Addenda to Peer Review Response

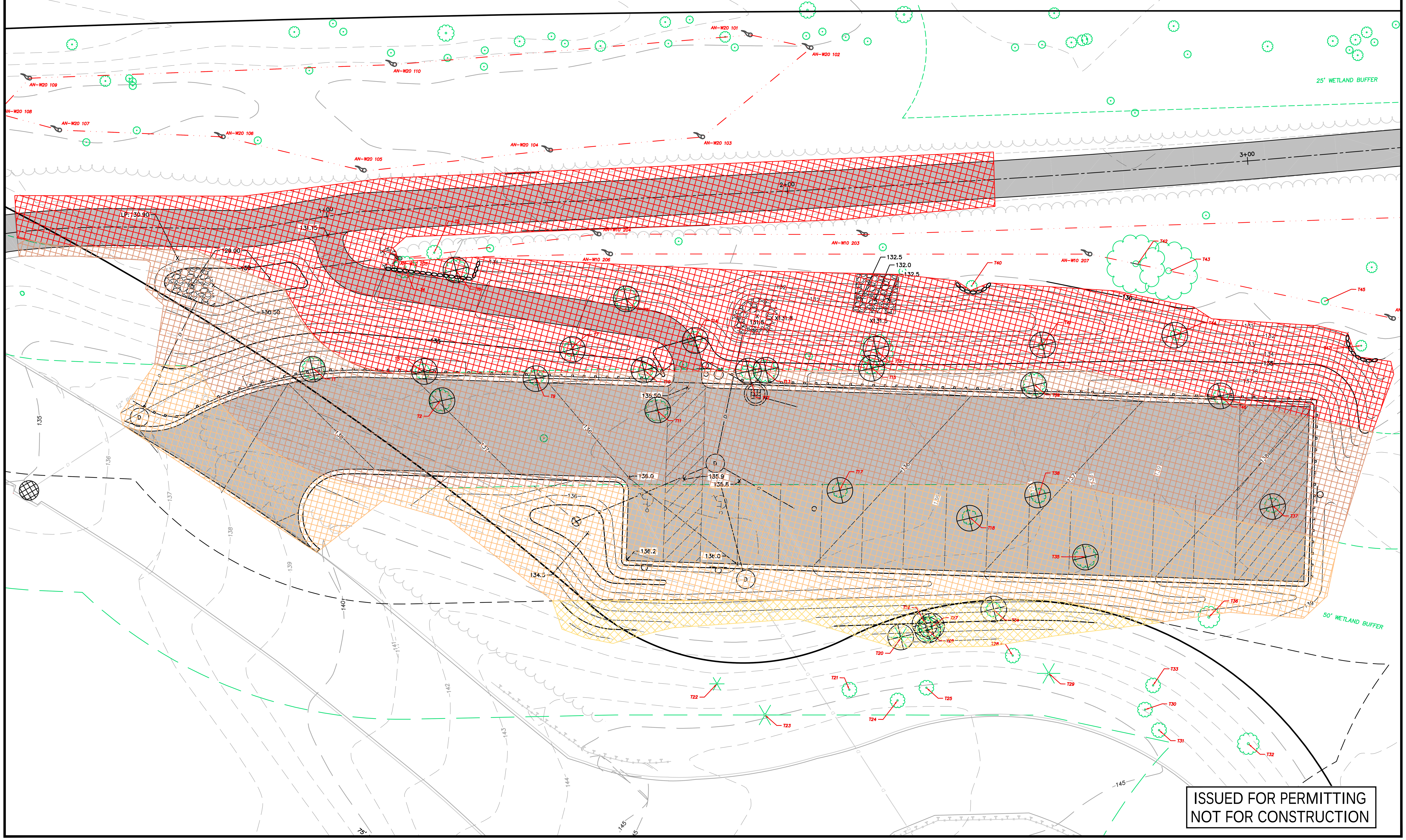
Haggetts Pond Rail Trail
Andover, Massachusetts

RESPONSE 9	9-1 HIGH PLAIN PARKING ALTERNATIVE #1 SITE PLAN 9-2 HIGH PLAIN PARKING ALTERNATIVE #2 SITE PLAN 9-3 HIGH PLAIN PARKING ALTERNATIVE #3 SITE PLAN 9-4 HIGH PLAIN PARKING ALTERNATIVE #4 SITE PLAN
RESPONSE 15	15-1 STREAMSTATS, NORTH PERENNIAL STREAM 15-2 STREAMSTATS, SOUTH PERENNIAL STREAM 15-3 HABITATS OF POTENTIAL REGIONAL OR STATEWIDE IMPORTANCE 15-4 WILDLIFE HABITAT EVALUATION FORM
RESPONSE 17	17-1 MOWING ADVISORY GUIDELINES IN RARE TURTLE HABITAT: PASTURES, SUCCESSIONAL FIELDS, AND HAYFIELDS
RESPONSE 23	23-1 WETLAND DELINEATION PLOT DATA SHEET
RESPONSE 33	33-1 NILES, ET AL., 2020 33-2 CRAWFORD, ET AL., 2023 33-3 KRIECH AND OSBORN, 2022 33-4 MCINTYRE, ET AL., 2016 33-5 ROWE AND O'CONNOR, 2011

ADDENDUM 9-1
HIGH PLAIN PARKING SITE PLAN
ALTERNATIVE #1

LEGEND	DISTURBANCE	DISTURBANCE
	0–25 FT WETLAND BUFFER	7,760 SF
	25–50 FT WETLAND BUFFER	6,836 SF
	50–75 FT WETLAND BUFFER	5,287 SF
	75–100 FT WETLAND BUFFER	908 SF
	TOTAL BUFFER DISTURBANCE	20,791 SF
⊕	SIGNIFICANT TREES LOST	28 TREES

SIGNIFICANT TREES = GREATER THAN 10" DIAMETER TAKEN BETWEEN 6–12 INCHES FROM THE GROUND.



ISSUED FOR PERMITTING
NOT FOR CONSTRUCTION

TOWN OF ANDOVER INCORPORATED MAY 6, 1646 MASSACHUSETTS

HAGGETTS POND RAIL TRAIL

IN

ANDOVER, MASSACHUSETTS

HIGH PLAIN ROAD PARKING LOT ALTERNATIVE #1 SITE PLAN

NOVEMBER 7, 2023

REVISIONS:

NO.	DATE	DESCRIPTION
1	12/21/23	REDUCED ENV. IMPACTS
2	3/1/24	LEGEND

PREPARED FOR:
TOWN OF ANDOVER
36 BARTLET STREET
ANDOVER, MA, 01810

BSC GROUP
300 Brickstone Square, Suite 203
Andover, Massachusetts
01810
617 896 4300

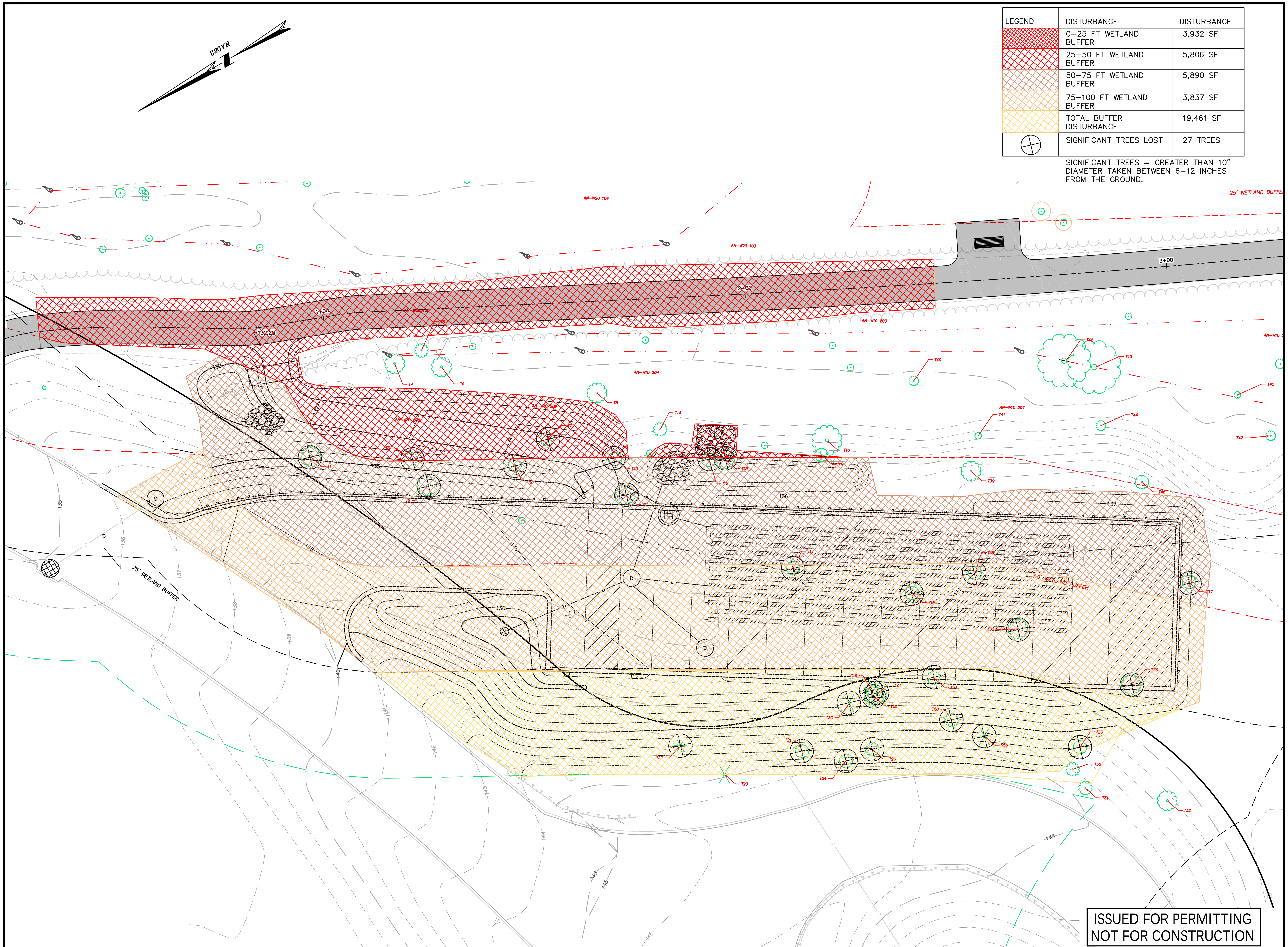
SCALE: 1" = 10'

0 5 10 20 FEET

FILE: P:\8998501\C_D
DWG.:
JOB. NO: 8-9985.01

ADDENDUM 9-2
HIGH PLAIN PARKING SITE PLAN
ALTERNATIVE #2

BSC GROUP



LEGEND	DISTURBANCE	DISTURBANCE
	0–25 FT WETLAND BUFFER	3,932 SF
	25–50 FT WETLAND BUFFER	5,806 SF
	50–75 FT WETLAND BUFFER	5,890 SF
	75–100 FT WETLAND BUFFER	3,837 SF
	TOTAL BUFFER DISTURBANCE	19,461 SF
	SIGNIFICANT TREES LOST	27 TREES

SIGNIFICANT TREES = GREATER THAN 10" DIAMETER TAKEN BETWEEN 6–12 INCHES FROM THE GROUND.

