRD analysis. CRM 171 contains 86% of quartz as the dominant mineral phase. The clay phase content is $\approx 3.9\%$, which includes kaolinite and muscovite. Non-clay phases K-feldspar ($\approx 4.9\%$), P-feldspar ($\approx 2.7\%$), calcite ($\approx 0.26\%$), dolomite ($\approx 0.51\%$), siderite ($\approx 1.2\%$), and pyrite ($\approx 0.64\%$) were found in the minority. On the other hand, the submarine sediment standard HS5 contains 65% of quartz, $\approx 8.5\%$ of clay phase illite and chlorite, and significant non-clay P-feldspar content ($\approx 15\%$). Other

non-clay phases K-feldspar ($\approx 5.2\%$), calcite ($\approx 0.26\%$), dolomite ($\approx 0.68\%$), siderite ($\approx 2.2\%$), and pyrite ($\approx 2.8\%$) are present.

Mössbauer spectroscopy. Iron minerals and iron phases in CRM171 and HS5 standards were identified by Mössbauer spectroscopy at 298 K and 4 K. The Mössbauer spectrum of CRM 171 at 298 K contains a main central doublet for Fe(III) attributed to structural iron in kaolinite with Mössbauer parameters: isomer shift (δ) 0.36 mm.s^{-1} and quadrupole splitting (Δ) 0.52 mm.s^{-1} , which represents 20% of total iron content. Ferrous iron Fe(II) doublet with $\delta = 1.14 \text{ mm.s}^{-1}$ and $\Delta = 2.61 \text{ mm.s}^{-1}$ was detected by Mössbauer spectroscopy ($\approx 15\%$ of total iron). Magnetically ordered hematite was observed in 298 K Mössbauer spectrum of CRM 171 with $\delta = 0.37 \text{ mm.s}^{-1}$, $\Delta = -0.23 \text{ mm.s}^{-1}$, and hyperfine splitting (Bhf) of 50.8 T ($\approx 32\%$ of total iron). The Mössbauer spectrum of CRM 171 taken at 4 K includes two doublets, Fe(III) $\approx 16\%$ and Fe(II) $\approx 8\%$ of total iron, respectively. Two sextets attributed to hematite ($\approx 28\%$, Bhf = 51.2 T) and magnetically ordered goethite ($\approx 25\%$, Bhf = 48.5 T) indicate the presence of an iron oxide and an iron oxyhydroxide. The Mössbauer spectrum of HS5 at 298 K expresses also the central doublet with Mössbauer parameters: $\delta = 0.32 \text{ mm.s}^{-1}$ and $\Delta = 0.62 \text{ mm.s}^{-1}$ dedicated to Fe(III) iron in kaolinite revealing a total iron content of 61% in the HS5 sample. Also, a Fe(II) doublet with $\delta = 1.13 \text{ mm.s}^{-1}$ and $\Delta = 2.63 \text{ mm.s}^{-1}$ is present ($\approx 15\%$) and no magnetically ordered phase was observed at 298 K. On the other hand, the 4 K Mössbauer spectrum of HS5 includes two doublets (one for Fe(III) $\approx 48\%$ and one for Fe(II) $\approx 31\%$) and one sextet attributed to paramagnetic goethite ($\approx 21\%$, Bhf = 47.9 T) blocked at ambient temperature

MIR. The CRM 171 loamy sand and HS5 submarine sediment standard were also characterized by FTIR spectroscopy for their mineral phase compositions. These two reference materials were chosen for their structural similarity to the studied samples. The CRM 171 standard contains kaolinite as a main mineral phase along with the quartz mineral visible in the middle infrared region (MIR) at 796 cm^{-1} and 778 cm^{-1} . The MIR spectrum of HS5 standard provides evidence of more components. As the main clay mineral phases the kaolinite, illite, and mix-layered clay mineral illite/smectite were found. In the minority, quartz and carbonates are present, in good agreement with XRD and Mössbauer spectroscopy results.

Chemical analysis of CRM 171 and HS5

PAH analysis. The quality control of PAH's determination was demonstrated via CRM171 and HS5 standards. Both reference materials were commercially spiked by total target 16 PAHs and delivered with the known total target 16 PAHs content certificate. On average, >90% recovery was reached for all 16 polycyclic aromatic hydrocarbons spiked by the manufacturer.

Determination of the clay mineralogy and PAH content of uncontaminated adjacent soils (CLIN 0003).

Mineralogy of the uncontaminated soils

XRD. Quantitative mineral phase analysis of the uncontaminated soils was accomplished by XRD measurements of oriented and randomly oriented patterns. The mineral content was determined in the <63 μm fraction, 63 μm - 125 μm fraction, 125 μm - 500 μm fraction, and greater than 500 μm fraction of background soil samples BF-BG and WF-BG. Both uncontaminated soils are similar in the mineral phase composition. Soil samples, the sandy soils, contain quartz as a dominant mineral phase ($\approx 94\%$) in all fractions. The average of the clay phase content is 1.3%. Other non-clay phases K-feldspar ($\approx 2.7\%$), P-feldspar ($\approx 1.4\%$), calcite ($\approx 0.30\%$), dolomite ($\approx 0.33\%$), and pyrite ($\approx 0.49\%$) were found in the minority in all fractions. The clay mineral phase analysis revealed the presence of illite ($\approx 47\%$), mix-layered clay mineral illite/smectite ($\approx 39\%$), kaolinite ($\approx 5.8\%$), and chlorite ($\approx 8.0\%$) in both background soils and all separated fractions. A separation of BF-BG soil sample caused a slight increase of the clay phases (from 1.3% in >500 μm fraction to 1.6% in the <66 μm fraction) as well as the K-feldspar phase content increased from 2.0% (>500 μm fraction) to 3.4% (<66 μm fraction) for BF-BG. Also, the K-feldspar content increased from 2.1% in >500 μm fraction to 3.8% in <66 μm fraction for WF-BG. A quantitative mineral phase analysis was also determined in the S1, S3, and S6 raw background soils. Uncontaminated soils S1 and S3 contained a similar mineral phase composition. Both contained a high calcite content 94.1% and 87.3%, respectively. S6 soil sample contained 69.1% of quartz and 21.2% of corundum as the dominant mineral phases. In the S1 sample were found minor phases as corundum ($\approx 3.0\%$), boehmite ($\approx 2.4\%$), and quartz ($\approx$

0.5%). S3 background soil contained beside calcite only just 6.0% of quartz and 6.7% of gibbsite. The admixtures in S6 soil were identified as albite (9.5%) and microcline ($\approx 0.2\%$). A mineral phase analysis of sample S8 provided 61.2% of calcite as a dominant mineral phase. Two other dominant mineral phases, corundum (18.7%) and kaolinite (10.5%), were found in the sample. Quartz ($\approx 5.2\%$) and pyrite ($\approx 4.3\%$) were found in minority. Other clay phases of very low content, $<0.10\%$, which includes illite and muscovite, were determined in the sample. Similar results were obtained for S10 sample with 64.5% of calcite as a major mineral phase. Corundum (17.3%) phase was present as well. Surprisingly, a considerable content of lead (7.0%) was determined in the sample, along with 9.6% of quartz, 1.6% of gibbsite, and no clay phase.

Mössbauer spectroscopy. Uncontaminated soils (S1, S2 and S3) were analyzed by Mössbauer spectroscopy at ambient (293 K) and the liquid helium (4.2 K) temperatures. The presence of iron species was confirmed in all background soils. Their spectra collected at 293 K exhibited a dominant central doublet of isomer shift (IS) 0.36 mm.s^{-1} and quadrupole splitting (QS) 0.56 mm.s^{-1} , attributed to octahedral coordination of Fe(III) in the kaolinite structure. At 293 K, magnetic ordering was observed in all spectra. The magnetically ordered magnetite was observed in 293 K Mössbauer spectra of S1 (14.4%) and S3 (19.1%) background soils with a hyperfine splitting (Bhf) of 48.6 T, while 17.3% of hematite (Bhf = 50.7 T) was found in S6. A negligible amount of octahedral coordination of Fe(II) was confirmed by a doublet at 1.10 mm.s^{-1} IS and 2.66 mm.s^{-1} QS. On the other hand, the 4.2 K spectra provided enormous development of magnetic relaxation in all three samples. S1 spectrum contained 55.2% of akaganeite (Bhf = 48.0 T), 18% of goethite (Bhf = 47.6 T) and 18.7% of ferrihydrite (Bhf = 51.7 T). Mössbauer spectrum of S3 soil contained just 3.6% of magnetically disordered Fe(III), but 76.3% and 20.1% of magnetically ordered Fe(III) belonged to akaganeite (Bhf = 48.2 T) and ferrihydrite (Bhf = 51.9 T), respectively. Ferrihydrite (20.1%) and akaganeite (30.7%) were present also in S6 sample.

MIR. FTIR spectroscopy in the middle infrared (MIR) region ($4000 \text{ cm}^{-1} - 400 \text{ cm}^{-1}$) was used for mineralogical characterization of three uncontaminated soils. Background soils S1 and S3 contained the main mineral phase carbonate (dolomite and calcite) with characteristic vibrations

at 2515 cm^{-1} , 1424 cm^{-1} , 874 cm^{-1} , and 712 cm^{-1} . Clay phase, kaolinite, was detected in the spectrum at 3699 cm^{-1} , 3620 cm^{-1} , 1066 cm^{-1} , and 1035 cm^{-1} . MIR spectrum of S6 soil sample provides an evidence of more components. As the main clay mineral phases the montmorillonite (1034 cm^{-1} , 914 cm^{-1} , 534 cm^{-1} , and 468 cm^{-1}), kaolinite (3699 cm^{-1}), and illite or mix-layered clay mineral illite/smectite (434 cm^{-1}). Also the small portions of quartz (799 cm^{-1} and 778 cm^{-1}) and carbonates (dolomite, calcite) (1420 cm^{-1}) were present.

Chemical analysis of the uncontaminated soils

Carbon content. The amounts of OC and IC of uncontaminated soils are summarized in Figure 6. In S1 background soil, TC, OC, and IC contents were determined to be 16.2%, 5.9%, and 10.3%, respectively. Similar inorganic carbon content was obtained for S3 soil 10.2%, which was confirmed by quantitative XRD analysis. Both background soil samples contained a high amount of calcite (94% and 87%). On the other hand, soil OC content in sample S3 was much lower just 1.1%, thus TC was then 11.3%. Lower total carbon content was observed in S6 soil sample, 5.8% only. IC was lower than in previous two soils just 5.5% and organic part represents 0.28% only. The water content was for all background samples uniform.