ISSUED FOR PERMITTING
NOT FOR CONSTRUCTION

TOWN OF ANDOVER
INCORPORATED MAY 6, 1646
MASSACHUSETTS

PROFESSIONAL ENGINEER DATE

HAGGETTS POND RAIL TRAIL

IN

ANDOVER, MASSACHUSETTS

HIGH PLAIN ROAD PARKING LOT ALTERNATIVE #2 SITE PLAN

FEBRUARY 15, 2024

REVISIONS:

NO.	DATE	DESCRIPTION
1.	3/1/24	LEGEND

PREPARED FOR:
TOWN OF ANDOVER
36 BARTLET STREET
ANDOVER, MA, 01810

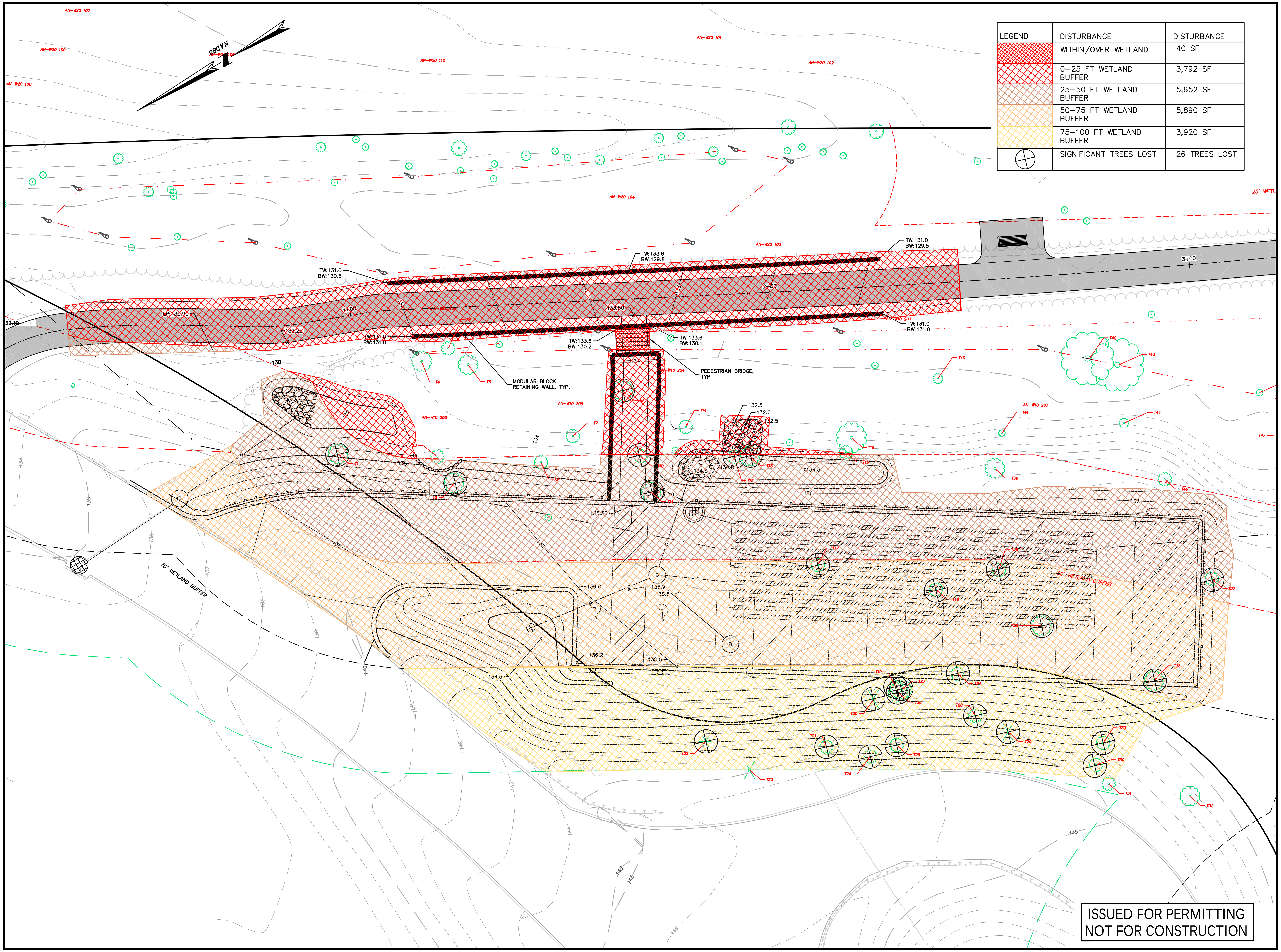
BSC GROUP
300 Brickstone Square, Suite 203
Andover, Massachusetts
01810
617 896 4300

SCALE: 1" = 10'
0 5 10 20 FEET

FILE: P:\8998501\C_D
DWG.:
JOB. NO: 8-9985.01
SHEET 2 OF 4

ADDENDUM 9-3
HIGH PLAIN PARKING SITE PLAN
ALTERNATIVE #3

BSC GROUP



LEGEND	DISTURBANCE	DISTURBANCE
	WITHIN/OVER WETLAND	40 SF
	0–25 FT WETLAND BUFFER	3,792 SF
	25–50 FT WETLAND BUFFER	5,652 SF
	50–75 FT WETLAND BUFFER	5,890 SF
	75–100 FT WETLAND BUFFER	3,920 SF
	SIGNIFICANT TREES LOST	26 TREES LOST

ISSUED FOR PERMITTING
NOT FOR CONSTRUCTION

TOWN OF ANDOVER
INCORPORATED MAY 6, 1646
MASSACHUSETTS

DRAFT

PROFESSIONAL ENGINEER DATE

HAGGETTS POND RAIL TRAIL

IN

ANDOVER, MASSACHUSETTS

HIGH PLAIN ROAD PARKING LOT ALTERNATIVE #3 SITE PLAN

FEBRUARY 15, 2024

REVISIONS:

NO.	DATE	DESCRIPTION
1.	3/1/24	LEGEND

PREPARED FOR:
TOWN OF ANDOVER
36 BARTLET STREET
ANDOVER, MA, 01810

BSC GROUP
300 Brickstone Square, Suite 203
Andover, Massachusetts
01810
617 896 4300

SCALE: 1" = 10'

0 5 10 20 FEET

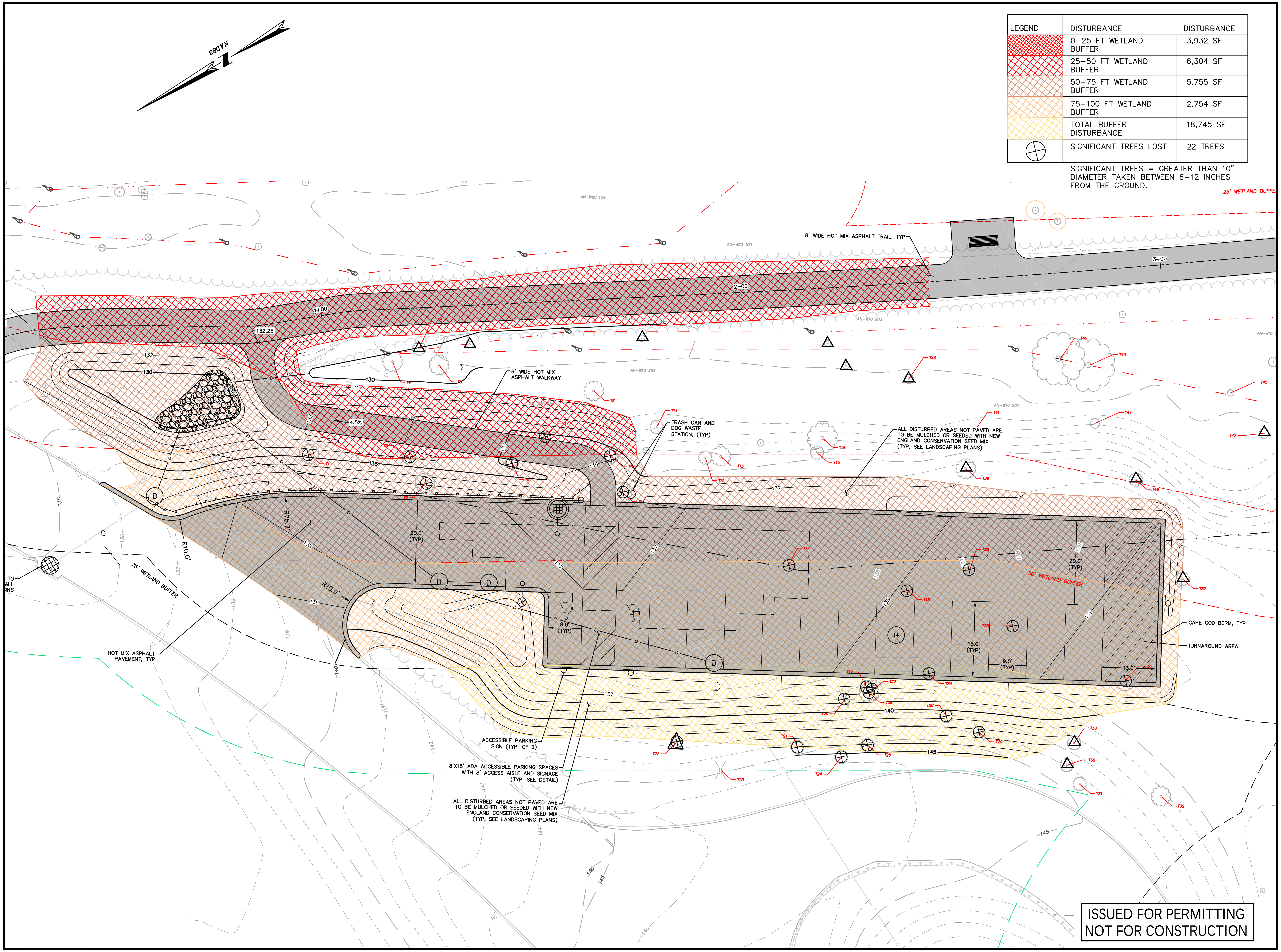
FILE: P:\8998501\C_D
DWG.:
JOB. NO: 8-9985.01

SHEET 3 OF 4

ADDENDUM 9-4
HIGH PLAIN PARKING SITE PLAN
ALTERNATIVE #4

LEGEND	DISTURBANCE	DISTURBANCE
	0–25 FT WETLAND BUFFER	3,932 SF
	25–50 FT WETLAND BUFFER	6,304 SF
	50–75 FT WETLAND BUFFER	5,755 SF
	75–100 FT WETLAND BUFFER	2,754 SF
	TOTAL BUFFER DISTURBANCE	18,745 SF
	SIGNIFICANT TREES LOST	22 TREES

SIGNIFICANT TREES = GREATER THAN 10" DIAMETER TAKEN BETWEEN 6–12 INCHES FROM THE GROUND.



ISSUED FOR PERMITTING
NOT FOR CONSTRUCTION

TOWN OF ANDOVER INCORPORATED MAY 6, 1646 MASSACHUSETTS

PROFESSIONAL ENGINEER DATE

HAGGETTS POND RAIL TRAIL

IN

ANDOVER, MASSACHUSETTS

HIGH PLAIN ROAD PARKING LOT ALTERNATIVE #4 SITE PLAN

FEBRUARY 15, 2024

REVISIONS:

NO.	DATE	DESCRIPTION
1.	3/1/24	LEGEND

PREPARED FOR:
TOWN OF ANDOVER
36 BARTLET STREET
ANDOVER, MA, 01810

BSC GROUP
300 Brickstone Square, Suite 203
Andover, Massachusetts
01810
617 896 4300

SCALE: 1" = 10'

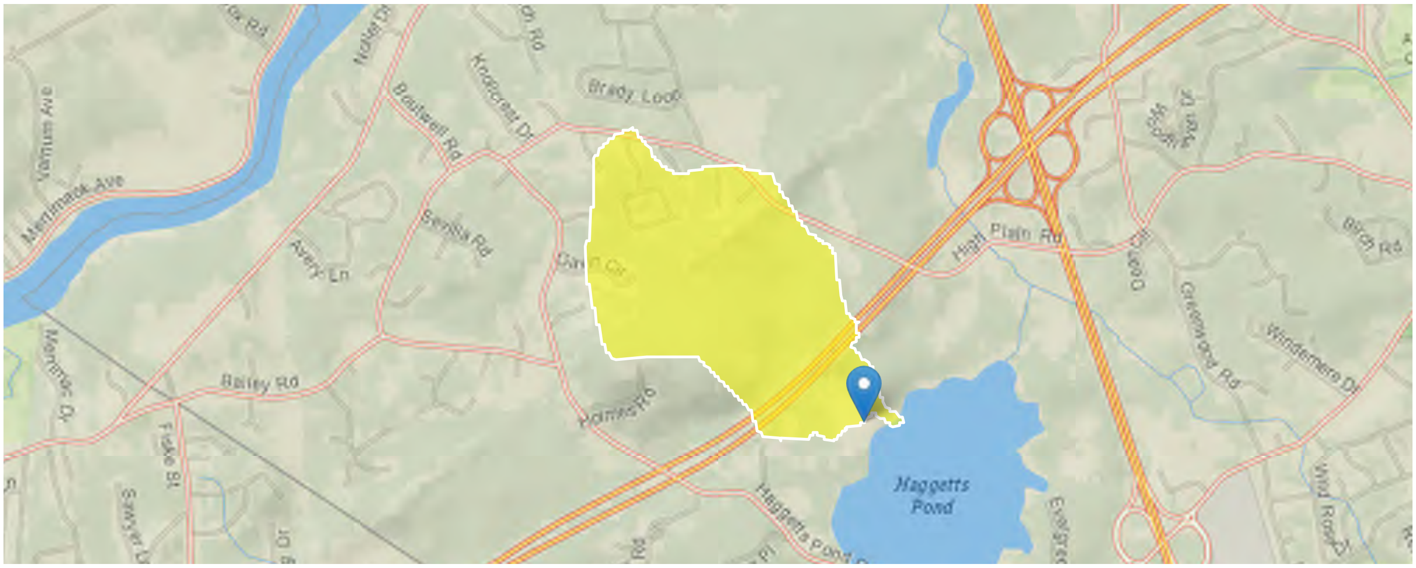
0 5 10 20 FEET

FILE: P:\8998501\C_D
DWG.:
JOB. NO: 8-9985.01

ADDENDUM 15-1
STREAMSTATS
NORTH PERENNIAL STREAM

StreamStats Report

Region ID: MA
Workspace ID: MA20240122185937657000
Clicked Point (Latitude, Longitude): 42.65165, -71.20443
Time: 2024-01-22 14:00:04 -0500



Collapse All

Basin Characteristics

Parameter Code	Parameter Description	Value	Unit
BSLDEM10M	Mean basin slope computed from 10 m DEM	8.599	percent
BSLDEM250	Mean basin slope computed from 1:250K DEM	5.05	percent
DRFTPERSTR	Area of stratified drift per unit of stream length	0.11	square mile per mile
DRNAREA	Area that drains to a point on a stream	0.55	square miles
MAREGION	Region of Massachusetts 0 for Eastern 1 for Western	0	dimensionless

Flow-Duration Statistics

Flow-Duration Statistics Parameters [Statewide Low Flow WRIR00 4135]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.55	square miles	1.61	149
DRFTPERSTR	Stratified Drift per Stream Length	0.11	square mile per mile	0	1.29
MAREGION	Massachusetts Region	0	dimensionless	0	1
BSLDEM250	Mean Basin Slope from 250K DEM	5.05	percent	0.32	24.6

Flow-Duration Statistics Disclaimers [Statewide Low Flow WRIR00 4135]

One or more of the parameters is outside the suggested range. Estimates were extrapolated with unknown errors.

Flow-Duration Statistics Flow Report [Statewide Low Flow WRIR00 4135]

Statistic	Value	Unit
50 Percent Duration	0.519	ft^3/s
60 Percent Duration	0.336	ft^3/s
70 Percent Duration	0.183	ft^3/s
75 Percent Duration	0.136	ft^3/s
80 Percent Duration	0.124	ft^3/s
85 Percent Duration	0.0903	ft^3/s
90 Percent Duration	0.0704	ft^3/s
95 Percent Duration	0.0386	ft^3/s
98 Percent Duration	0.0231	ft^3/s
99 Percent Duration	0.0159	ft^3/s

Flow-Duration Statistics Citations

Ries, K.G., III,2000, Methods for estimating low-flow statistics for Massachusetts streams: U.S. Geological Survey Water Resources Investigations Report 00-4135, 81 p. (http://pubs.usgs.gov/wri/wri004135/)

Bankfull Statistics

Bankfull Statistics Parameters [Bankfull Statewide SIR2013 5155]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.55	square miles	0.6	329
BSLDEM10M	Mean Basin Slope from 10m DEM	8.599	percent	2.2	23.9

Bankfull Statistics Parameters [Appalachian Highlands D Bieger 2015]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.55	square miles	0.07722	940.1535

Bankfull Statistics Parameters [New England P Bieger 2015]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.55	square miles	3.799224	138.999861

Bankfull Statistics Parameters [USA Bieger 2015]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.55	square miles	0.07722	59927.7393

Bankfull Statistics Disclaimers [Bankfull Statewide SIR2013 5155]

One or more of the parameters is outside the suggested range. Estimates were extrapolated with unknown errors.

Bankfull Statistics Flow Report [Bankfull Statewide SIR2013 5155]

Statistic	Value	Unit
Bankfull Width	12.3	ft
Bankfull Depth	0.82	ft
Bankfull Area	9.94	ft^2
Bankfull Streamflow	27.3	ft^3/s

Bankfull Statistics Flow Report [Appalachian Highlands D Bieger 2015]

Statistic	Value	Unit
Bieger_D_channel_width	11.9	ft
Bieger_D_channel_depth	0.944	ft
Bieger_D_channel_cross_sectional_area	11.3	ft^2

Bankfull Statistics Disclaimers [New England P Bieger 2015]

One or more of the parameters is outside the suggested range. Estimates were extrapolated with unknown errors.

Bankfull Statistics Flow Report [New England P Bieger 2015]

Statistic	Value	Unit
Bieger_P_channel_width	21.4	ft
Bieger_P_channel_depth	1.21	ft
Bieger_P_channel_cross_sectional_area	25.5	ft^2

Bankfull Statistics Flow Report [USA Bieger 2015]

Statistic	Value	Unit
Bieger_USA_channel_width	10	ft
Bieger_USA_channel_depth	1.06	ft
Bieger_USA_channel_cross_sectional_area	12.4	ft^2

Bankfull Statistics Flow Report [Area-Averaged]

Statistic	Value	Unit
Bankfull Width	12.3	ft
Bankfull Depth	0.82	ft
Bankfull Area	9.94	ft^2
Bankfull Streamflow	27.3	ft^3/s
Bieger_D_channel_width	11.9	ft
Bieger_D_channel_depth	0.944	ft
Bieger_D_channel_cross_sectional_area	11.3	ft^2
Bieger_P_channel_width	21.4	ft
Bieger_P_channel_depth	1.21	ft
Bieger_P_channel_cross_sectional_area	25.5	ft^2
Bieger_USA_channel_width	10	ft
Bieger_USA_channel_depth	1.06	ft
Bieger_USA_channel_cross_sectional_area	12.4	ft^2

Bankfull Statistics Citations

Bent, G.C., and Waite, A.M.,2013, Equations for estimating bankfull channel geometry and discharge for streams in Massachusetts: U.S. Geological Survey Scientific Investigations Report 2013–5155, 62 p., (http://pubs.usgs.gov/sir/2013/5155/)

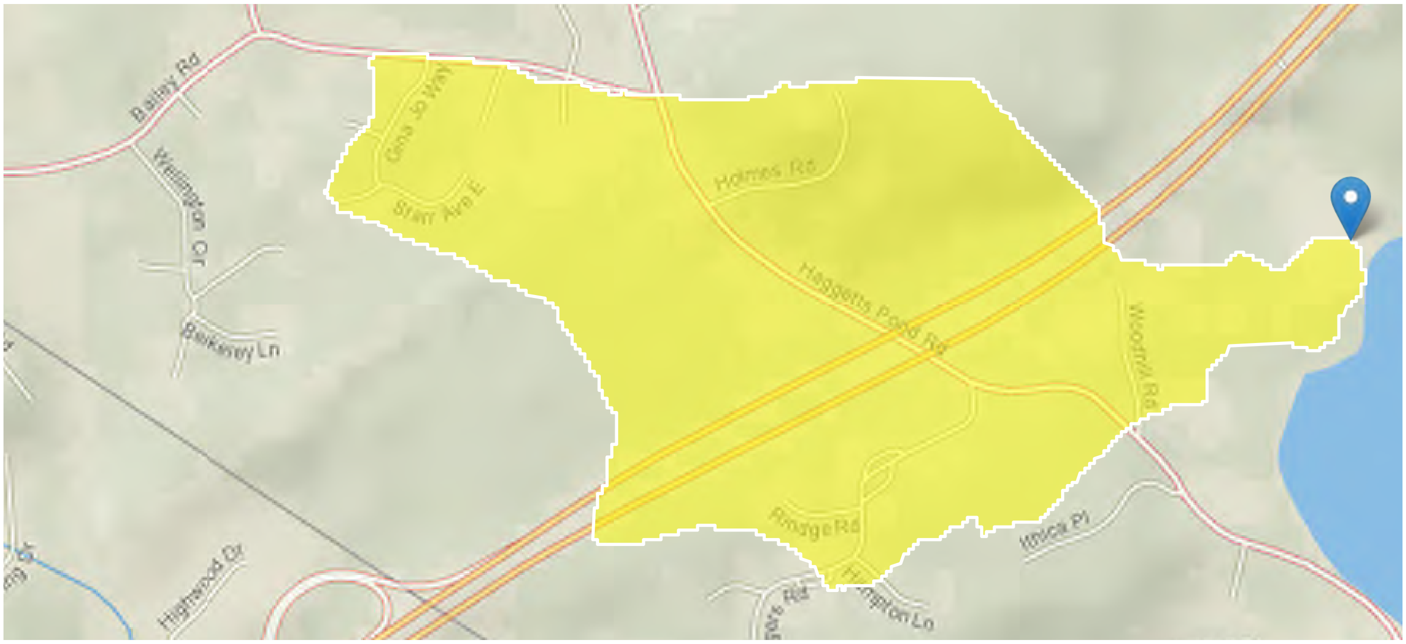
Bieger, Katrin; Rathjens, Hendrik; Allen, Peter M.; and Arnold, Jeffrey G.,2015, Development and Evaluation of Bankfull Hydraulic Geometry Relationships for the Physiographic Regions of the United States, Publications from USDA-ARS / UNL Faculty, 17p. (https://digitalcommons.unl.edu/usdaarsfacpub/1515?utm_source=digitalcommons.unl.edu%2Fusdaarsfacpub%2F1515&utm_medium=PDF&utm_campaign=PDFCoverPages)

Application Version: 4.19.3
StreamStats Services Version: 1.2.22
NSS Services Version: 2.2.1

ADDENDUM 15-2
STREAMSTATS
SOUTH PERENNIAL STREAM

StreamStats Report

Region ID: MA
Workspace ID: MA20240122190312295000
Clicked Point (Latitude, Longitude): 42.65137, -71.20445
Time: 2024-01-22 14:03:40 -0500



Collapse All

Basin Characteristics

Parameter Code	Parameter Description	Value	Unit
BSLDEM10M	Mean basin slope computed from 10 m DEM	7.388	percent
BSLDEM250	Mean basin slope computed from 1:250K DEM	3.72	percent
DRFTPERSTR	Area of stratified drift per unit of stream length	0.17	square mile per mile
DRNAREA	Area that drains to a point on a stream	0.57	square miles
MAREGION	Region of Massachusetts 0 for Eastern 1 for Western	0	dimensionless

Flow-Duration Statistics

Flow-Duration Statistics Parameters [Statewide Low Flow WRIR00 4135]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.57	square miles	1.61	149
DRFTPERSTR	Stratified Drift per Stream Length	0.17	square mile per mile	0	1.29
MAREGION	Massachusetts Region	0	dimensionless	0	1
BSLDEM250	Mean Basin Slope from 250K DEM	3.72	percent	0.32	24.6

Flow-Duration Statistics Disclaimers [Statewide Low Flow WRIR00 4135]

One or more of the parameters is outside the suggested range. Estimates were extrapolated with unknown errors.

Flow-Duration Statistics Flow Report [Statewide Low Flow WRIR00 4135]

Statistic	Value	Unit
50 Percent Duration	0.538	ft^3/s
60 Percent Duration	0.36	ft^3/s
70 Percent Duration	0.208	ft^3/s
75 Percent Duration	0.158	ft^3/s
80 Percent Duration	0.145	ft^3/s
85 Percent Duration	0.105	ft^3/s
90 Percent Duration	0.0831	ft^3/s
95 Percent Duration	0.0449	ft^3/s
98 Percent Duration	0.0274	ft^3/s
99 Percent Duration	0.0189	ft^3/s

Flow-Duration Statistics Citations

Ries, K.G., III,2000, Methods for estimating low-flow statistics for Massachusetts streams: U.S. Geological Survey Water Resources Investigations Report 00-4135, 81 p. (http://pubs.usgs.gov/wri/wri004135/)

Bankfull Statistics

Bankfull Statistics Parameters [Bankfull Statewide SIR2013 5155]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.57	square miles	0.6	329
BSLDEM10M	Mean Basin Slope from 10m DEM	7.388	percent	2.2	23.9

Bankfull Statistics Parameters [Appalachian Highlands D Bieger 2015]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.57	square miles	0.07722	940.1535

Bankfull Statistics Parameters [New England P Bieger 2015]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.57	square miles	3.799224	138.999861

Bankfull Statistics Parameters [USA Bieger 2015]

Parameter Code	Parameter Name	Value	Units	Min Limit	Max Limit
DRNAREA	Drainage Area	0.57	square miles	0.07722	59927.7393

Bankfull Statistics Disclaimers [Bankfull Statewide SIR2013 5155]

One or more of the parameters is outside the suggested range. Estimates were extrapolated with unknown errors.

Bankfull Statistics Flow Report [Bankfull Statewide SIR2013 5155]

Statistic	Value	Unit
Bankfull Width	12.1	ft
Bankfull Depth	0.812	ft
Bankfull Area	9.72	ft^2
Bankfull Streamflow	25	ft^3/s

Bankfull Statistics Flow Report [Appalachian Highlands D Bieger 2015]

Statistic	Value	Unit
Bieger_D_channel_width	12	ft
Bieger_D_channel_depth	0.954	ft
Bieger_D_channel_cross_sectional_area	11.6	ft^2

Bankfull Statistics Disclaimers [New England P Bieger 2015]

One or more of the parameters is outside the suggested range. Estimates were extrapolated with unknown errors.