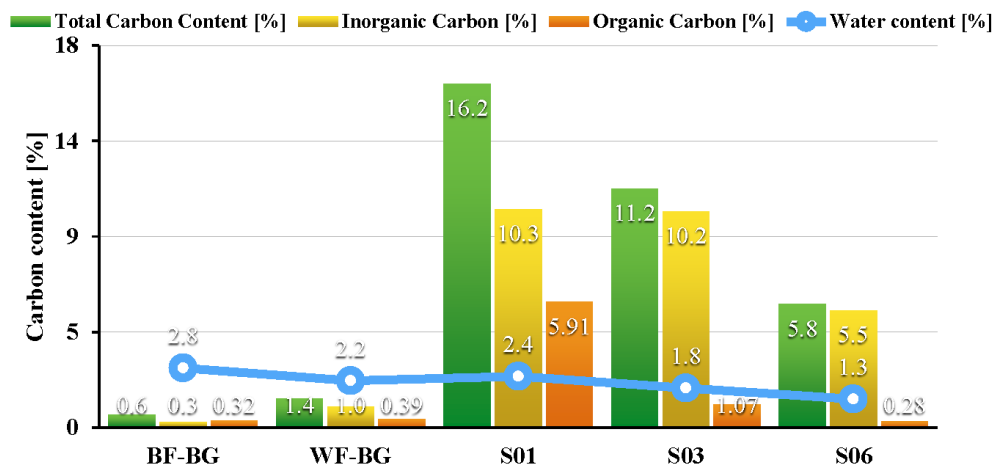


Figure 6. Carbon analysis and water content of the background soils.

PAH analysis. The total PAH's content in background soil was determined (Table 6). The content of various 16 PAHs in background soils was variable. Some traces of PAHs were observed, despite of the highest concentration was recorded in S6 sample with 21.2 mg/kg and the lowest concentration in S1 soil sample with just 0.15 mg/kg of 16 PAHs (Figure 7). This result is opposite that revealed by the carbon content analysis (see Figure 6).

Table 6. 16 target PAH concentrations in the background soils.

Sample		BF-BG	WF-BG	S1	S3	S6	S8	S10
PAH		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	Nap	<0.01	<0.01	0.034	0.020	0.145	0.215	0.325
2	Aty	<0.01	<0.01	<0.001	0.016	0.040	0.038	<0.001
3	Ath	<0.01	<0.01	<0.001	0.010	0.019	0.012	<0.001
4	Flu	<0.01	<0.01	0.010	0.005	0.024	0.067	2.765
5	Phe	<0.01	<0.01	0.006	0.001	1.079	0.563	0.555
6	Anth	<0.01	<0.01	0.003	0.001	0.181	0.032	0.070
7	Fla	<0.01	<0.01	0.002	0.055	1.460	0.245	0.051
8	Py	<0.01	<0.01	0.003	<0.001	1.241	0.256	0.057
9	BA	0.28	0.27	0.006	0.006	4.119	2.984	0.633
10	Chr	<0.01	<0.01	0.003	0.003	1.049	0.152	0.182
11	BbF	0.19	0.18	0.003	0.006	3.796	0.606	<0.001
12	BkF	<0.01	<0.01	0.014	0.006	2.335	0.040	<0.001
13	BaP	0.14	<0.01	0.002	0.012	0.293	0.277	0.256
14	IP	<0.01	<0.01	0.018	0.025	3.957	1.687	<0.001
15	DBahA	<0.01	<0.01	0.019	0.105	0.299	2.402	<0.001
16	BghiP	<0.01	<0.01	0.023	1.348	1.171	3.124	<0.001
Total Target PAH		0.60	0.45	0.147	1.620	21.208	12.700	4.893
MDL* [ppm]		0.01	0.01	0.001	0.001	0.001	0.001	0.001

* Minimal Detection Limit

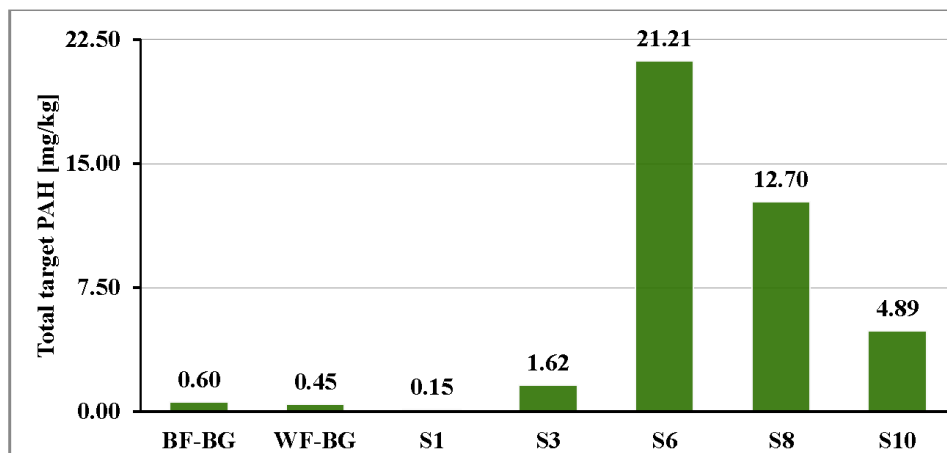


Figure 7. Total PAH content in the background soils.

Characterization of the mineralogy, total PAH content, and rate of PAH leaching of each particle-size fraction of clay-target contaminated soils (CLIN 0004).

Mineralogy of clay-target contaminated soils

XRD. The XRD patterns of BF and WF soil samples (Figure 8) revealed that the differences between the contaminated (SA) and uncontaminated (BG) forms of the BF soil were very small, which suggests that the extent of contamination was not large. An exception, however, was the relative intensity of the quartz peaks at about 21 and $36^\circ 2\theta$. This ratio was smaller in both of the contaminated soils than in their uncontaminated counterparts. Soil WF exhibited some further differences in its XRD pattern when comparing contaminated with uncontaminated forms. Not only was the quartz peak ratio different, but peaks for calcite and dolomite were also observed, indicating that the level of contamination of this soil is greater than that of the BF soil.

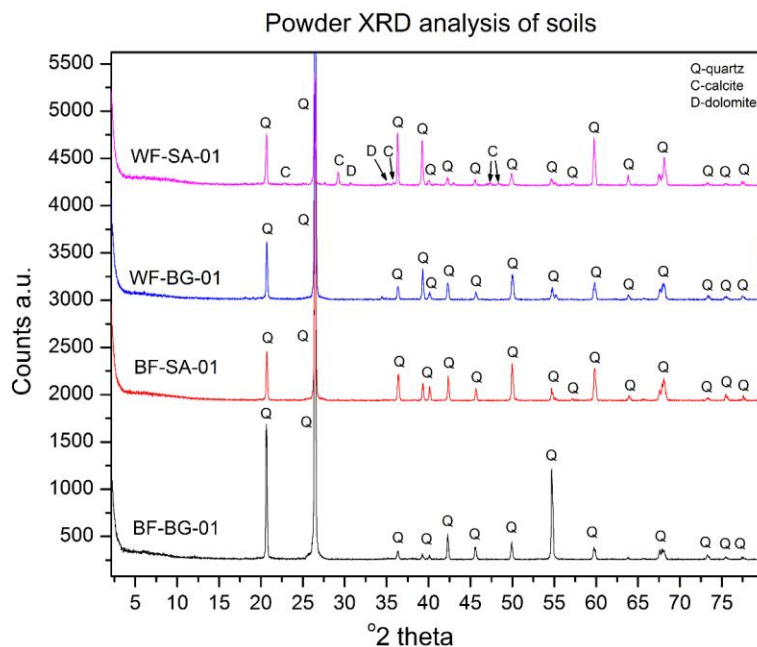


Figure 8. X-ray diffraction patterns of soils uncontaminated (BF-BG and WF-BG) and skeet-contaminated (BF-SA and WF-SA) states. The main crystalline phase is quartz. Notice, however, that some dolomite and calcite is visible in the pattern for the contaminated soil WF-SA. Another interesting feature is the relative intensities of the quartz peaks at about 21 and 36°2 θ differ between the uncontaminated (BG) and contaminated (SA) soils.

A qualitative mineral phase analysis of oriented XRD patterns of clay-target contaminated soils <66 μm fraction of BF-SA and WF-SA was performed. Similar results for the <63 μm fraction of the clay-target contaminated soils have been accomplished. Beside the major quartz phase and clay components, i.e. smectite, mica, and kaolinite), a non-clay phase feldspar was found. The presence of the clay phases in the <63 μm particle size fraction also confirmed that their PAH content was higher than in the raw fractions (Figure 9).

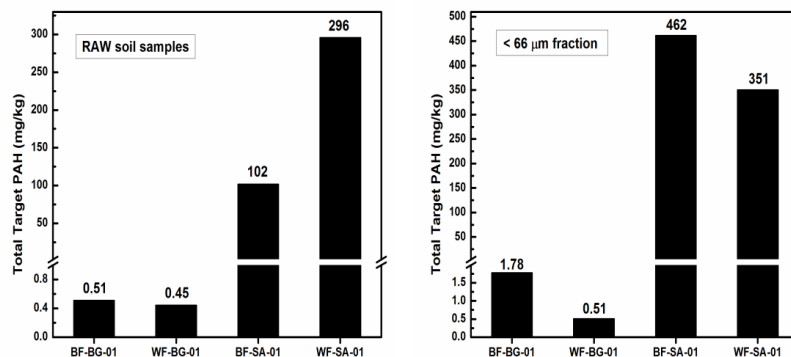


Figure 9. A comparison of the PAH content in a raw and the <66 μ m fractions of the BF and WF soil samples.

On the other hand, the quantitative mineral phase analysis of BF-SA and WF-SA performed by XRD measurements of oriented and randomly oriented patterns revealed similar mineral phase compositions. The mineral content was determined in the <63 μ m fraction, 63 - 125 μ m fraction, 125 - 500 μ m fraction, and >500 μ m fraction of contaminated soil samples BF-SA and WF-SA, respectively. Quartz was the dominant mineral phase in all fractions. The clay phase content (1.4%), K-feldspar ($\approx$ 2.7%), P-feldspar ($\approx$ 1.6%), calcite ($\approx$ 3.72%), dolomite ($\approx$ 1.12%), and pyrite ($\approx$ 0.62%) were determined in BF-SA and WF-SA. The clay targets (with the dolomite and calcite main mineral phases) weathering caused a significant increase of dolomite and calcite content in the WF-SA with the maximum calcite (22.8%) and dolomite (3.9%) content in >500 μ m fraction. The clay mineral phase analysis of contaminated soils also provided the presence of illite ($\approx$ 45%), mix-layered clay mineral illite/smectite ($\approx$ 40%), kaolinite ($\approx$ 5.8%), and chlorite ($\approx$ 9.0%) in all fractions. The separation of contaminated soils resulted in a significant increase of the K-feldspar (from 2.1% in >500 μ m fractions to 3.8% in the <66 μ m fractions) and pyrite (from 0.42% in >500 μ m fractions to 0.86% in the <66 μ m fractions) phases in BF-SA and WF-SA. The S13 soil sample contained the high calcite content (75.8%) and significant corundum content (17.3%) was present in the sample. Lower contents of quartz (5.0%) and aragonite (1.9%) were determined.