Bankfull Statistics Flow Report [New England P Bieger 2015]

Statistic	Value	Unit
Bieger_P_channel_width	21.6	ft
Bieger_P_channel_depth	1.22	ft
Bieger_P_channel_cross_sectional_area	26	ft^2

Bankfull Statistics Flow Report [USA Bieger 2015]

Statistic	Value	Unit
Bieger_USA_channel_width	10.2	ft
Bieger_USA_channel_depth	1.07	ft
Bieger_USA_channel_cross_sectional_area	12.6	ft^2

Bankfull Statistics Flow Report [Area-Averaged]

Statistic	Value	Unit
Bankfull Width	12.1	ft
Bankfull Depth	0.812	ft
Bankfull Area	9.72	ft^2
Bankfull Streamflow	25	ft^3/s
Bieger_D_channel_width	12	ft
Bieger_D_channel_depth	0.954	ft

Statistic	Value	Unit
Bieger_D_channel_cross_sectional_area	11.6	ft^2
Bieger_P_channel_width	21.6	ft
Bieger_P_channel_depth	1.22	ft
Bieger_P_channel_cross_sectional_area	26	ft^2
Bieger_USA_channel_width	10.2	ft
Bieger_USA_channel_depth	1.07	ft
Bieger_USA_channel_cross_sectional_area	12.6	ft^2

Bankfull Statistics Citations

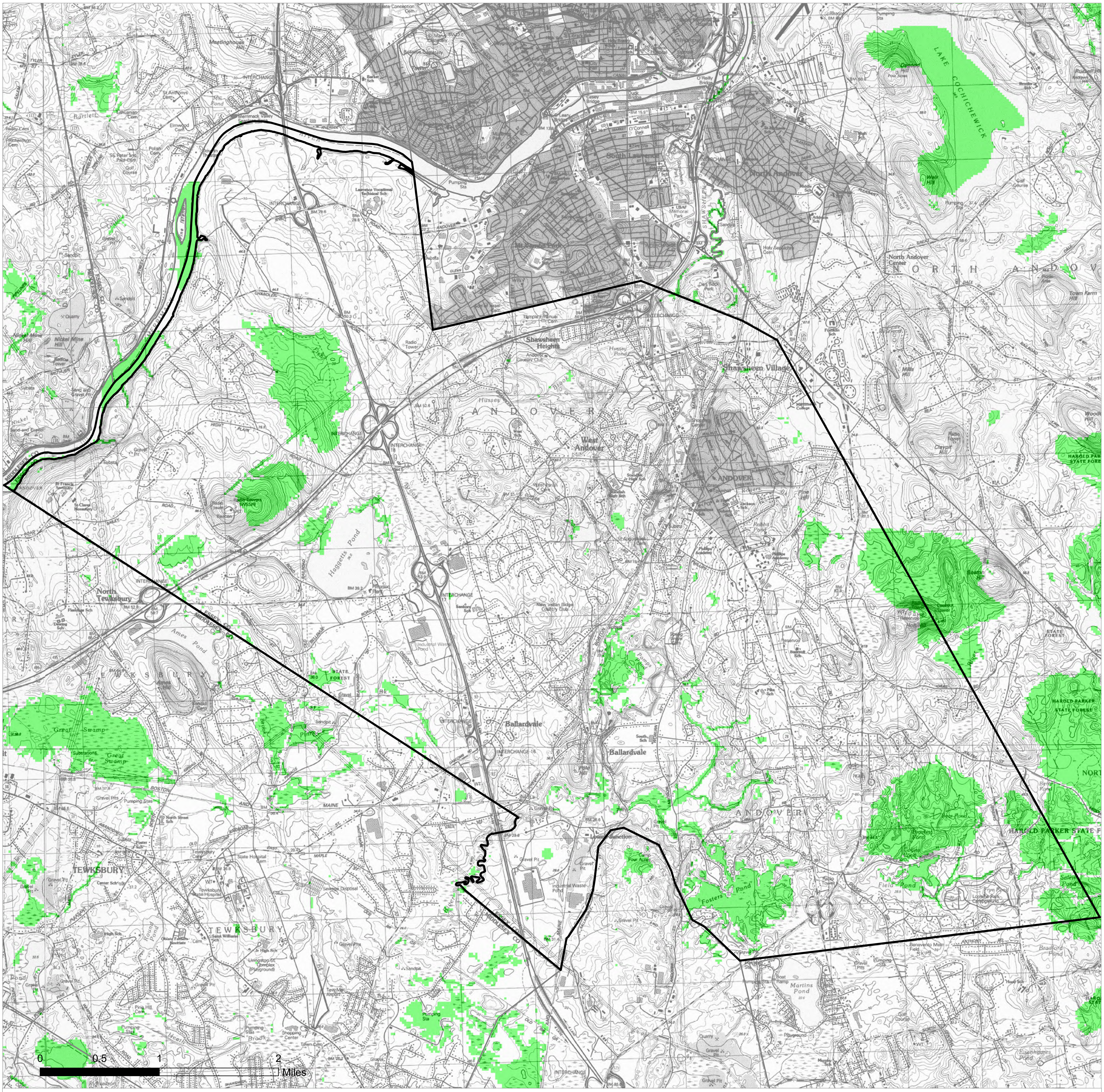
Bent, G.C., and Waite, A.M.,2013, Equations for estimating bankfull channel geometry and discharge for streams in Massachusetts: U.S. Geological Survey Scientific Investigations Report 2013–5155, 62 p., (http://pubs.usgs.gov/sir/2013/5155/)

Bieger, Katrin; Rathjens, Hendrik; Allen, Peter M.; and Arnold, Jeffrey G.,2015, Development and Evaluation of Bankfull Hydraulic Geometry Relationships for the Physiographic Regions of the United States, Publications from USDA-ARS / UNL Faculty, 17p. (https://digitalcommons.unl.edu/usdaarsfacpub/1515?utm_source=digitalcommons.unl.edu%2Fusdaarsfacpub%2F1515&utm_medium=PDF&utm_campaign=PDFCoverPages

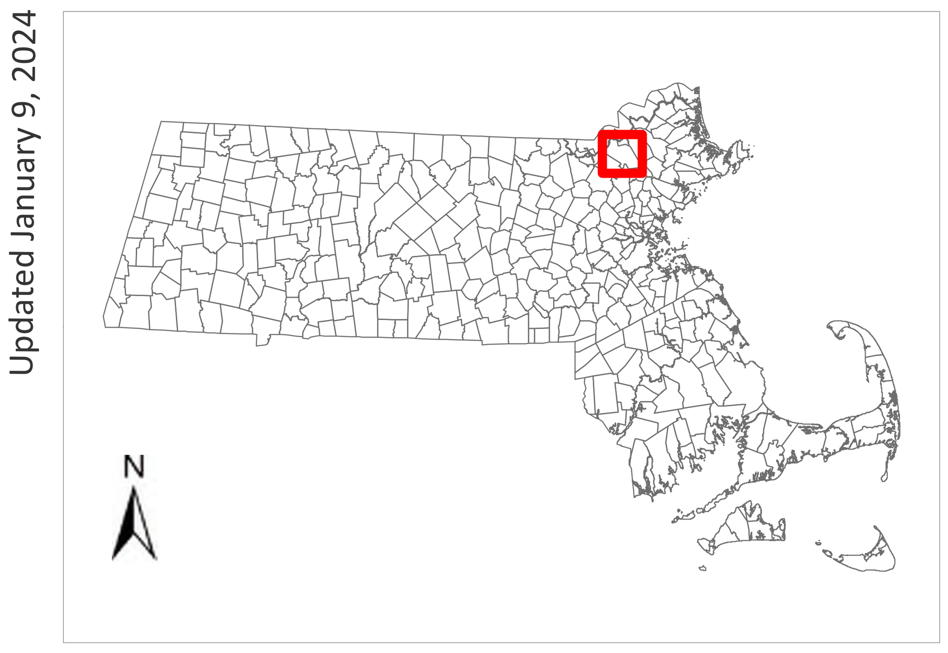
Application Version: 4.19.3
StreamStats Services Version: 1.2.22
NSS Services Version: 2.2.1

ADDENDUM 15-3
HABITATS OF POTENTIAL REGIONAL OR STATEWIDE IMPORTANCE

Habitat of Potential Regional or Statewide Importance
Town of ANDOVER, MA



Habitat of Potential Regional or Statewide Importance



MassDEP's Massachusetts Wildlife Habitat Protection Guidance for Inland Wetlands (June 2006) adopted a new approach for assessing wildlife habitat impacts associated with work in wetlands. This approach utilizes maps developed at the University of Massachusetts Amherst using the Conservation Assessment and Prioritization System (CAPS). The maps depict Habitat of Potential Regional or Statewide Importance that may trigger more intensive review under the MA Wetlands Protection Act. For more information on how to assess wildlife habitat impacts, see Section III of the Guidance document: https://www.mass.gov/doc/massachusetts-wildlife-habitat-protection-guidance-for-inland-wetlands/download.

CAPS is an approach to prioritizing land for conservation/protection based on the assessment of ecological integrity for various ecological communities (e.g. forested wetland, shrub swamp, headwater stream) within an area. The CAPS model assesses ecological integrity of the Massachusetts landscape as influenced by environmental stressor metrics (e.g. pollution, fragmentation). It relies on data that are broadly available across Massachusetts. Ecological features which are not consistently surveyed or uniformly available, such as certified vernal pools, rare species habitat, and contamination sites are not included in the CAPS analysis. When available, this more specific ecological information may be used in conjunction with the CAPS outputs to better understand particular sites in Massachusetts and support informed conservation decision-making. For more information on the statewide maps produced by the CAPS model, see: http://www.umasscaps.org.

These maps were prepared by the University of Massachusetts Amherst, with funding from the Massachusetts Department of Environmental Protection.

UMass Amherst

MassDEP

UMass Extension

CENTER FOR AGRICULTURE

ADDENDUM 15-4
WILDLIFE HABITAT EVALUATION FORM

Massachusetts Department of Environmental Protection
Bureau of Resource Protection - Wetlands Program

Wildlife Habitat Protection Guidance

Appendix B: Detailed Wildlife Habitat Evaluation

Part 1. Summary Sheet

Important: When filling out forms on the computer, use only the tab key to move your cursor - do not use the return key.

Haggett's Pond Rail Trail
Project Name

Andover, MA
Location

8,491 SF
Size of Area Being Impacted

1/25/2024
Date

Impact Areas (linear feet, square feet, or acres for each of the impact areas within the site)

Name	Waterbody/ Waterway	Wetland	Upland*	Total Area
1. Haggett's Brook			8,491 SF	8,491 SF
2.				
3.				
4.				
5.				
6.				
7.				

*Riverfront Area/BLSF

Attach Sketch map and/or photos of the Impact Areas

Narrative Description of Site (attach separate page if necessary)

Two perennial streams merge in a cattail swamp with poorly defined channels. Impact area on existing railbed trail within Riverfront Area only, no impacts to wetland expected. Soil data is for Riverfront Area/wetland; impact area soils are human transported material/compacted gravel railbed. Presumed beaver/muskrat in adjacent marsh. Emergent wetland immediately adjacent to work area. Habitat degradation present-- dog waste bags observed, beaver management causing regular dramatic fluctuations of water.

Certification

I hereby certify that this project has been designed to avoid, minimize, and mitigate adverse effects on wildlife habitat, and that it will not, following two growing seasons of project completion and thereafter, substantially reduce its capacity to provide important wildlife habitat functions.

Signature of Wildlife Specialist (per 310 CMR 10.60 (1) (b))

Matt Burne
Typed or Printed Name

Massachusetts Department of Environmental Protection
Bureau of Resource Protection - Wetlands Program

Wildlife Habitat Protection Guidance

Appendix B: Detailed Wildlife Habitat Evaluation

Part 2. Field Data Form (for each wetland or non-wetland resource area)

I. General Information

0 High Plain Road (42.651440, -71.204066)
Project Location (from NOI page 1)

8,491 SF/Riverfront Area
Impact Area (number/name)

1/25/2021
Date(s) of Site Visit(s) and Data Collection

Overcast, light rain
Weather Conditions During Site Visit (if snow cover, include depth)

Matt Burne
Person completing form per 310 CMR 10.60(1)(b)

1/25/2024
Date this form was completed

The information on this data sheet is based on my observations unless otherwise indicated

Signature

II. Site Description (complete A or B under Classification - see instructions for full description)

A. Classification

1. For Wetland Resource Areas, complete the following:

System: ______ Subsystem: ______

Class: ______ Subclass: ______

Hydrology/Water Regime

☐ Permanently flooded ☐ Saturated

☐ Intermittently exposed ☐ Temporarily flooded

☐ Semi-permanently flooded ☐ Intermittently flooded

☐ Seasonally flooded ☐ Artificially flooded

2. For Riverfront or Bordering Land Subject to Flooding Resource Areas, complete the following. Use a terrestrial classification system such as one of the two listed below:
   a. "Classification of the Natural Communities of Massachusetts (Draft)" by Patricia C. Swain and Jennifer B. Kearsley, MA DFW NHESP, Westborough, MA. July 2000. (Department of Fish & Game Website)
   b. "New England Wildlife: Habitat, Natural History, and Distribution" by Richard M. DeGraaf and Deborah D. Rudis, USDA Forest Service, Northeastern Forest Experiment Station. General Technical Report NE-108. August 1992. 491 pages.