The quantitative mineral phase analysis of the new set of the clay-target contaminated soils was performed by XRD analysis of oriented and randomly oriented patterns. The mineral content was determined in the raw contaminated soil samples S2, S4, S5, and S7. Clay-target contaminated soils S2 and S4 contained similarly high calcite contents 94.4% and 98.0%, respectively. In both soil samples an admixture quartz was found 4.3% and 2.0%, respectively. S2 sample contained also a small portion of corundum (1.2%). On the other hand, the S7 soil contained no calcite but well crystallized mineral quartz (53.7%) as a major mineral phase, together with the other mineral phases such as corundum (16.9%), muscovite (18.1%), or albite (11.3%) were found in the sample. Very low calcite (4.3%) and dolomite (5.9%) contents were identified in S5. The presence of aluminum rich phases gibbsite (61.5%) or boehmite (12.4%) and an Fe(III) oxide phase hematite (8.6%) indicated a mineral variability in soil sample S5. Further, semi-quantitative mineral XRD analysis of S9, S11, and S12 was performed. Sample S9 contained 77.6% of calcite. This content is higher than for uncontaminated S8 background soil (61.2%), caused probably by broken clay target particles weathered in the field. Minerals corundum (10.7%) and quartz (7.3%) were also present in the sample. The presence of lead (4.3%) was also determined in sample S9. The presence of carbonates in sample S11 was confirmed by 64.5% of calcite and 25.4% of dolomite. A lower, but still significant, content of corundum (10.9%) was present as well. Admixtures of lead (2.5%), quartz (2.8%), and gibbsite (0.30%) were determined in the sample. Contaminated sample S12 contained 53.2% of calcite and just 8.7% of dolomite. The quartz content was 16.1%. Other mineral phases including corundum (13.9%) and aragonite (8.1%) were also found in this sample.

MIR. Mineralogical characterization of three contaminated soils was also performed by FTIR spectroscopy in the middle infrared (MIR) region ($4000\text{ cm}^{-1} - 400\text{ cm}^{-1}$). Contamination in S2 soil caused a significant increase in organic carbon phases. Intense bands of C-H aromatic groups between 3002 cm^{-1} and 3103 cm^{-1} and aliphatic C-H vibrations at 2900 cm^{-1} and 2850 cm^{-1} , respectively, confirmed a large organic carbon uptake by soil S2. The carbonate (dolomite and calcite) content considerably decreased, as revealed by the lower intensities of the characteristic vibrations at 2515 cm^{-1} , 1422 cm^{-1} , 874 cm^{-1} , and 713 cm^{-1} . A similar trend was observed in the MIR spectrum of contaminated soil S5. The MIR spectra of soil samples S4 and

S7 contain the same mineralogy as their background soils, and have a very low organic content attributable skeet-fragment weathering in the field.

Chemical analysis of clay-target contaminated soils

Carbon analysis. The carbon content of contaminated soil samples was very different. The organic and inorganic C contents of the BF soil changed very little between the background and contaminated samples. The WF soil, on the other hand, changed dramatically when contaminated. Therefore, the C content profile or total organic matter content (TOC) served as strong indicators of the extent of soil contamination by skeet material.

The total carbon contents (TC) were determined in contaminated soil samples S2, S4, S5, and S7, and were measured by CHN analysis before and after acid treatment. In soil S2, TC was 13.4% and, surprisingly, the OC content was much lower, just 1.6%, than in the uncontaminated sample but IC content was similar at 11.8%. Relatively high TC before acid treatment was determined in contaminated soil sample S4, at 15.4%. Inorganic carbon (6.5%) was leached from the sample and 8.9% of OC remained after acid treatment in S4. Samples S5 and S7 represent soils with the lowest carbon content. TC for S5 and S7 were just 3.4% and 1.6%, respectively. After acid treatment, OC of S5 was just 0.64% while 0.08% of OC remained in sample S7. Inorganic carbon contents dissolved from soil samples were the lowest at 2.6% in S5 and 1.5% in S7 (Figure 10).

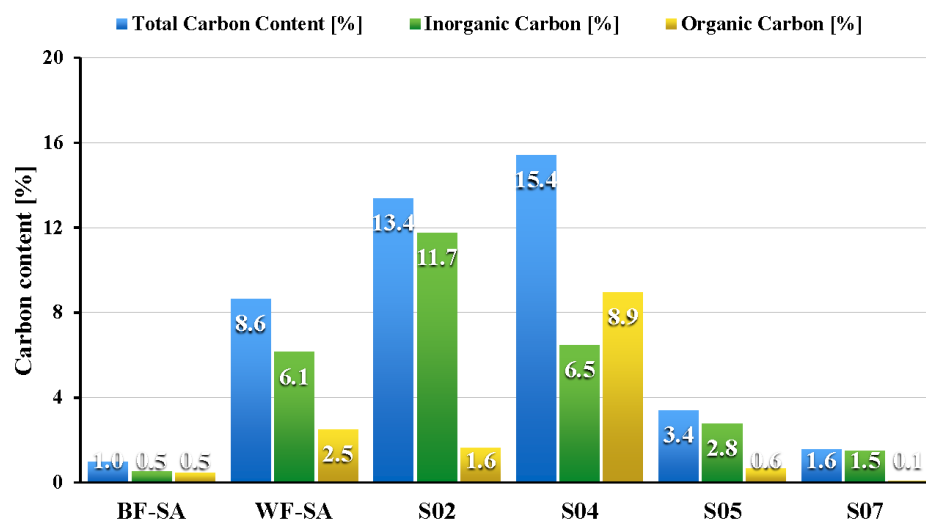


Figure 10. Carbon content analysis of BF-SA, WF-SA, S2, S4, S5, and S7 contaminated soil samples.

Acid treatment of S8, S9, S10, S11, S12, and S13 wasn't performed due to a large portion of soluble minerals present in these samples, which could negatively affect the calculation of IC or OC in the samples. The TOC of all samples, together with their corresponding water contents, are included in Figure 11.

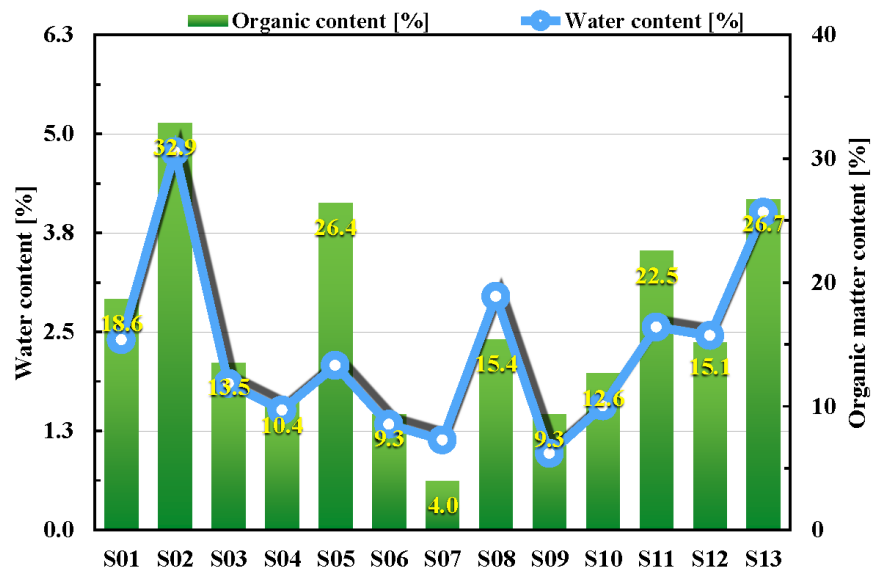


Figure 11. The total organic content (TOC) and water content of soil samples S1 - S13.

PAH analysis. The total target 16 PAHs determination provided the extent of contamination of skeet range soils. Samples BF-SA (102 mg/kg), S7 (169 mg/kg), S9 (151 mg/kg), and S13 (65 mg/kg) contained a relatively low impact of skeet contamination. A higher level of PAHs was observed in soils WF-SA with 296 mg/kg, S2 with 332 mg/kg, and S4 with (832 mg/kg). The most contaminated soils were, then, S11 and S12 with an enormous level of PAH contamination – 7828 and 12081 mg/kg for S11 and S12, respectively (Figure 12). Surprisingly, the lowest contamination in samples rich in quartz, which indicates that PAH compounds were preferentially adsorbed on carbonates (calcite, dolomite -- more porous surfaces) than on quartz. All other 16 target PAH contents of uncontaminated soil samples are included in Table 7. The total PAH content in contaminated soils was determined by GC-MS measurements. Results correspond with the visually observed small weathered skeet particles in the contaminated soil samples.

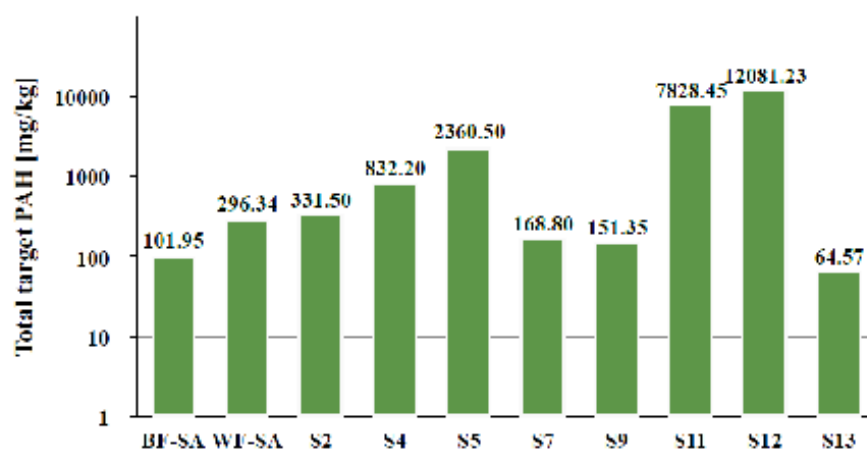


Figure 12. The total PAH content in the contaminated soils.

Table 7. 16 target PAH content in the contaminated soils.