Terrestrial - Forested
Community Name

Mixed Coniferous – Deciduous
Vegetation Description

Riverfront area within the project footprint is a historic rail bed.
Physical Description

Wildlife Habitat Protection Guidance

Appendix B: Detailed Wildlife Habitat Evaluation

Part 2. Field Data Form (continued)

B. Inventory (Plant community)

% Cover:

Trees (> 20')	Shrubs (< 20')	Woody vines	Mosses	Herbaceous
85	0	0	0	0

Plant Lists (species that comprise 10% or more of the vegetative cover in each strata; "*" designates a dominant plant species for the strata):

Strata	Plant Species	Strata	Plant Species
Overstory	White pine		
Overstory	Red oak		

C. Inventory (Soils)

52A- Freetown muck, 0 to 1 percent slopes
Soil Survey Unit

Very poorly drained
Drainage Class

Mucky peat, muck
Texture (upper part)

0-2 in, 2-79 in
Depth

0-6 in
Depth to Water Table

III. Important Habitat Features (complete for all resource areas)

If the following habitat characteristics are present, describe & quantify them on a separate sheet & attach.

Wildlife Food

Important Wetland/Aquatic Food Plants (smartweeds, pondweeds, wild rice, bulrush, wild celery)

☒ Abundant ☐ Present ☒ Absent

Important Upland/Wetland Food Plants (hard mast and fruit/berry producers)

☐ Abundant ☒ Present ☐ Absent

Shrub thickets or streambeds with abundant earthworms (American woodcock)

☐ Present ☒ Absent

Shrub and/or herbaceous vegetation suitable for veery nesting

☐ Present ☒ Absent

Wildlife Habitat Protection Guidance

Appendix B: Detailed Wildlife Habitat Evaluation

Part 2. Field Data Form (continued)

Number of trees (live or dead) > 30" DBH: 0

Number (or density) of Standing Dead Trees (potential for cavities and perches):

6-12" dbh	12-18" dbh	18-24" dbh	> 24" dbh
5	1	2	1

Number of Tree Cavities in trunks or limbs of:

1
6-12" diameter (e.g., tree swallow, saw whet owl, screech owl, bluebird, other songbirds)

0
12-18" diameter (e.g., hooded merganser, wood duck, common goldeneye, mink)

5
>18" diameter (e.g., hooded merganser, wood duck, common goldeneye, common merganser, barred owl, mink, raccoon, fisher)

Small mammal burrows

☐ Abundant ☒ Present ☐ Absent

Cover/Perches/Basking/Denning/Nesting Habitat

☐ Dense herbaceous cover (voles, small mammals, amphibians & reptiles)

☒ Large woody debris on the ground (small mammals, mink, amphibians & reptiles)

☐ Rocks, crevices, logs, tree roots or hummocks under water's surface (turtles, snakes, frogs)

☐ Rocks, crevices, fallen logs, overhanging branches or hummocks at, or within 1m above the water's surface (turtles, snakes, frogs, wading birds, wood duck, mink, raccoon)

☐ Rock piles, crevices, or hollow logs suitable for:

☐ otter ☐ mink ☐ porcupine ☐ bear ☐ bobcat ☐ turkey vulture

☐ Live or dead standing vegetation overhanging water or offering good visibility of open water (e.g., osprey, kingfisher, flycatchers, cedar waxwings)

Depressions that may serve as seasonal (vernal/autumnal) pools

☐ Present ☒ Absent

Standing water present at least part of the growing season, suitable for use by

☐ Breeding amphibians ☐ Non-breeding amphibians (foraging, re-hydration)

☐ Turtles ☐ Foraging waterfowl

Sphagnum hummucks or mats, moss-covered logs or saturated logs, overhanging or directly adjacent to pools of standing water in spring (four-toed salamander)

☐ Present ☒ Absent

Part 2. Field Data Form (continued)

Important habitat characteristics (if present, describe and quantify them on a separate sheet)

Medium to large (> 6”), flat rocks within a stream (cover for stream salamanders and nesting habitat for spring & two-lined salamanders)

☐ Present ☒ Absent

Flat rocks and logs on banks or within exposed portions of streambeds (cover for stream salamanders and nesting habitat for dusky salamanders)

☐ Present ☒ Absent

Underwater banks of fine silt and/or clay (beaver, muskrat, otter)

☐ Present ☒ Absent

Undercut or overhanging banks (small mammals, mink, weasels)

☐ Present ☒ Absent

Vertical sandy banks (bank swallow, kingfisher)

☐ Present ☒ Absent

Areas of ice-free open water in winter

☐ Present ☒ Absent

Mud flats

☐ Present ☒ Absent

Exposed areas of well-drained, sandy soil suitable for turtle nesting

☒ Present ☐ Absent

Wildlife dens/nests (if present, describe & quantify them on the back of this sheet)

Turtle nesting sites

☐ Present ☒ Absent

Bank swallow colony

☐ Present ☒ Absent

Nest(s) present of ☐ Bald Eagle ☐ Osprey ☐ Great Blue Heron

Den(s) present of ☐ Otter ☐ Mink ☐ Beaver

Wildlife Habitat Protection Guidance

Appendix B: Detailed Wildlife Habitat Evaluation

Part 2. Field Data Form (continued)

Project area is within:

☒ 100' of beaver, mink or otter den, bank swallow colony or turtle nesting area

☐ 200' of Great Blue Heron or osprey nest(s)

☐ 1400' of a Bald Eagle nest[1]

Emergent Wetlands (if present, describe & quantify them on a separate sheet)

Emergent wetland vegetation at least seasonally flooded during the growing season (wood duck, green heron, black-crowned night heron, king rail, Virginia rail, coot, etc.)

Flooded > 5 cm	☐ Present	☒ Absent
Flooded > 25 cm (pied-billed grebe)	☐ Present	☒ Absent

Persistent emergent wetland vegetation at least seasonally flooded during the growing season (mallard, American bittern, sora, common snipe, red-winged blackbird, swamp sparrow, marsh wren)

Flooded > 5 cm	☐ Present	☒ Absent
Flooded > 25 cm (least bittern, common moorhen)	☐ Present	☒ Absent

Cattail emergent wetland vegetation at least seasonally flooded during the growing season

Flooded > 5 cm (marsh wren)	☐ Present	☒ Absent
Flooded > 25 cm (least bittern, common moorhen)	☐ Present	☒ Absent

Fine-leafed emergent vegetation (grasses and sedges) at least seasonally flooded during the growing season (common snipe, spotted sandpiper, sedge wren)

Flooded > 5 cm	☐ Present	☒ Absent
Flooded > 25 cm (least bittern, common moorhen)	☐ Present	☒ Absent

IV. Landscape Context

A. **Habitat Continuity** (if present, describe the landscape context on a separate sheet and its importance for area-sensitive species)

Is the impact area part of an emergent marsh at least	1.0 acre in size?	☐ Yes	☒ No
(marsh and waterbirds)	2.0 acres in size?	☐ Yes	☒ No
	5.0 acres in size?	☐ Yes	☒ No
	10.0 acres in size?	☐ Yes	☒ No

[1] 1400 feet is the distance used by NHESP for evaluating potential disturbance impacts on eagle nests under MESA. Keep in mind, however, that this doesn't give jurisdiction within 1400' of an eagle's nest; it only identifies it on the checklist so that adverse effects can be avoided if work in a resource area is within 1400 feet.

Part 2. Field Data Form (continued)

Is the impact area part of a wetland complex at least	2.5 acres in size?	☐ Yes	☒ No
(turtles, frogs, waterfowl, mammals)	5.0 acres in size?	☐ Yes	☒ No
	10.0 acres in size?	☐ Yes	☒ No
	25.0 acres in size?	☒ Yes	☐ No

For upland resource areas is the impact area part of contiguous forested habitat at least

(forest interior nesting birds)	50 acres in size?	☐ Yes	☒ No
	100 acres in size?	☐ Yes	☒ No
	250 acres in size?	☒ Yes	☐ No
	500 acres in size?	☐ Yes	☒ No
(grassland nesting birds)	> 1.0 acre in size?	☐ Yes	☒ No
(special habitat such as gallery floodplain forest, alder thicket, etc.)	> 1.0 acre in size?	☐ Yes	☒ No

B. **Connectivity with adjoining natural habitats**

☐ No direct connections to adjacent areas of wildlife habitat (little connectivity function)

☒ Connectors numerous or impact area is embedded in a large area of natural habitat (limited connectivity function)

☐ Impact area contributes to a limited number of connectors to adjacent areas of habitat (somewhat important for connectivity function)

☐ Impact area serves as *part of* a sole connector to adjacent areas of habitat (important for connectivity function)

☐ Impact area serves as *only* connector to adjacent areas of habitat (very important for connectivity function)

V. Habitat Degradation (describe degradation and wildlife impacts on the back of the sheet)

☐ Evidence of significant chemical contamination

☐ Evidence of significant levels of dumping

☐ Evidence of significant erosion or sedimentation problems

☐ Significant invasion of exotic plants (e.g., purple loosestrife, *Phragmites*, glossy buckthorn)

☒ Disturbance from roads or highways ☒ Other human disturbance

☐ Is the site the only resource area in the vicinity of an otherwise developed area

Note: These are not the only important habitat features that may be observed on a site. If the wildlife specialist identifies other features they should be noted in the application.

Part 2. Field Data Form (continued)

VI. Quantification Table for Important Habitat Characteristics

Habitat Characteristic	Amount Impacted in Impact Area	Current (entire site)	Post-Construction (entire site)
Standing dead 6-12	0	5	5
Standing dead 12-18	0	1	1
Standing dead 18-24	0	2	2
Standing dead >24	0	1	1
Coarse woody debris			Replace in kind

ADDENDUM 17-1
MOWING ADVISORY GUIDELINES IN RARE TURTLE HABITAT: PASTURES, SUCCESSIONAL FIELDS, AND HAYFIELDS

MOWING ADVISORY GUIDELINES IN RARE TURTLE HABITAT: PASTURES, SUCCESSIONAL FIELDS, AND HAYFIELDS

by
The Natural Heritage and Endangered Species Program
Massachusetts Division of Fisheries and Wildlife

Grasslands, shrublands, pastures and hayfields are important habitats for turtles, particularly the Wood Turtle and Eastern Box Turtle. Turtles require sparsely vegetated areas with some bare soil for nesting and many prefer early successional areas as feeding areas during the late spring and summer months. The natural succession of grasslands, shrublands, old pastures, and fields reduces the availability of these critical habitat types forcing turtles to travel longer distances to find similar habitat elsewhere. As the travel distance increase so does the likelihood that they will cross roads putting them at risk of being hit and killed by cars. Therefore, the maintenance of these habitat types is important and often requires periodic mowing, although other methods of control are possible (e.g. prescribed burns, grazing). Mowing during the spring and summer months can also cause significant turtle mortality; up to 10% of a western Massachusetts population of Wood Turtles (Jones 2007). In fact, researchers in rural areas are finding that the percent of mortality due to mowing and agricultural machinery is much higher than the mortality rate due to roads.

The following guidelines are intended to avoid or minimize any detrimental effect of habitat management on Wood Turtle or Box Turtle populations. These measures will likely also benefit other turtle species, such as the Stinkpot and Spotted Turtle. Native plant communities and all native species, particularly MESA-listed species, should be considered when developing management plans for conservation lands. These guidelines provide a suite of options, each of which we believe will help reduce turtle mortality. We recognize that all options will not be appropriate for every circumstance and that land managers may need to modify these guidelines to manage sites to accommodate the needs of other species.

For more information about Wood Turtles and Box Turtles and the types of habitat they use, see the NHESP Fact Sheets:
Wood Turtle http://www.mass.gov/eea/docs/dfg/nhesp/species-and-conservation/nhfacts/glyptemys-insculpta.pdf
E. Box Turtle http://www.mass.gov/eea/docs/dfg/nhesp/species-and-conservation/nhfacts/terrapene-carolina.pdf

An information request form can be submitted to the NHESP for private persons interested in finding out if they have state-listed turtle species on their property; the form may be found at http://www.mass.gov/eea/docs/dfg/nhesp/regulatory-review/inforequform-elect.pdf

For more information on management of these habitats, land managers can refer to the recently released *Managing Grasslands, Shrublands, and Young Forest Habitats for Wildlife: a Guide for the Northeast* available for download at: http://www.wildlife.state.nh.us/habitat/management-guide.html

For more information about Habitat Management for Amphibians and Reptiles see the *Habitat Management guidelines for Amphibians and Reptiles of the Northeastern United States* available for order at http://northeastparc.org/habitat-management-guidelines/

Areas Managed as Turtle Habitat: Lands where the primary objective is turtle habitat (such as nature preserves, wildlife refuges or private lands where the landowners wish to optimize turtle habitat and abundance).

1) ***Timing*** **- The best solution** is to avoiding mowing during the peak time when turtles are using fields.

Peak Time for Field Use by Turtles
May 15^{th} – September 15^{th}

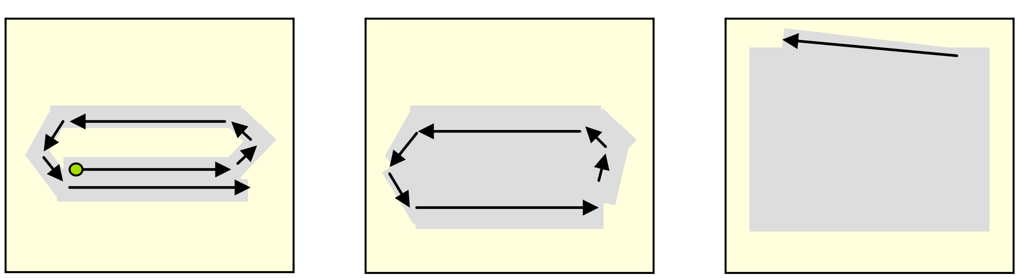
2) *Mowing Rotation* – Mowing to maintain field habitat for conservation reasons should only require multi-year rotations (e.g. mowing once every 2-3 years)*. If mowing is combined with another maintenance method such as chemical control** of invading woody plants, mowing during the turtle active season may not be necessary. If periodic mowing is the sole method used for maintenance, woody plant cover on the site will likely increase over the long-term, and mowing during the active season will be necessary to inhibit woody plant invasion. In some years, very frequent mowing may be required to reduce woody plant abundance. If this repeated mowing treatment is required in a given year, vegetation should be mowed frequently enough that it does not provide habitat for turtles in that year, provided that turtle habitat is present adjacent or nearby to mitigate the temporary loss of use of the site

3) *Percent Mowed* - For sites with > 10 acres of grassland/fields it is recommended that no more than 25%-50% be mowed in any given year. For example, when possible mowing that occurs during the active season should be limited to approximately 25% and areas mowed during the inactive season approximately 50%.

4) *Mower Style* – If mowing on a multi-year rotation, avoid flail mower heads with guide bars that ride along the ground. Sickle-bar mowers will likely have the least impact if mowing grassland and fields every 1-5 years. In areas with more woody vegetation >1-2" diameter a Brontosaurus-style mower will likely have the least impact on turtles.

5) *Mowing Height* – If mowing during the active season is necessary, retention of mowing stubble to 7 or even 12 inches will reduce mortality, reduce blade wear, and will leave important cover for animals.

6) *Directionality* - If mowing during the active season is necessary, start mowing from the center of the field and use a back-and-forth approach, or large circular pattern, to avoid concentrating fleeing animals where they may be killed or stranded. In addition, leave an unmowed 30 ft strip around the perimeter of the field and mow this area last. Most turtles are found in these areas and this provides time for them to react to the mowing activity and move out of the area (see diagram below).



There are three exceptions to this general rule. The first is when a stream is near the field; in these cases it is best to start mowing the side furthest from the streams edge first and work your way towards the stream. The second exception is when the field is bordered by woodland, start mowing the sections of the field furthest from the woods and mow towards the woods. The third exception is when the field is bordered by a road; In this case start mowing the section next to the road first and work your way across the field.

7) *Mower Speed* – Mowing in low gear or at slow speeds will allow turtles to react and move out of the field.

8) *Unmowed Edge* - Leaving an unmowed field edge in high turtle use areas until after September 15th. Eastern box turtles are usually along field edges adjacent to forest and wood turtle are often in field edges closest to nearby streams.

*We recognize that this mowing rotation may be beyond the capacity of the mowing equipment to which a land manager has access. Grant programs are available that may assist in providing funds to assist in hiring a contractor with appropriate mowing equipment, including the NRCS WHIP Program (http://www.nrcs.usda.gov/Programs/whip/) and MassWildlife LIP Program (http://www.mass.gov/eea/agencies/dfg/dfw/wildlife-habitat-conservation/habitat-grant.html). However, these programs are often temporary and intended to recover the capacity of the landowner to manage the property on their own.

** In some cases herbicide applications may be the best alternative to control woody plants and avoid impacts to turtles. Make sure that you read and follow all state and federal regulations. Use the minimum amount and least toxic herbicide possible for desired outcome. Spot application to individual woody plants is preferred. Most of the herbicides used today are amino acid inhibitors acting on amino acids found only in plants. These prevent the plant from performing metabolically.

Land with Multiple Uses: Land where turtles and turtle habitat management is secondary to other management objectives (such as sportsmen's clubs, farmland, recreational areas, etc).

1) *Mower Style* – If mowing on a multi-year rotation, avoid flail mower heads with guide bars that ride along the ground. Sickle-bar mowers will likely have the least impact if mowing grassland and fields every 1-5 years. In areas with more woody vegetation >1-2" diameter a Brontosaurus-style mower will likely have the least impact on turtles.

2) *Blade Height* - Elevating the mowing deck height to 7 or even 12 inches (particularly during the 1st haying of the season) will reduce mortality and will leave important cover for animals. Shorter cuts during late summer second hay harvests are less likely to impact turtles.

*Note: It is actually economically wise to mow fields using higher blade heights. The lower portions of the stem have relatively low nutritional value, it reduces blade wear, increases soil moisture retention which can increase yield of the second harvest, and reduces soil erosion (*Saumure 2006*).*

3) *Directionality* - If mowing during the active season is necessary, start mowing from the center of the field and use a back-and-forth approach, or large circular pattern, to avoid concentrating fleeing animals where they may be killed or stranded. In addition, leave an unmowed 10m strip around the perimeter of the field and mow this area last (see diagram in #5 above). Most turtles are found in these areas and this provides time for them to react to the mowing activity and move out of the area.

There are three exceptions to this rule. The first is when a stream is within 100 m; in these cases it is best to start mowing the side furthest from the streams edge first and work your way towards the stream. The second exception is when the field is bordered by woodland, start mowing the sections of the field furthest from the woods and mow towards the woods. The third exception is when the field is bordered by a road; In this case start mowing the section next to the road first and work your way across the field.

4) *Mower Speed* – Mowing in low gear or at slow speeds will allow turtles to react and move out of the field.

5) *Unmowed Edge* - Leaving an unmowed field edge in high turtle use areas until after September 15th. Eastern box turtles are usually along field edges adjacent to forest and wood turtle are often in field edges closest to nearby streams.

Research Needs:

1) <u>Behavior Data</u> – We need data on the behavioral responses of turtles in reaction to mowers.
2) <u>Blade Height Tests During Actual Field Mowing Events</u> – We need to do tests on the blade height in fields as they are actually being mowed as part of regular maintenance at various sites.
3) <u>The optimum mowing rotation for turtle habitat management.</u>

References:

Jones, M. 2006. Personal Communication. University of Massachusetts, Amherst, MA

Parren, S. Personal Communication. Vermont Fish and Wildlife

Saumure, R.A., and J.R. Bider. 1998. Impact of agricultural development on a population of wood turtles (*Clemmys insculpta*) in southern Québec, Canada. Chelonian Conservation and Biology 3: 37-45.

Saumure, R.A., Herman, T.B., and R.D. Titman. 2006. Effects of haying and agricultural practices on a declining species: The North American wood turtle, *Glyptemys insculpta*. Biological Conservation *in press*

Addendum 23-1
Wetland Delineation Plot
Data Sheet

BORDERING VEGETATED WETLAND DETERMINATION FORM

Project/Site: Hapgood Wright Rail Trail City/Town: Andover, MA Sampling Date: 12/8/2023

Applicant/Owner: Town of Andover Sampling Point or Zone: WF101 - WF115

Investigator(s): Matt Burne, PWS Latitude / Longitude: 42.650617, -71.204476

Soil Map Unit Name: Hinckley and Windsor; Freetown NWI or DEP Classification: NA

Are climatic/hydrologic conditions on the site typical for this time of year? Yes ☑ No ☐ (If no, explain in Remarks)

Are Vegetation ☐, Soil ☐ , or Hydrology ☐ significantly disturbed? (If yes, explain in Remarks)

Are Vegetation ☐, Soil ☐ , or Hydrology ☐ naturally problematic? (If yes, explain in Remarks)

SUMMARY OF FINDINGS – Attach site map and photograph log showing sampling locations, transects, etc.

Wetland vegetation criterion met?	Yes ☐ No ☑	**Is the Sampled Area within a Wetland?**	**Yes** ☐ **No** ☑
Hydric Soils criterion met?	Yes ☑ No ☐		
Wetlands hydrology present?	Yes ☐ No ☐		

Remarks, Photo Details, Flagging, etc.:

Local bylaw wetland only. Fac Up dominated community. Hydric sandy soils and evidence of hydrology, but veg is not wet.

HYDROLOGY

Field Observations:			
Surface Water Present?	Yes ☐	No ☑	Depth (inches)______
Water Table Present?	Yes ☐	No ☑	Depth (inches)______
Saturation Present (including capillary fringe)?	Yes ☐	No ☑	Depth (inches)______

Wetland Hydrology Indicators

Reliable Indicators of Wetlands Hydrology	Indicators that can be Reliable with Proper Interpretation	Indicators of the Influence of Water
☑ Water-stained leaves	☐ Hydrological records	☐ Direct observation of inundation
☐ Evidence of aquatic fauna	☐ Free water in a soil test hole	☐ Drainage patterns
☐ Iron deposits	☐ Saturated soil	☐ Drift lines
☐ Algal mats or crusts	☑ Water marks	☐ Scoured areas
☐ Oxidized rhizospheres/pore linings	☐ Moss trim lines	☐ Sediment deposits
☐ Thin muck surfaces	☐ Presence of reduced iron	☐ Surface soil cracks
☐ Plants with air-filled tissue (aerenchyma)	☐ Woody plants with adventitious roots	☐ Sparsely vegetated concave surface
☐ Plants with polymorphic leaves	☐ Trees with shallow root systems	☐ Microtopographic relief
☐ Plants with floating leaves	☐ Woody plants with enlarged lenticels	☐ Geographic position (depression, toe of slope, fringing lowland
☐ Hydrogen sulfide odor		

Remarks (describe recorded data from stream gauge, monitoring well, aerial photos, previous inspections, if available):

Area has waterstained leaves and some evidence of water marks on tree trunks.

This form is only for BVW delineations. Other wetland resource areas may be present and should be delineated according to the applicable regulatory provisions.

Form Revised July 2023

VEGETATION – Use both common and scientific names of plants.

Tree Stratum Plot size 30'

Common name	Scientific name	Indicator Status	Absolute % Cover	Dominant? (yes/no)	Wetland Indictor? (yes/no)
1. Red Pine	Pinus resinosa	FACU	70.0	Yes	No
2. Black Oak	Quercus velutina	UPL	10.0	No	No
3. White Pine	Pinus strobus	FACU	10.0	No	No
4. Red Maple	Acer rubrum	FAC	5.0	No	Yes
5.					
6.					
7.					
8.					
9.					

95.0 = Total Cover

Shrub/Sapling Stratum Plot size 15'

Common name	Scientific name	Indicator Status	Absolute % Cover	Dominant? (yes/no)	Wetland Indictor? (yes/no)
1. White Pine	Pinus strobus	FACU	1.0	No	No
2. High bush blueberry	Vaccinium corymbosum	FACW	5.0	No	Yes
3. Unknown			1.0	No	
4.					
5.					
6.					
7.					
8.					
9.					

7.0 = Total Cover

Herb Stratum Plot size 5'

Common name	Scientific name	Indicator Status	Absolute % Cover	Dominant? (yes/no)	Wetland Indictor? (yes/no)
1. NA					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					

0.0 = Total Cover

VEGETATION – continued.