Sample		BF-SA	WF-SA	S2	S4	S5	S7	S9	S11	S12	S13
Units		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	Nap	0.12	0.16	69.6	40.2	9.4	27.7	0.106	5.771	2.276	0.251
2	Aty	<0.01	<0.1	61.2	37.4	6.0	14.7	0.020	0.642	0.281	0.019
3	Ath	<0.01	0.34	17.4	<0.1	9.1	5.8	0.283	6.840	11.462	0.078
4	Flu	<0.01	0.16	15.1	<0.1	2.4	1.1	0.046	9.233	1.468	0.016
5	Phe	3.21	7.19	<0.1	17.3	50.4	0.4	0.965	43.152	67.439	0.307
6	Anth	0.58	1.11	<0.1	4.1	10.2	2.0	0.228	24.325	14.646	0.024
7	Fla	13.33	5.99	<0.1	40.2	115.9	1.6	3.127	106.531	210.007	1.188
8	Py	12.62	46.43	3.3	49.2	155.1	2.1	4.147	170.786	264.161	1.365
9	BA	9.41	25.18	<0.1	48.6	160.9	2.4	6.564	390.239	566.164	1.451
10	Chr	11.43	35.30	<0.1	41.2	109.9	1.5	3.616	288.954	352.774	1.323
11	BbF	11.85	29.85	<0.1	112.7	359.7	<0.1	28.860	1140.933	2031.847	7.902
12	BkF	8.71	13.56	<0.1	22.3	47.1	<0.1	3.130	154.049	378.275	0.792
13	BaP	11.27	74.92	48.0	146.8	350.3	32.9	27.357	1994.014	2581.929	6.817
14	IP	8.57	3.83	116.8	151.5	552.1	76.5	47.741	1441.081	3415.970	33.378
15	DBahA	1.78	12.00	<0.1	55.0	225.7	<0.1	7.652	563.375	718.311	3.854
16	BghiP	9.06	40.32	<0.1	65.6	196.3	<0.1	17.504	1488.524	1464.223	5.808
Total Target PAH		101.95	296.34	331.5	832.2	2360.5	168.8	151.347	7828.448	12081.232	64.573
MDL* [ppm]		0.01	0.01	0.1	0.1	0.1	0.1	0.001	0.001	0.001	0.001

Conclusion

☼ Identification of the skeets fragments in the contaminated soils.

The XRD analysis.

The qualitative XRD powder analysis was successfully utilized for the identification of the skeet fragments weathered on the skeet range fields BF-SA and WF-SA. This method was used for the identification and comparison of the commercial skeets (SK1 thru SK7). The skeet fragments in BF-SF and WF-SF matched with SK1 and SK4, respectively (Figure 13).

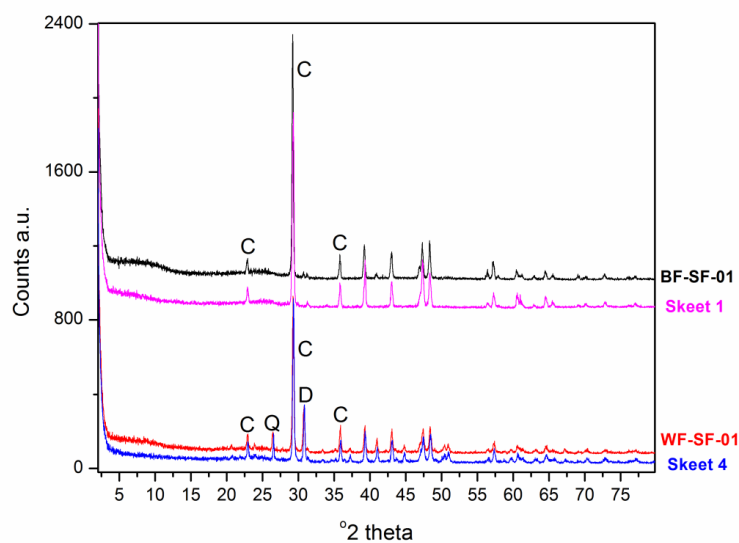


Figure 13. Identification of skeet fragments BF-SF-01 and WF-SF-01 collected from the skeet range areas.

☼ Calibration of the carbon content in the soil samples.

The XRD calibration method

The XRD calibration method for determination of the contamination extent in contaminated soils by clay targets has been tested on SK3. The calibration mixtures of SK3 and the background soil WF-BG provided a good correlation between the total carbon content and the calcite XRD peak area vs. the skeet content for the contaminated soil sample WF-SA (skeet content = 13.1% ± 2.69) (Figure 14).

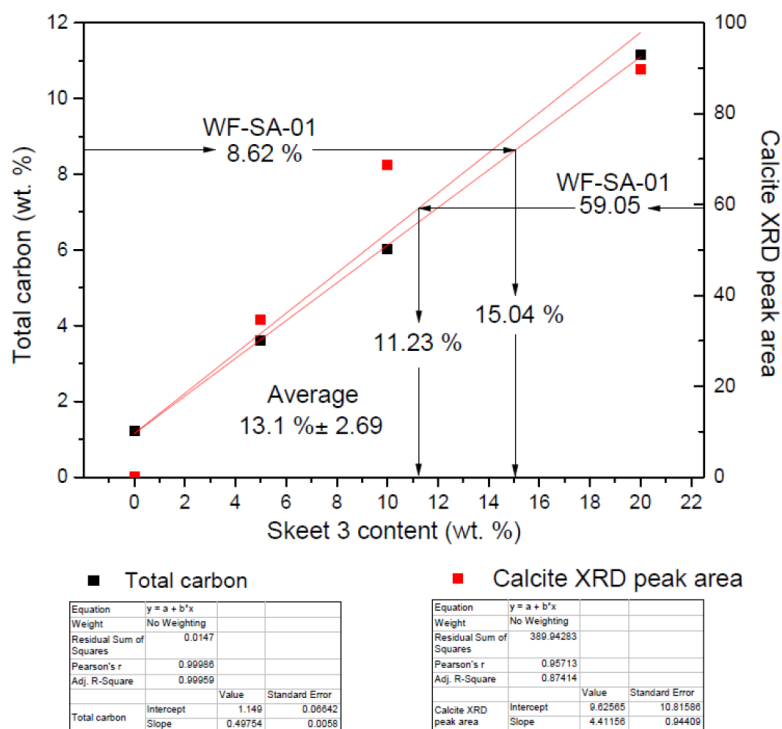


Figure 14. The relationship of total carbon content vs. SK3 content and the calcite XRD peak area vs. SK3 content. The carbon content in the WF-SA sample is 11.23 wt.% and 15.04 wt.% calculated from total carbon analysis and the calcite XRD peak area integration, respectively.

Also the other skeets were tested using the XRD calibration method. From SK 1 (with calcite content only) and skeets SK2 and SK7 (not shown) (with dolomite content) the calibration mixtures with background soil WF-BG were prepared (Figure 15). Dolomite presence in WF-SA contaminated sample gives a premise to use the dolomite peak for the XRD calibration. The R^2 values from the linear regression calibrations for WF-BG/SK1, WF-BG/SK2, and WF-BG/SK7 were 0.99, 0.96, and 0.99, respectively. This calibration data provided a database very useful for the estimation of the clay target content in the contaminated soils by XRD measurement. This calibration method could also be used for samples which contain primarily quartz and generally no carbonates (dolomite, calcite).

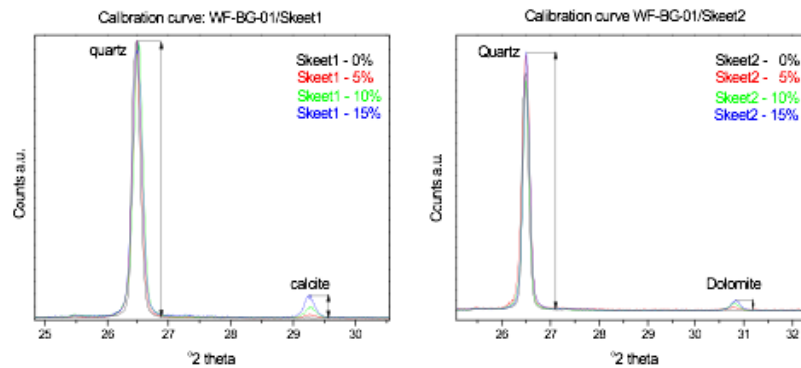


Figure 14. The normalized XRD patterns of WF-BG soil with the SK1 and SK2 loadings on a quartz diffraction.

☼ Soils summary

A summary of investigated soils (background and contaminated) is included in Table 8. Soils are of several origins with different dominant main minerals divided into two groups, those containing primarily quartz and those containing primarily carbonates. Both groups represent soil members with different particle size distributions and minor mineral components. The presence of clay fractions, very often found in the finest fractions, in all soils was in the minority. This conclusion also confirms the low water content in all soil samples. Preferably, particles are distributed in the mid-size or larger-size fractions, which supports the hypothesis that weathered clay particles could be better distributed and penetrated into the soil (Figure 15).

Table 8. A summary of the background a contaminated soil samples.

Soil	Mineralogical composition		Total Organic Content	Total PAH Target
	main mineral	admixtures	[%]	[mg/kg]
BF-BG	quartz	illite, illite/smectite, feldspar, calcite, dolomite	0.32	0.60
BF-SA	quartz	calcite, illite, illite/smectite, feldspar	0.45	101.95
WF-BG	quartz	illite, illite/smectite, feldspar, calcite, dolomite	0.39	0.45
WF-SA	quartz	dolomite, calcite	2.49	296.34
S1	calcite	quartz, corundum, boehmite	18.6	0.15
S2	calcite	quartz, corundum	32.9	331.50
S3	calcite	quartz, gibbsite	13.5	1.62
S4	calcite	quartz	10.4	832.20
S5	gibbsite	boehmite, hematite, goethite, dolomite, calcite	26.4	2360.50
S6	quartz	corundum, albite, microcline	9.3	21.21
S7	quartz	muscovite/illite, corundum, albite	4.0	168.80
S8	calcite	quartz, corundum, muscovite/illite, kaolinite, pyrite	15.4	12.70
S9	calcite	quartz, corundum, lead	9.3	151.35
S10	calcite	quartz, corundum, lead, gibbsite	12.6	4.89
S11	calcite, dolomite	quartz, corundum, lead, gibbsite	22.5	7828.45
S12	calcite	dolomite, quartz, corundum, aragonite	15.1	12081.23
S13	calcite	dolomite, quartz, corundum, aragonite	26.7	64.57

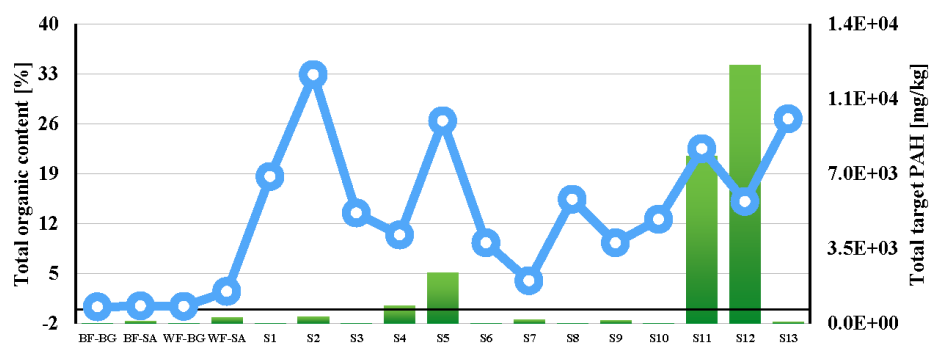


Figure 15. Total organic content vs. total target PAH content of all studied soil samples.

Report:

Mineralogical and chemical characterization of FAFB-G1, FAFB-G2, and FAFB-G3 soils.

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Team of investigators: Martin Pentrak, Linda Pentrakova, and Joseph W. Stucki

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Report 10-20-2016

MATERIALS AND METHODS

Soil samples origin. Soil samples investigated were sampled and delivered by the department of the Navy. The labeling of samples is included in Table 1.

Table 1. Labeling of studied soil samples.

#	Soil Sample	Label
1	FAFB-G1	G1
2	FAFB-G2	G2
3	FAFB-G3	G3

Mineralogy

X-Ray Diffraction (XRD). The mineralogical characteristics of the soil samples were determined by X-ray powder diffraction (XRD) using a Siemens Bruker D5000 diffractometer and analyzed by Jade 9 software for XRD mineral identification and quantification at the Material Research Laboratory (MRL), University of Illinois at Urbana-Champaign.

Infrared spectroscopy (FTIR). The FTIR spectra in the middle infrared (MIR) region (4000 cm^{-1} - 400 cm^{-1}) were collected in transmission mode using a MIDAC M2000 FTIR spectrometer from MIDAC Corp. (Westfield, Massachusetts, USA) equipped with a DTGS detector. The resolution of 2 cm^{-1} and 128 scans were used to analyze samples prepared as KBr pellets (0.5 mg of the sample powder mixed with 200 mg KBr) pressed up to 109,267 PSI and heated overnight at 150°C to minimize water content in the sample and KBr. The raw spectra were processed using the OPERANT LLC Essential FTIR software package.

Near infrared spectroscopy (NIR). NIR spectra were collected using a UV-Vis-NIR spectrometer Varian 5E by measuring the solid phase samples in diffuse reflectance mode. All spectra were recorded in the NIR region from 8000 cm^{-1} to 4000 cm^{-1} and manipulated by the Essential FTIR software package.

Mössbauer spectroscopy. Mössbauer spectra were recorded using a Web Research, Inc. (Edina, Minnesota) spectrometer equipped with a Janis model SHI-850-5 (Janis, Inc., Woburn, Massachusetts) closed cycle low temperature cryostat. The transducer operated in the triangular waveform mode with a 50 mCi ^{57}Co source dispersed as 10 wt.% in a thin Rh foil (Ritverc, Inc. St. Petersburg, Russia). Calibration of the velocity scale was performed by measuring the magnetic hyperfine field (B_{hf}) of a 7-mm thick α -Fe foil at the sample temperature (Stucki *et al.*, 2014). The data were analyzed by the WinNormos-for-IGOR (Brand, 2008) extension software pack within IGOR Pro (WaveMetrics Inc., Lake Oswego, Oregon, USA) using Lorentzian lineshapes (Murad and Cashion, 2004).

Chemical analysis.

Calibration of the skeet content in the soil samples.

The XRD calibration method for determination of the skeet contamination extent in G1, G2, and G3 soils was used. XRD patterns of all three soils were compared with calibration pattern of skeets SK1, SK2, SK3, and SK7 with respect to dolomite and calcite as the identification admixture in studied soils.

Total organic content (TOC). The portion of organic matter in the soil samples was determined by a thermal treatment in a furnace at 440°C overnight.

Water content (WC). The amount of physically adsorbed water on the soil and skeet surfaces was determined by weighing before and after drying at 105°C overnight.

PAH analysis. The polyaromatic hydrocarbon (PAH) contents in the skeet and soil samples were determined following the EPA method 3545 using a pressurized fluid extraction (PFE) and method 8270C with gas chromatograph/mass spectrometer (GC/MS) in the full scan mode for analyzing a cocktail containing 16 target PAH standards (Table 2).

Table 2. Abbreviations, ion mass, and retention times (Rt) of 16 target PAH standards.

PAH compound	PAH abbrev.	Ion [m/z]	Rt [s]
Naphthalene	Nap	128	5.71
Acenaphthylene	Aty	152	7.42
Acenaphthene	Ath	154	7.66
Fluorene	Flu	166	8.52
Phenanthrene	Phe	178	10.94
Anthracene	Anth	178	11.11
Fluoranthene	Fla	202	15.55
Pyrene	Py	202	16.56
Benzene (a) anthracene	BA	228	22.84
Chrysene	Chr	228	23.00
Benzo (b) fluroanthene	BbF	252	28.59
Benzo (k) fluoranthene	BkF	252	28.77
Benzo (a) pyrene	BaP	252	30.40
Indeno (1,2,3,c,d) perylene	IP	276	36.13
Dibenzo (a,h) anthracene	DBahA	278	36.37
Benzo (g,h,i) perylene	BghiP	276	37.28

RESULTS AND DISCUSSION

Mineralogy of soils G1, G2, and G3

XRD. The mineralogical characteristics of the soil samples were determined by XRD, FTIR, NIR, and Mössbauer spectroscopy. The XRD patterns of G1, G2, and G3 (Figure 1) revealed that the dominant crystalline phases is quartz (Q) in all three samples. Sample G2 contained a significant amount of dolomite (MgCO_3) and just a trace of calcite (CaCO_3), indicating an enormous level of contamination in that sample.

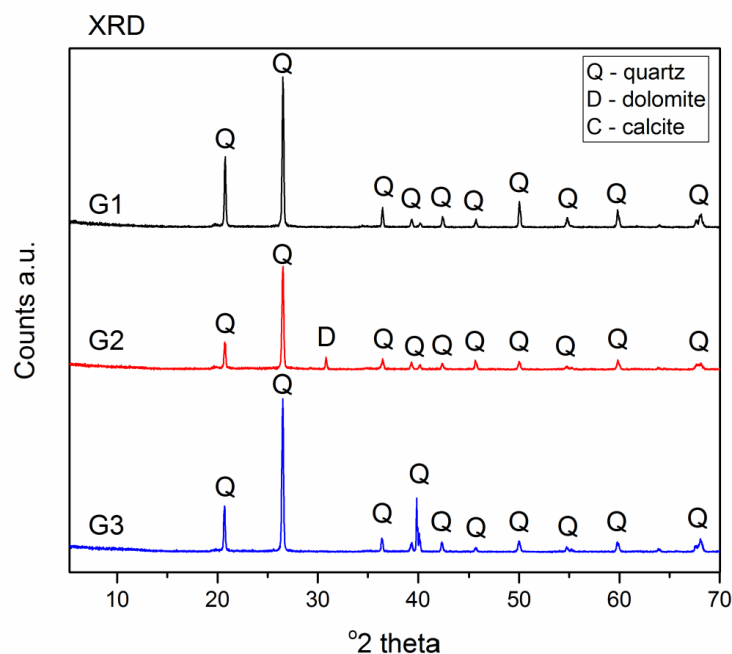


Figure 1. X-ray diffraction patterns of samples G1, G2, and G3. The main crystalline phase in all samples is quartz (Q).

FTIR. FTIR spectroscopy in the middle infrared (MIR) region ($4000\text{ cm}^{-1} - 400\text{ cm}^{-1}$) confirmed (Figure 2) that the main mineral phase was quartz (Q), but also detected some kaolinite (K) with characteristic vibrations at 799 cm^{-1} and 778 cm^{-1} for Q and 3699 cm^{-1} , 1066 cm^{-1} , 1035 cm^{-1} and 434 cm^{-1} for kaolinite, respectively. Adsorbed water molecules on the clay phase surface were confirmed by two vibrations near 3400 cm^{-1} and 1600 cm^{-1} . The group vibration of C-H near 2900 cm^{-1} was found in all samples. In the MIR spectrum for sample G2, a

visible intensive band was observed near 1400 cm^{-1} , which is related to carbonates (dolomite, calcite). They have characteristic vibrations at 1424 cm^{-1} , 873 cm^{-1} , and 745 cm^{-1} (Figure 2).

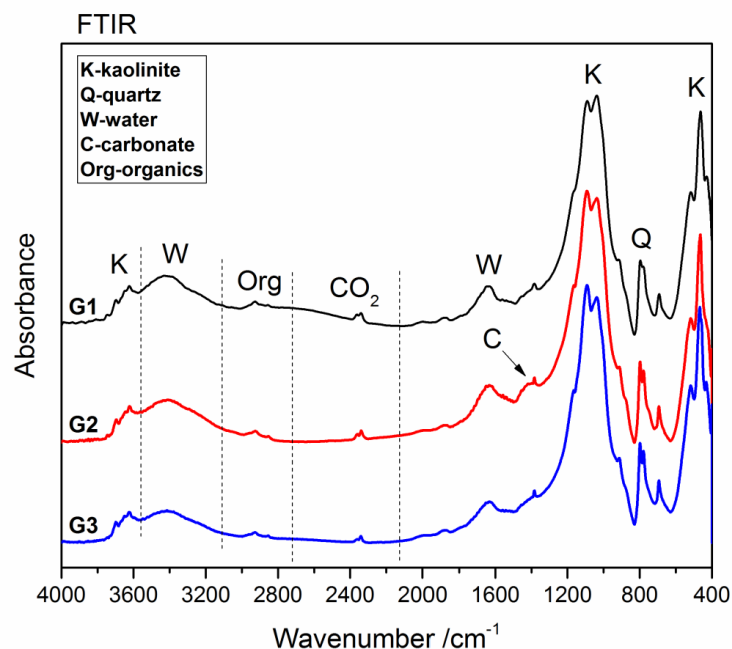


Figure 2. FTIR spectra of G1, G2 and G3.

The second derivative of the MIR spectra (SDS) provided detailed information about the carbonate content in the soil samples analyzed (Figure 3). Samples G1 and G3 contained low amounts of carbonates, on the other hand a significant carbonate content was confirmed in G2 sample by bands at 873 cm^{-1} and 745 cm^{-1} .