Woody Vine Stratum Plot size 30' Common name	Scientific name	Indicator Status	Absolute % Cover	Dominant? (yes/no)	Wetland Indictor? (yes/no)
1. NA					
2.					
3.					
4.					
		0.0 = Total Cover			

Rapid Test:	Do all dominant species have an indicator status of OBL or FACW?			Yes ☐ No ☑
Dominance Test:	Number of dominant species	Number of dominant species that are wetland indicator plants		Do wetland indicator plants make up ≥ 50% of dominant plant species?
	1	0		Yes ☐ No ☑
Prevalence Index:		Total % Cover (all strata)	Multiply by:	Result
	OBL species	0	X 1	= 0.00
	FACW species	5	X 2	=10.00
	FAC species	5	X 3	=15.00
	FACU species	81	X 4	=324.00
	UPL species	10	X 5	=50.00
	Column Totals	(A) 101		(B)399
	Prevalence Index	B/A = 3.95		Is the Prevalence Index ≤ 3.0? Yes ☐ No ☑
Wetland vegetation criterion met?	**Yes** ☐ **No** ☑			

Definitions of Vegetation Strata

Tree - Woody plants 3 in. (7.62 cm) or more in diameter at breast height (DBH), regardless of height

Shrub / Sapling - Woody plants less than 3 in. (7.62 cm) DBH and greater than or equal to 3.3 ft. (1 m) tall

Herb - All herbaceous (non-woody plants, regardless of size, and woody plants less than 3.3 ft. (1 m) tall

Woody vines - All woody vines greater than 3.3 ft. (1 m) in height

Cover Ranges	
Range	Midpoint
1-5 %	3.0 %
6-15 %	10.5 %
15-25 %	20.5 %
26-50 %	38.0 %
51-75 %	63.0 %
76-95 %	85.5 %
96-100 %	98.0 %

Sampling Point WF101 - WF115

SOIL

Profile Description: (Describe to the depth needed to document the indicator or confirm the absence of indicators)

Depth (inches)	Matrix		Redox Features				Texture	Remarks
	Color (moist)	%	Color (moist)	%	Type[1]	Location[2]		
0-1"	7.5YR 2.5/1	100.00	NA				Fibric	
1 - 2.5"	10YR 3/1						Loamy Sand	
2.5 - 4.5"	10 YR 2/1	100.00					Loamy Sand	
4.5 - 20"	10 YR 6/2	65.00	10 YR 2/2	20.00	C	M	Loamy Sand	
			10 YR 4/6	15.00	C	M	Loamy Sand	

[1]Type: C=Concentration, D=Depletion, RM=Reduced Matrix, MS=Masked Sand Grains [2]Location: PL=Pore Lining, M=Matrix

Hydric Soil Indicators (Check all that apply)

- ☐ Histosol (A1)
- ☐ Histic Epipedon (A2)
- ☐ Black Histic (A3)
- ☐ Hydrogen Sulfide (A4)
- ☐ Stratified Layers (A5)
- ☐ Depleted Below Dark Surface (A11)
- ☐ Thick Dark Surface (A12)
- ☐ Sandy Mucky Mineral (S1)
- ☐ Sandy Gleyed Matrix (S4)
- ☐ Sandy Redox (S5)
- ☐ Stripped Matrix (S6)
- ☑ Dark Surface (S7)
- ☐ Polyvalue Below Surface (S8)
- ☐ Thin Dark Surface (S9)
- ☐ Loamy Gleyed Matrix (F2)
- ☐ Depleted Matrix (F3)
- ☐ Redox Dark Surface (F6)
- ☐ Depleted Dark Surface (F7)
- ☐ Redox Depressions (F8)

Indicators for Problematic Hydric Soils

- ☐ 2 cm Muck (A10)
- ☐ 5 cm Mucky Peat or Peat (S3)
- ☐ Iron-Manganese Masses (F12)
- ☐ Mesic Spodic (A17)
- ☐ Red Parent Material (F21)
- ☐ Very Shallow Dark Surface (F22)
- ☐ Other (Include Explanation in Remarks)

Restrictive Layer (if observed) Type: ________ Depth (inches): ________

Remarks:

Hydric Soils criterion met? **Yes** ☑ **No** ☐

ADDENDUM 33-1
NILES, ET AL., 2020

Environmental Science & Technology

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Characterization of an Asphalt Binder and Photoproducts by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Reveals Abundant Water-Soluble Hydrocarbons

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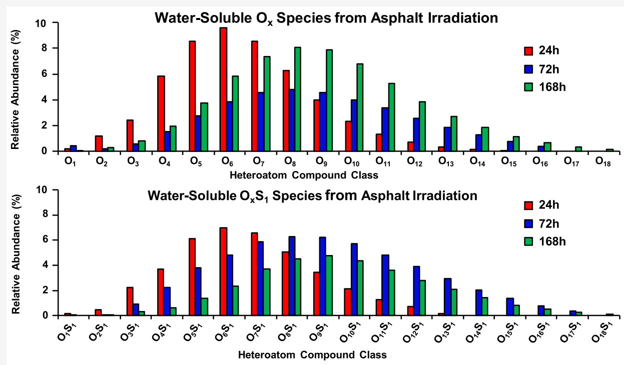

ABSTRACT: Road asphalt is comprised of aggregate (rocks) mixed with a binder composed of high-boiling petroleum-derived compounds, which have been thought to be relatively inert (unreactive) and thus leach small amounts of polyaromatic hydrocarbons (PAHs) into water from the built environment. However, recent studies have demonstrated that petroleum readily undergoes photooxidation and generates water-soluble oxygen-containing hydrocarbons. Therefore, here, we investigate the effects of solar irradiation on an asphalt binder. Upon irradiation in a photooxidation microcosm, thin films of the asphalt binder produce abundant oil- and water-soluble oxygenated hydrocarbons, which we hypothesize are also leached from roads and highways through photooxidation reactions. Ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables extensive compositional characterization of the virgin asphalt binder, irradiated asphalt binder, and the water-soluble photoproducts. The results reveal the production of water-soluble species that resemble the molecular composition of petroleum-derived dissolved organic matter, including abundant hydrocarbons and S-containing species with up to 18 oxygen atoms. The results also confirm photo-induced oxidation, fragmentation, and potentially polymerization as active processes involved in the production of water-soluble organic pollutants from asphalt.

■ INTRODUCTION

Crude oil samples have been shown to produce a plethora of oxygenated oil- and water-soluble hydrocarbons after solar irradiation in the environment as well as in laboratory studies.[1−5] Previous work focused on photochemical and subsequent solubility changes to light crude oil following a large oil spill such as Deepwater Horizon; however, limited work regarding the photochemical weathering of high boiling point petroleum products has been done. Road asphalt (also known as hot mix asphalt) is comprised of aggregate (rocks, etc.) and an asphalt binder/cement, comprised of the highest boiling point species in crude oil, which holds the aggregate together. These high boiling point species remain after high-temperature vacuum distillation and are thus referred to as "vac-bottoms" or residuum. Further processing of the residuum (e.g., addition of a polymer blend) may be required to meet road specifications, which vary by geographic location to ensure high integrity of the asphalt at extreme temperatures (e.g., higher ambient temperatures and intensity of solar irradiation in the southern US). Testing procedures include measurement of viscosity, as well as hardening and cracking tendencies. Once the asphalt binder meets these requirements, it is mixed with aggregate to pave roads.[6]

The heaviest (highest-boiling) fractions of petroleum contain higher proportions of asphaltenes, which are defined as the fraction of crude oil that is insoluble in short alkanes (e.g., *n*-pentane and *n*-heptane) but soluble in an aromatic solvent (e.g., toluene and benzene), and are enriched in polarizable compounds with higher aromaticity and heteroatom content.[7] Asphaltenes have been shown to generate water-soluble organic compounds through photooxidation processes that are structure-dependent. High-resolution mass spectrometry has revealed two structural motifs in asphaltenes: an aromatic core with alkyl side chains (single-core) or several covalently linked aromatic cores (multicore).[8] Asphaltenes with high concentration of multicore motifs were shown to "crack" to produce small water-soluble polyaromatic hydrocarbons (PAHs) through photofragmentation reactions, whereas samples enriched in single-core motifs were not.[8] The photochemically produced oxidized PAHs can then

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undergo polymerization reactions to produce water-soluble compounds with up to 18 oxygen atoms and increased carbon number.[8] Due to the high proportion of asphaltenes in the asphalt binder, we therefore hypothesize that photooxidation of road asphalt could be a potential source of water-soluble, oxidized hydrocarbons, which may be toxic to ecosystems.[9,10] Previous work has indicated that photochemically weathered crude oil produces toxic water-soluble species.[11] Furthermore, previous studies have reported ultraviolet (UV) photooxidation of asphalt;[12] a recent study has identified UV aging and subsequent leaching as a source of dissolved organic carbon (DOC).[13]

An asphalt binder has been previously analyzed by positive-ion (+) electrospray (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to reveal abundant sulfur-containing species, including sulfides, thiophenes, and dibenzothiophenes.[14] The authors also report 19−34 wt % asphaltenes for three asphalt binders. Another study detected and quantified PAHs, which have known carcinogenic and mutagenic properties, in asphalt mixtures by use of liquid chromatography mass spectrometry (LCMS).[15,16] Leaching of unoxidized PAHs into water and soil from asphalt has been previously reported, but the PAH concentrations were well below the water limits allowed in Europe.[17−19]

To determine whether or not asphalt binders produce a complex mixture of water-soluble products upon photoirradiation, an asphalt binder (provided by Capital Asphalt, Tallahassee, FL) is irradiated (in water) with a solar simulator. The water- and oil-soluble components are subsequently analyzed by ultra-high-resolution FT-ICR MS, which reveals molecular-level changes to the asphalt and provides detailed insight into the composition of the water-soluble components. The nonpurgeable organic carbon (NPOC) is quantified at several time periods to provide a measure of the amount of water-soluble organic carbon produced as a function of the irradiation period. Finally, the asphaltene and maltene (alkane-soluble) fractions from the asphalt binder are isolated and subsequently characterized by (+) atmospheric pressure photoionization (APPI) FT-ICR MS to provide insight into the asphalt binder composition prior to irradiation. Mass spectral analysis by (+) APPI is optimal for highly aromatic compounds (e.g., asphaltenes) and is therefore employed for analysis of the oil-soluble fractions.[20,21] Conversely, acidic water-soluble species have been demonstrated to form through photooxidation of hydrocarbons, and therefore (−) ESI is employed for analysis of water-soluble extracts.[22] Future work will investigate the contributions from each component (asphaltene versus maltene) to the formation of water-soluble photoproducts.

■ EXPERIMENTAL METHODS

Asphalt Binder. An asphalt binder (performance grade (PG) 76-22) was obtained directly from a heated delivery truck (Capital Asphalt, Tallahassee, FL) and was stored in the dark in an airtight container. The binder is a PG 76-22 rated asphalt, modified with a polymer to increase the rutting resistance at higher temperatures (up to 76 °C) and is widely used in the southeast United States.[23]

Solar Simulation Microcosm. Thin films of the asphalt binder were prepared by spreading a saturated solution of the asphalt binder in dichloromethane (DCM) over a glass slide. Thin films were allowed to dry under a stream of nitrogen gas, and subsequent additional layers were added until a mass of ~30 mg was achieved. Once DCM was evaporated, the film was placed in a jacketed beaker (attached to a water chiller, which circulated water at 25 °C) on a glass ring, which allowed for a stir bar to sit below the glass slide. Deionized water (HPLC grade, JT Baker) (30 mL) was added to cover the asphalt film and was allowed to stir throughout irradiation (and dark control) experiments. The samples were then placed in an ATLAS Suntest CPS solar simulator, where they were irradiated by artificial sunlight for 24, 72, and 168 h. A dark control was prepared similarly; the beaker was covered with aluminum foil and allowed to stir for 168 h (1 week) prior to isolation of oil- and water-soluble components. Following irradiation, the water was removed by a pipet, and the oil-soluble layer (asphalt film) was dissolved in DCM. All oil and water samples were stored under nitrogen in the dark (at 3 °C) until analysis to prevent further oxidation.

Extraction of Water Solubles. Water samples were subjected to filtration (120 μm) to remove any asphalt film "flakes" from the water. Samples were then eluted through a 0.45 μm nylon filter; a portion of the water samples (~20 mL) was stored in vials for NPOC analysis, and the remaining portion was subjected to a solid-phase extraction (SPE) method to isolate organic compounds for mass spectral analysis. The SPE method employed a PriorityPoLlutant (PPL) column (Agilent) according to a previously published method.[24] The resultant water-soluble extract (in methanol) was stored in glass vials until mass analysis. All glassware that came into contact with water samples (e.g., pipets, vials, funnels) was cleaned with solvent (toluene and methanol) and then subjected to combustion in a muffle furnace (BF51800 Series, Thermo Fisher Scientific) where it was heated to a maximum temperature of 550 °C, held at this temperature for 4 h, and then cooled to room temperature.

NPOC Analysis. A Shimadzu TOC-L instrument was employed for NPOC measurement of filtered water samples. Samples were quantified against a calibration curve of anhydrous potassium hydrogen phthalate (Sigma-Aldrich). All samples were acidified with hydrochloric acid (Fisher Scientific) to 1.5% (v/v) acid and then sparged with ultrazero air (Airgas Inc.) for 90 s to remove inorganic content. After sparging, samples were injected into the furnace for catalysis, and carbon was measured by nondispersive infrared spectroscopy.