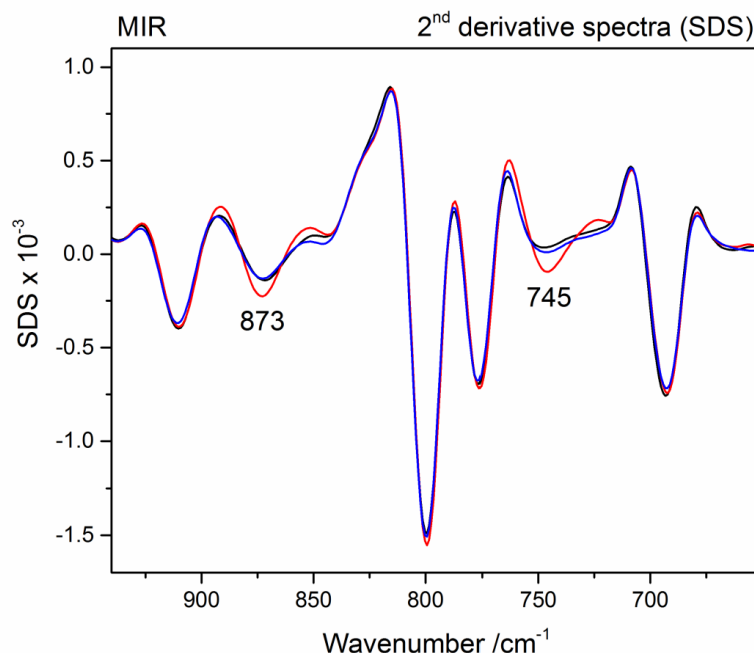


Figure 3. FTIR SDS spectra of samples G1 (black line), G2 (red line), and G3 (blue line).

NIR. The NIR spectra of G1, G2, and G3 revealed more information about the levels of skeet contamination and the corresponding hydrophobic character in the samples. Observed in this region for kaolinite were the combination stretching and bending vibrations of AlAlOH at 4562 cm^{-1} and the first overtone $2\nu(\text{OH})$ at 7076 cm^{-1} , and for water the stretching and bending combination band $(\nu+\delta)\text{H}_2\text{O}$ near 5240 cm^{-1} (Figure 4). The very intense water band $(\nu+\delta)\text{H}_2\text{O}$ in sample G1 compared to the lower intensity of this particular band for soils G3 and G2 indicated that soil G1 has higher hydrophilic properties than soils G3 and G2, due to no or very low organic (contamination) content. The water band observed in the spectrum for sample G3 was less intense due to higher skeet contamination compared with G1, and the water content of sample G2 was even lower, as seen by the lowest intensity of the water band, which confirmed the highest hydrophobicity in soil G2 caused by the highest contamination. The hydrophobic character of the samples thus decreases in the order $\text{G2} > \text{G3} > \text{G1}$. This is also consistent with the region of the first overtones of OH groups ($2\nu_{\text{OH}}$) near 7076 cm^{-1} . Increasing contamination decreased the intensity of $2\nu_{\text{OH}}$. A gentle uplifted background of the G2 and G3 spectra around 6000 cm^{-1} indicates the presence of the first overtones of C-H groups (this region is attributed to $2\nu\text{CH}_3$ (5925 cm^{-1}) and $2\nu\text{CH}(\text{aromatic})$ (6000 cm^{-1})) (Figure 4).

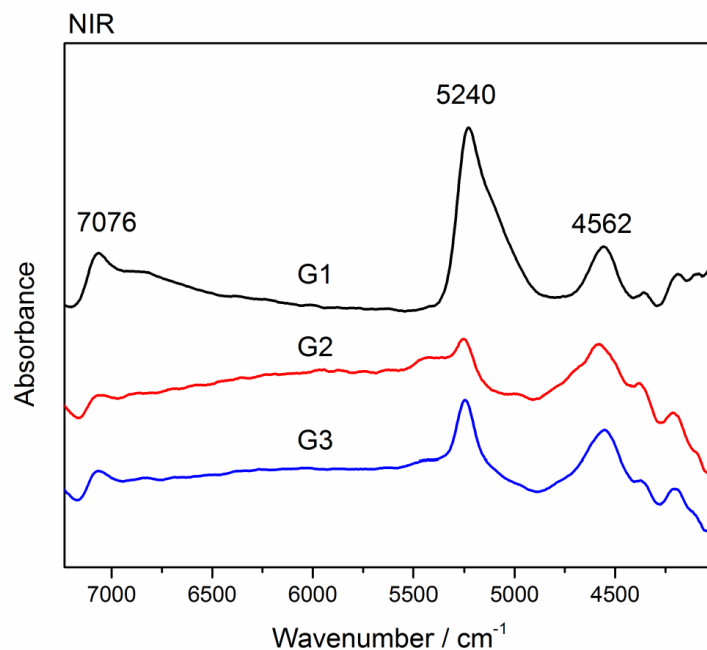


Figure 4. Near-infrared (NIR) spectra of the soils and two skeet samples

SDS spectra provided more information about the carbon contamination in G2 (Figure 5). The G2 spectrum contained more intense vibrations of the C-H groups at 4383 cm⁻¹ and 4616 cm⁻¹, which are attributed to combination vibrations of $(\nu+\delta)\text{CH}_2\text{-C}$ and $(\nu_{\text{CH}}+\nu_{\text{CC}})\text{aromatic}$, respectively. A set of intense bands at 4000 cm⁻¹, 4500 cm⁻¹, 4600 cm⁻¹, and 3000 cm⁻¹ attributed to organic compounds is evidence for higher contamination in sample G2 (Figure 5).

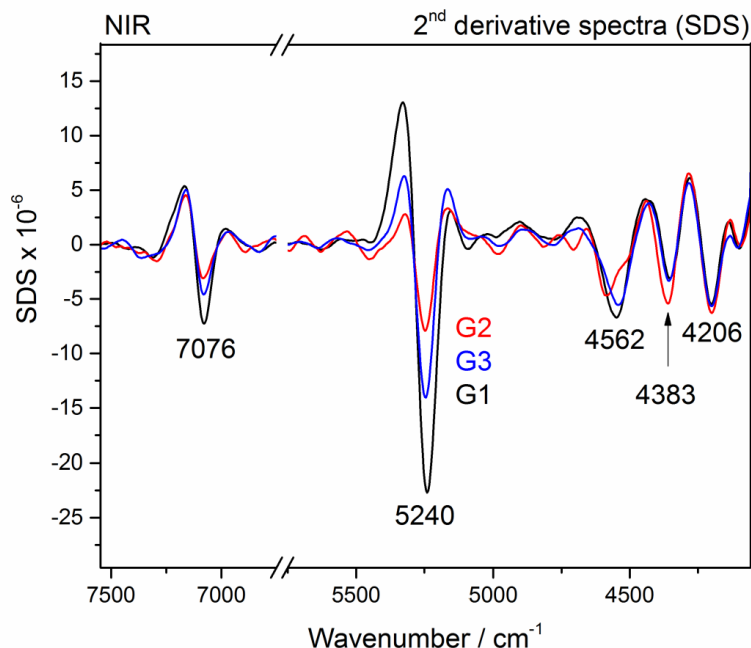


Figure 5. NIR SDS spectra of G1, G2, and G3.

Mössbauer spectroscopy. Soils (G1, G2, and G3) were analyzed by Mössbauer spectroscopy at ambient (293 K) temperature. The presence of iron species was confirmed in all soils. The Mössbauer spectrum of sample G1 provided a dominant central doublet with an isomer shift (IS) of 0.24 mm s^{-1} and a quadrupole splitting (QS) of 0.52 mm s^{-1} , attributed to octahedral coordination of Fe(III) in the kaolinite structure (Figure 6A). The presence of ferrous iron (2.5 %) in sample G2 was confirmed by a doublet with an IS of 1.03 mm s^{-1} and a QS of 2.59 mm s^{-1} , which can be attributed to an illite admixture (Figure 6B). The Mössbauer spectrum of sample G3 contained, besides a doublet due to kaolinite, also another Fe(III) doublet attributed to other possible clay admixtures (mica, smectite) (Figure 6C). The Mössbauer parameters of G1, G2, and G3 samples are included in Table 3.

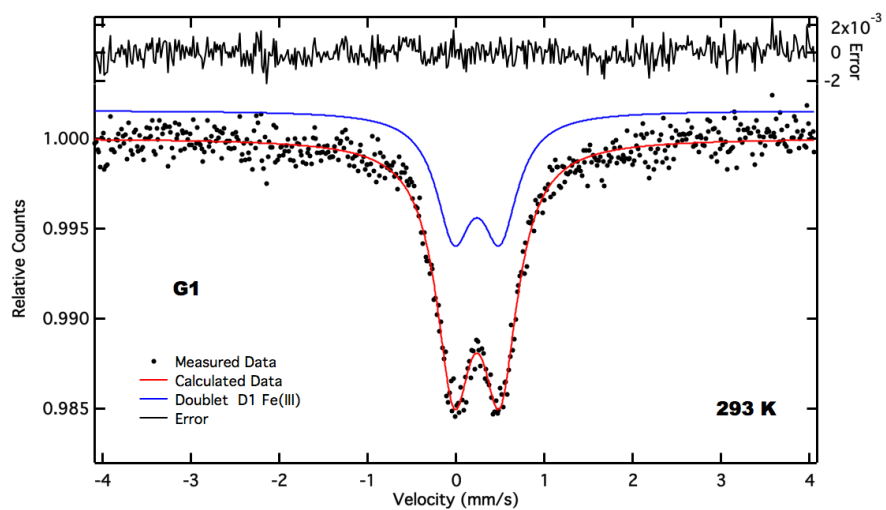


Figure 6A. Mössbauer spectra of sample G1 recorded at 293 K.

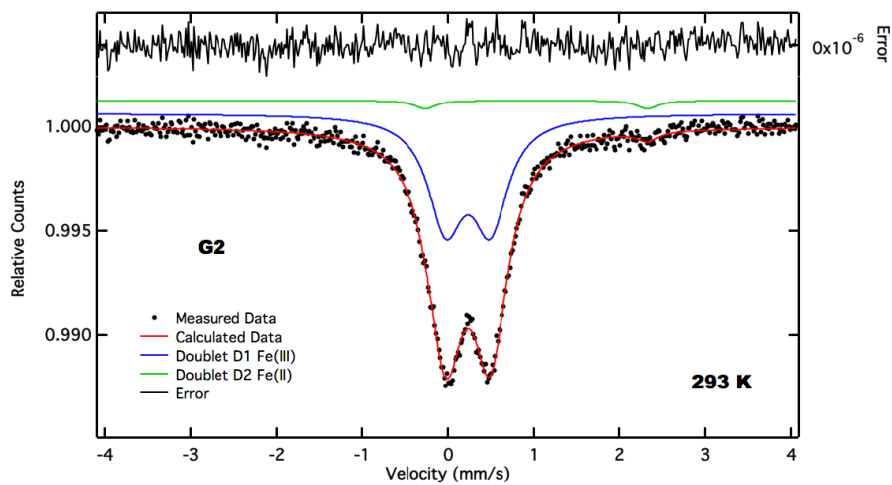


Figure 6B. Mössbauer spectra of sample G2 recorded at 293 K.

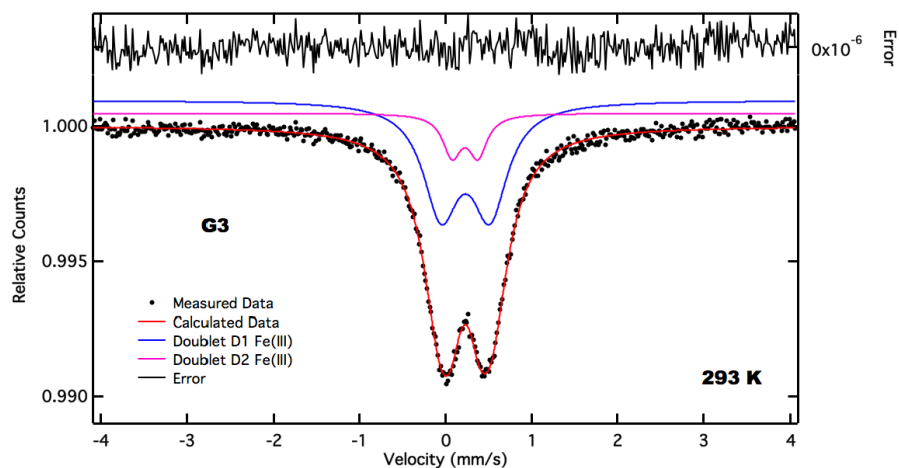


Figure 6C. Mössbauer spectra of sample G3 recorded at 293 K.

Table 3. The Mössbauer parameters of G1, G2, and G3 samples.

Sample	Sub-component	Isomer Shift (corrected) [mm s ⁻¹]	Quadrupole Splitting [mm s ⁻¹]	Relative Area [%]
G1	Doublet D1 Fe(III)	0.238 (3)	0.520 (5)	100
G2	Doublet D1 Fe(III)	0.234 (1)	0.520 (2)	97.5
	Doublet D2 Fe(II)	1.03 (3)	2.59 (5)	2.5
G3	Doublet D1 Fe(III)	0.226 (3)	0.30 (3)	90.8
	Doublet D2 Fe(III)	0.232 (6)	0.57 (7)	9.2

Chemical analysis of soils G1, G2, and G3

Total organic content. The total organic content (TOC) of all samples, together with their corresponding water contents are displayed in Figure 7.

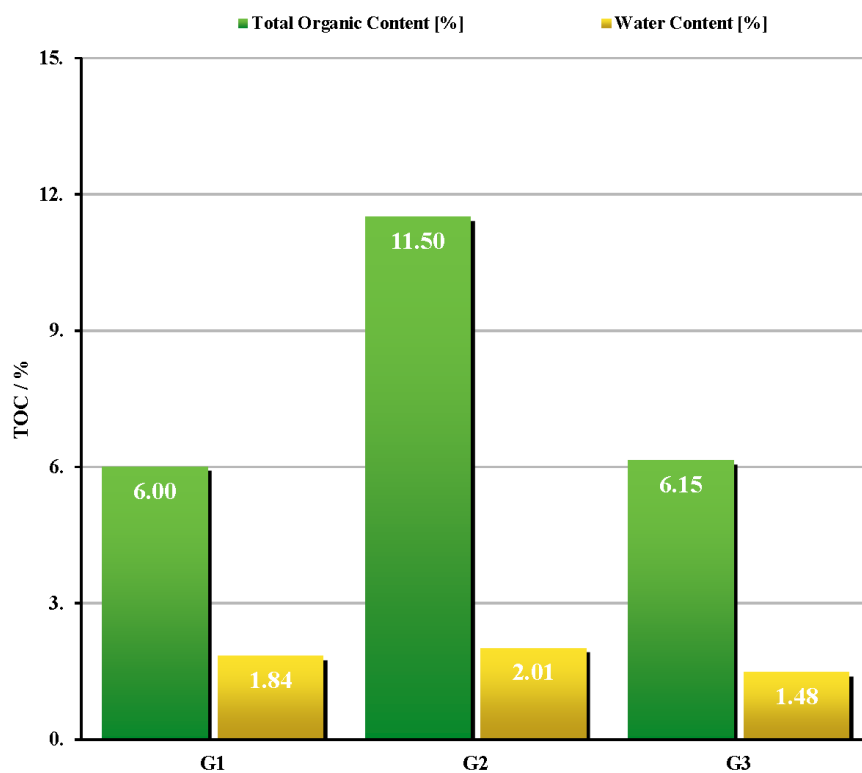


Figure 7. The total organic content and water content of samples G1, G2, and G3.

PAH analysis. The PAH content was determined in all three soil samples. For all samples a triplicate analysis was performed and 16 target PAHs were calculated from powder samples dried at 105°C (Table 4). The highest contamination was found in soil sample G1 with 2345 mg/kg of total target PAH content (Figure 8).

Table 4. Concentration of the 16 target PAHs determined in soil samples.

Sample	G1	G2	G3
PAHs	mg/kg	mg/kg	mg/kg
1 Nap	1.259	1.710	0.473
2 Aty	0.221	0.367	0.236
3 Ath	0.067	6.903	0.725
4 Flu	0.124	1.821	0.237
5 Phe	3.238	101.667	14.527
6 Anth	0.321	21.284	2.579
7 Fla	11.777	246.411	44.993
8 Py	11.214	231.456	42.649
9 BA	14.870	214.672	36.211
10 Chr	8.546	193.481	52.936
11 BbF	6.765	472.002	80.814
12 BkF	3.314	106.190	24.482
13 BaP	6.514	496.799	74.774
14 IP	5.002	828.347	107.417
15 DBahA	1.826	75.562	18.369
16 BghiP	3.384	284.348	49.549
Total target PAH	78.443	3283.019	550.971
MDL* [ppm]	0.001	0.001	0.001

* a minimal detection limit

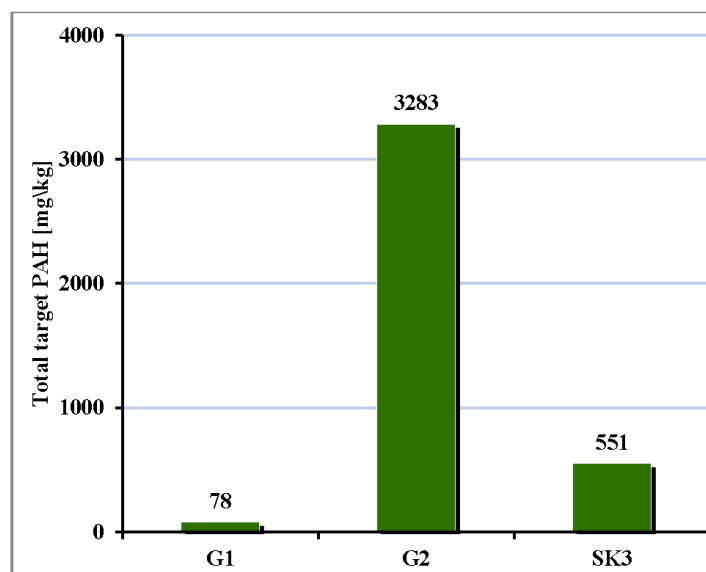


Figure 8. Total target PAHs determined in three soil samples.

Conclusion

☼ Calibration of the carbon content in the soil samples.

The XRD calibration method

The XRD calibration method for determination of the contamination extent in contaminated soils by clay targets was applied. The carbonates were used to identify which manufactured clay target was present, and was thus used as a tracer of the contamination in the studied soil samples. The XRD pattern of sample G2 revealed the presence of well-crystalized quartz and admixtures of dolomite (high content) and calcite (low content) (Figure 9). Previously prepared calibration curves by mixing of skeet material (SK1, SK2, SK3, and SK7) with a background soil WF-BG containing highly crystallized quartz were used for the estimation of the clay target content in the contaminated soil by XRD measurement. (Figure 10).

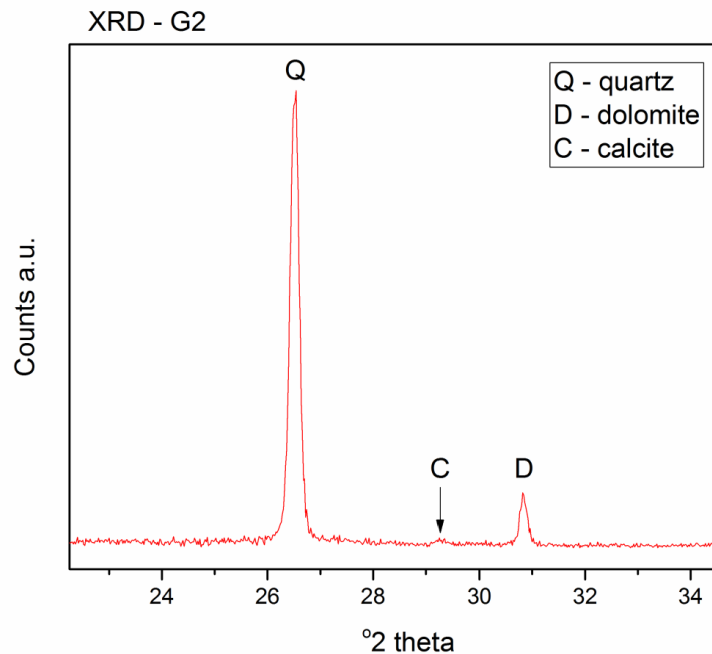


Figure 9. Detailed X-ray diffraction pattern of G2 sample. Beside of the main crystalline phase quartz (Q), the minor phases are dolomite (D) and calcite (C).

The XRD patterns of samples G1 and G3 showed no evidence of calcite or dolomite, so the XRD calibration method couldn't be applied. On the other hand, sample G2 contains a significant dolomite content and a trace of calcite were found (Figure 1). The results revealed that 33.6 % of dolomite (calibration via Skeet 2), 4.9 % of calcite (calibration via Skeet 1), and 4.0 % of calcite (calibration via Skeet 3).

☼ Soils summary

A summary of investigated soils (G1, G2, and G3) is included in Table 4. Soils are of similar composition with quartz as the dominant main mineral. The highest contamination was in sample G2, as confirmed by XRD, FTIR, NIR, and PAHs analysis. Lower contamination in sample G3 was confirmed by SDS NIR and FTIR analysis. The extent of contamination was determined by clay target PAHs analysis in order G2 > G3 > G1 (Figure 11)

Table 4. A summary of the G1, G2, and G3 soil samples.

Soil	Mineralogical composition		Total Organic Content (%)	Total PAH Target (mg/kg)
	main mineral	admixtures		
G1	quartz	N.A.	6.0	0.60
G2	quartz	dolomite, calcite, illite	11.5	101.95
G3	quartz	smectite, mica	6.15	0.45

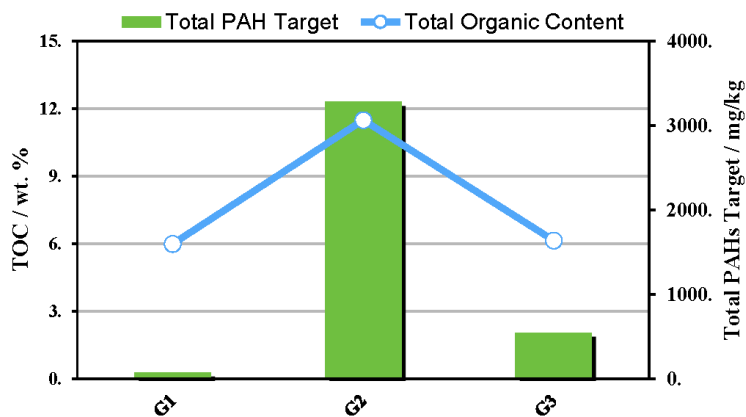


Figure 11. The total organic content vs. total target PAH content of G1, G2, and G3 soil samples.

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Brand (2008) ????

Murad, E., and Cashion, J. (2004) Mössbauer spectroscopy of environmental materials and their industrial utilization. (Norwell, MA: Kluwer), ISBN 1-4020-7726-2.

Stucki, J.W., Su, K., Pentrakova, L., Pentrak, M. (2014) Methods for handling redox-sensitive smectite dispersions. *Clay Minerals*, **49**, 359 – 377.

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APPENDIX C

TYPE OF INFORMATION INCLUDED IN EXWC RANGE DATA FILE

Overview – This section provides examples of data compiled in Skeet Range EXCEL data file.

Table C-1. EXWC RANGE DATA FILE- List of Bases by Region.

Region	State	Military		Branch	Status	Range ID
		Installation	Facility			
HAWAII	Hawaii	Joint Base	Pearl Harbor Hickam	Navy	Active	
	Hawaii	Naval Magazine	Lualualei (Oahu)	Navy	As of 2000, referred to as Naval Magazine Pearl Harbor	
	Hawaii	Naval Air Station (NAS)	Barbers Point	Navy	Closed under BRAC in 1990s	Former Northern Trap and Skeet Range
	Hawaii	Marine Corps Base	Hawaii	Marine Corps	Active	
Marianas	zGuam	Naval Base	NB Guam	Navy	Active	Orote
	zGuam	Naval Base	NB Guam	Navy	Active	NCTAMS Finegayan
MID ATLANTIC	Maine	Naval Air Station (NAS)	NAS Brunswick	Navy	BRAC	Brunswick Skeet Range
	Maine	NAS	NAS Brunswick	Navy	BRAC	Topsham Skeet Range
	New Jersey	Naval Warfare Station (NWS)	NWS Earle	Navy	Active	Skeet Range
	New Jersey	Naval Air Engineering Station (NAES)	NAES Lakehurst	Navy	Active	
	North Carolina	Marine Corps Air Station	Cherry Point	Marine Corps	Active	Former Range #1
	North Carolina	Marine Corps Base	Camp Lejeune	Marine Corps	Active	D-9 Skeet Range
	Virginia	Naval Surface Warfare Center (NSWC)	Dahlgren Division (NSWCDD)	Navy	Active	

	Virginia	Formally Naval Air Base (NAB) ; currently Joint Expeditionary Base (JEB)	Formally Little Creek; currently Little Creek-Fort Story	Navy	Active	Former MWR Skeet Range
	Virginia	Naval Air Station (NAS)	Oceana	Navy	Active	
	Virginia	Naval Warfare Station (NWS)	Yorktown	Navy	Active	MWR Skeet Range
MIDWEST	Illinois	Naval Station (NS)	RTC Great Lakes	Navy	Active	TSA (Trap, Skeet, & Archery)
	Indiana	Naval Support Activity (NSA)	Crane	Navy	Active	Former West Trap Range
	Tennessee	NSA	Mid-South	Navy	Active	Horse Stables Skeet Range (HSSR) #1 & #2
NORTHEAST	Rhode Island	Naval Station (NS)	Newport	Navy	Active	
NORTHWEST	Alaska	Naval Air Facility (NAF)	Adak	Navy	Closed under BRAC 1997	
	Washington State	NAS	Whidbey Island	Navy	Active	
	Washington State	Naval Base Kitsap (NBK)	Bangor	Navy	Active	Old Trap Range
SOUTHEAST	Florida	Formally Naval Outlying Field	Bronson	Navy	Closed	Bronson Field Skeet Range
	Florida	Naval Technical Training Center (NTTC)	Corry Station	Navy	As of 2007, Center for Information Dominance	
	Florida	NAS	Jacksonville	Navy	Active	Former Skeet Range Site 23
	Florida	NAS	NAS Cecil Field	Navy	NAS Cecil Field Decommissioned in 1999 under BRAC	Former Range at Bldg 804 ROD ref: OU5, Site 49
	Florida	NAS	OLF White House	Navy		
	Florida	NAS	Key West Boca Chica Site	Navy	Active	Skeet Range #820, North Boca Chica

	Florida	NS	Mayport	Navy	Active	
	Florida	NAS	Pensacola	Navy	Active	Fort Redoubt Skeet Range
	Florida	NAS	Pensacola	Navy	Active	National Cemetery Skeet and Trap Range
	Florida	Naval Outlying Field	Saufley	Navy	Active	Saufley Field
	Florida	NAS	Whiting Field	Navy	Active	Whiting Field Skeet Range
	Florida	NAS	Whiting Field	Navy	Active	Whiting Field Gunnery & Skeet Range
	Georgia	Marine Corps Logistics Base (MCLB)	Albany	Marine Corps	Active	
	Louisiana	Naval Air Station Joint Reserve Base (NASJRB)	New Orleans	Navy	Active	Active Range
	Mississippi	NAS	Meridian	Navy	Active	
	South Carolina	Joint Base (JB)	Charleston	Navy	Active	
	South Carolina	MCAS	Beaufort	Marine Corps	Active	
	Texas	NAS	Navy Auxiliary Landing Field (NALF) Cabaniss	Navy	Partially Active	Former Skeet Range NALF Cabaniss
	Texas	NAS	Corpus Christi	Navy	Active	North Trap Range
	Texas	NAS	Corpus Christi	Navy	Active	South Trap Range
	Texas	NAS Corpus Christi	NOLF Waldron	Navy	NOLF Closed	Waldron Skeet Range
	Texas	NAS	Dallas	Navy	BRAC	Former NASD Skeet Range
	Texas	NAS	Kingsville	Navy	Active	
SOUTHWEST	Arizona	MCAS	Yuma	Marine Corps	Active	
	California	NAS	Alameda	Navy	Closed under BRAC 1997	Former Skeet Range Alameda Point ROD ID "IR Site 29"
	California	Naval Base (NB)	North Island	Navy	Active	

	California	NB	Naval Outlying landing Field (NOLF) Imperial Beach	Navy	Active	SI designation: Skeet and Shotgun Target Ranges
	California	Naval Air Facility (NAF)	El Centro	Navy	Active	Skeet and Trap Range
	California	NAF	El Centro	Navy	Active	Turret and Skeet Range
	California	NAS	Lemoore	Navy	Active	San Joaquin Valley Rod and Gun club
	California	Naval Weapons Station (WPNSTA)	Seal Beach	Navy	Active	Site 74 Old Skeet Range
	California	WPNSTA Detachment	Fallbrook	Navy	Active	Fallbrook Skeet Range
	California	NS	Treasure Island	Navy	BRAC	Former Clipper Cove Skeet Range Identified in ROD as Site 27
	California	NB	Point Mugu	Navy	merged w/NB Ventura County in 2000	
	California	Marine Corps Logistics Base (MCLB)	Barstow	Marine Corps	Active	
	California	MCB	Camp Pendleton	Marine Corps	Active	Area 25 Skeet Range
	California	MCAS	Miramar	Marine Corps	Active	
	California	MCAS	Miramar	Marine Corps	Active	
Washington District	Maryland	Naval Station Warfare Facility (NSWF)	Indian Head	Navy	Active	Old Skeet & Trap Range
	Maryland	NSWF	Indian Head	Navy	Active	Rum Point
	Maryland	NAS	Patuxent River	Navy	Active	
	Virginia	MCB	MCB Quantico	Marine Corps	Active	Chopawamsic Creek Skeet Range No.1 (MRP 29)

Table C-2. Additional Data Included in Data Files.

Data Fields	Type of Information
Range Type	Skeet, Trap, Gunnery, Archery
Quantity	No. ranges
No. Arc	No firing arcs
Range Status	active or closed
Remedial Status	IR site, collecting samples, active, current remediation, closed
Regulatory Related Actions	Action Levels for cPAHs in Soil (mg/kg)
Contamination levels	cPAHs in Soil Contamination Levels (mg/kg) posted for site
Contaminated Area	total impacted acreage
Remediation method	cPAHs Contaminated Soil Remediation Method
NIRIS DATABASE	Skeet Range Related Documents Available
Geographical Soil Type	soil type listed in area/
Additional Reference	Related to base or range history
Misc Notes	Close to water body, info about references

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DoD liability for PAH-impacted soils at skeet ranges is in excess of \$100M over more than 40 sites. Current PAH cleanup goals often assume that 100% of PAHs in soil are bioavailable for uptake, resulting in > \$1M per site and overly-protective cleanup approaches. Recent research indicates lower bioavailability of skeet-derived PAHs (Relative Bioavailability (RBA) of 10-80%), that, when applied on a site-specific basis, would reduce costs cleanups by \$100K-\$1M per site (Lowney et al., 2017; Ruby et al., 2016; Xia et al., 2016; Magee et al., 2014). In vivo studies in which rodents are fed contaminated soils, are used to quantify site-specific RBA. However, these studies are not cost and time effective for all sites (\$>200-300K/site; personal communications Schoolfield, 2017, Meyer, 2019). To that end, the overarching objective of this study was to develop, optimize and demonstrate simple and rapid in vitro approaches using benchtop animal-free methods that can be used to provide site-specific RBA estimates. Results of this study shows potential for these methods as low cost, robust, and rapid methods to evaluate RBA of PAHs in skeet-impacted soil across sites with different soil types. To reach the overarching objective of this work, the four main sub-objectives (tasks) were as follows: (1) to provide an improved ability to discern clay target particles from soil particles; (2) to better inform PAH fate and transport processes of skeet impacted soils; (3) to demonstrate and calculate more realistic, site specific RBAs for PAHs instead of default RBAs; and (4) to provide defensible technical information that RPMs can use to negotiate lower risk-based clean-up levels.					
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