Asphaltene Precipitation. The asphalt binder was briefly heated for 30 min in an oven (~90 °C) to facilitate transfer of 150 mg of asphalt binder to a vial. C_7 asphaltenes were isolated by the standard ASTM method D6560-12 to yield 25.8 mg of asphaltenes and 122.2 mg of maltenes from 150.0 mg of asphalt binder.

FT-ICR MS Analysis. A custom-built 9.4 Tesla FT-ICR MS was used for mass analysis.[25] Oil-soluble asphalt binder samples were dissolved in toluene to a final concentration of 150 μg/mL for analysis by (+) APPI FT-ICR MS, as previously described.[26] Water-soluble extracts (in methanol) were infused directly into the mass spectrometer at 0.5 μL/min for (−) ESI FT-ICR MS, as previously described.[25] Predator and PetroOrg computer software were employed for molecular formula assignments.[27,28]

■ RESULTS AND DISCUSSION

Photooxidation of the Asphalt Binder. Following irradiation of the virgin asphalt binder for each of three time periods (24, 72, 168 h), (+) APPI FT-ICR MS was employed

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for analysis of the oil-soluble species. Each mass spectral peak is assigned a unique molecular formula, which is possible due to the ultrahigh mass accuracy of FT-ICR MS. Compounds containing the same numbers of heteroatoms can then be grouped into heteroatom compound classes (O_o, N_n, S_s). The heteroatom compound class distribution for virgin asphalt (starting material) (Figure S1) demonstrates high relative abundances of HC and S_1 compounds, as well as appreciable N_1 species. Therefore, asphalt should theoretically yield abundant O_x and O_xS_1 products derived from the photooxidation of hydrocarbons (HC) and S-containing compounds and N_1O_x species from the N_1-containing compounds. The O_x and O_xS_1 classes are shown for virgin asphalt and the oil-soluble photoproducts in Figure 1, which displays the isoabundance-contoured plots of double-bond equivalents (DBE = number of rings + double bonds to carbon) versus carbon number for the O_1−O_3 and S_1O_1−S_1O_3 classes. Oil-soluble products from irradiated asphalt samples exhibit elevated levels of O_x and O_xS_1 (x = 1−2) relative to virgin asphalt, as shown in Figure S2, and contain species with up to three oxygen atoms (O_3 and O_3S_1), which are not present in appreciable amounts for the virgin asphalt sample or a dark control. The presence of higher-order oxygenated species in the irradiated samples is consistent with photooxidation products previously observed from crude oil samples.[29] However, oxygenated species with more than three oxygen atoms (e.g., O_4 and O_4S_1) are not observed in oil-soluble fractions, whereas previous results from a light crude oil yielded species with up to 10 oxygens that remained oil-soluble.[22] All asphalt samples (virgin, dark control, and irradiated oil-soluble) also contain high amounts of N_1 and N_1O_1. The irradiated fractions contain elevated amounts of N_1O_2, which suggests photooxidation reactions involving nitrogen-containing compounds (as demonstrated by Figure S2, right, N_1−N_1O_3 series).

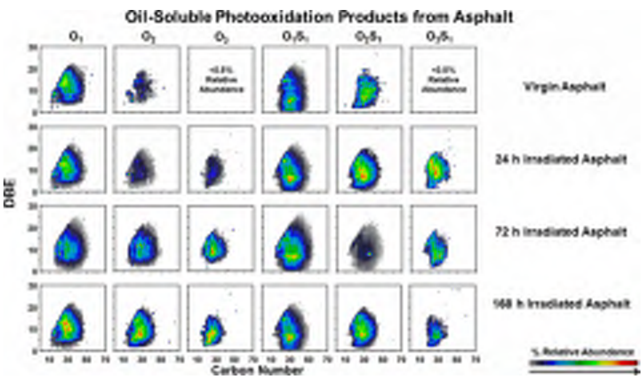

Figure 1. Isoabundance-contoured plots of double-bond equivalents (DBE = number of rings plus double bonds to carbon) versus carbon number for the O_x and O_xS_1 classes for (+) APPI FT-ICR MS analysis of virgin asphalt and oil-soluble products from 24, 72, and 168 h irradiated asphalt.

Dark Control. A dark control was prepared as a thin film on a glass slide (as for the irradiated samples) and was allowed to sit in water for 1 week prior to extraction and analysis of oil- and water-soluble components. The dark control occupies a similar compositional range as the virgin asphalt, illustrated in Figure S3, which displays the isoabundance-contoured plots of DBE versus carbon number for virgin asphalt, a dark control, and a 168 h irradiated asphalt sample (oil-soluble). The 168 h irradiated asphalt exhibits higher amounts of O_x and O_xS_1 relative to the dark control and virgin asphalt (Figure S2), indicating that photooxidation is responsible for the formation of higher-order oxygenated compounds (e.g., O_3S_1) and higher relative abundances for lower-order oxygenated compounds (e.g., O_1, O_2, O_1S_1, O_2S_1).

Quantification of Dissolved Carbon from Irradiation of the Asphalt Binder. High-resolution mass spectrometry can provide identification (at the level of elemental composition assignment) of tens-of-thousands of photochemically produced compounds in water samples but does not provide bulk quantification of the mass of organic species generated by photoirradiation of asphalt. Thus, total organic carbon (TOC) measurement was employed for the quantification of hydrocarbons in water samples.[30] The photochemically produced water-soluble fractions and the dark control were subjected to nonpurgeable organic carbon (NPOC) measurement to quantify the mass of asphalt transferred to water due to photochemical weathering, as displayed in Table 1. Each irradiation involves roughly the same amount of asphalt starting material (∼25−30 mg) and the same volume of water (30 mL); however, the mass of dissolved carbon that is produced varies greatly between a dark control (0.061 mg) and the irradiated samples (0.495−1.588 mg). The mass of dissolved carbon increases with irradiation period for each of the time points. For example, the 168 h irradiated asphalt produces ∼25 times as much dissolved carbon as the dark control and ∼3 times as much as the 24 h irradiated sample.

Comparison of Oil- and Water-Soluble Photoproducts. The water-soluble organic species were isolated and the resulting fractions analyzed by negative-ion (−) ESI FT-ICR MS for the characterization of photooxidation products. It is important to note that the SPE method employed has been shown to extract more than 40% of the DOM from environmental water samples, and therefore the SPE extracts of the water-soluble species may not represent all of the compounds present in the water due to recovery constraints and limitations in ionization efficiency. Figure S4 displays isoabundance plots of DBE versus carbon number for virgin

Table 1. Nonpurgeable Organic Carbon (NPOC) for Water (30 mL) Collected from 24, 72, 168 h Irradiated Asphalt Films and a 168 h Dark Control

sample	NPOC (mg/L)	mass of dissolved carbon (mg)	mass of asphalt starting material (mg)	mass of oil-soluble asphalt after irradiation (mg)	water solubles (wt %)
168 h asphalt dark control	2.0	0.061	34.9	34.0	0.17
24 h irradiated asphalt	16.5	0.495	27.6	29.2	1.79
72 h irradiated asphalt	42.1	1.262	27.2	20.5	4.64
168 h irradiated asphalt	52.9	1.588	24.2	25.2	6.56

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asphalt [(+) APPI], 168 h irradiated asphalt [oil-soluble fraction, (+) APPI], and water-soluble photoproducts from 168 h irradiation of asphalt [(−) ESI]. This plot illustrates a shift from lower-order oxygenated photoproducts (e.g., O_3S_1) in the oil-soluble fraction to higher-order oxygenated species, which become water soluble and extend from O_3S_1 to $O_{16}S_1$. Water-soluble products exhibit lower carbon number (<40) and DBE (<20) ranges than the oil-soluble species, which contain compounds with up to 50 carbons and DBE values up to 25. The lower carbon number and aromaticity ranges of water-soluble photoproducts have been previously reported.[8] Furthermore, the oxygenated species in the water-soluble fraction reveal a shift to higher carbon number and aromaticity as more oxygen atoms are incorporated (e.g., from O_3S_1 to $O_{16}S_1$). This phenomenon has been highlighted in previous studies and suggests photopolymerization reactions.[8] Another possible explanation for this shift is that as the number of oxygen atom increases, alkylated (nonpolar) species with higher DBE become increasingly polarizable and thus water soluble. Furthermore, ketone- and aldehyde-containing photoproducts have been shown to form upon solar irradiation of light crude oils, providing another explanation for higher aromaticity as the oxygen number increases.[29]

Asphalt Binder Produces Dissolved Organic Sulfur. Previous studies report the abundance of sulfur-containing species in asphalt binder,[14] which is confirmed for this sample (Figure S1); thus, we focus on sulfur-containing photoproducts (O_xS_1) in the water-soluble extract from irradiated asphalt. The sulfur-containing water-soluble photoproducts from 168 h irradiated asphalt are illustrated in Figure 2 by

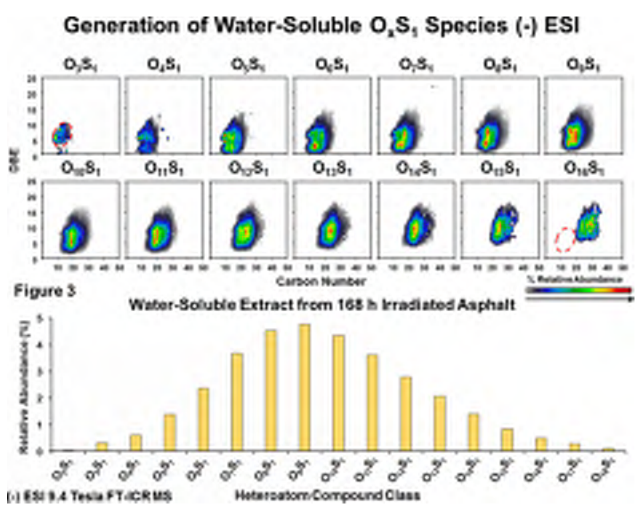

Figure 2. Isoabundance-contoured plots of DBE versus carbon number (top) for the sulfur-containing (O_xS_1) water-soluble photooxidation products from 168 h irradiated asphalt and their heteroatom compound class distribution (bottom).

isoabundance-contoured plots of DBE versus carbon number (top panel) and the corresponding heteroatom compound class distribution (bottom panel) showing the relative abundance (%) for each compound class. Abundant, sulfur-containing photoproducts (from O_2S_1 to $O_{18}S_1$) are readily detected in the water after asphalt irradiation, and the plots of DBE and C# (top) reveal the previously described shift of O_xS_1 species to higher carbon numbers and aromaticity (DBE) as the number of oxygen atoms increases, illustrated by the dashed circle (red) that represents the compositional range for the O_3S_1 class. Note that the most abundant species from the S_1O_3−S_1O_{10} classes are comprised of oxidized products that are at or below C_{20}, which is below that for S_1−S_3 containing "starting material" identified in the original asphalt binder. Thus, photocracking reactions are implicated in the production of these species. Finally, the relative abundances for each O_xS_1 class (bottom panel) follow a pseudo-Gaussian distribution, for which O_9S_1 is the most abundant O_xS_1 class (~4.7% relative abundance).

O_x Compounds in Water. Previous photooxidation studies focus on the O_x class of photoproducts because crude oil is dominated by hydrocarbons that contain no heteroatoms (O, N, S) and, upon irradiation, yield abundant O_x transformation products. As previously noted (Figure S1), virgin asphalt is also comprised of abundant hydrocarbon (HC) species and yields abundant O_x species in the oil-soluble fraction (Figure S2). Unsurprisingly, we observe abundant O_x photoproducts in the water upon (−) ESI FT-ICR MS analysis; the water-soluble extract from the 168 h irradiated asphalt binder reveals an oxygen continuum for O_x compounds (from O_1 to O_{18}) and resembles that for O_xS_1 compounds, as shown by DBE versus carbon number plots in Figure 3 (top

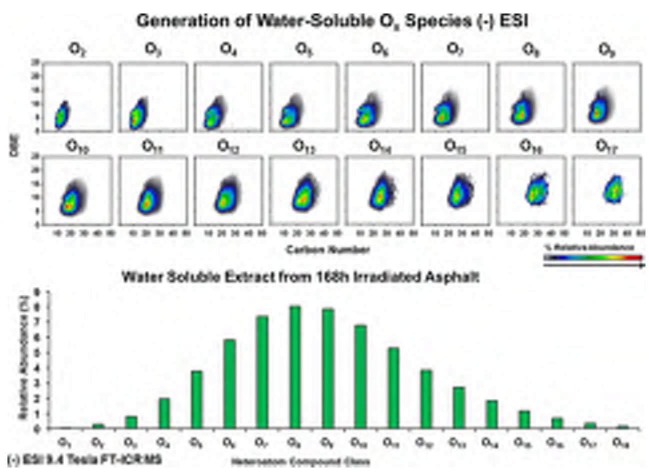

Figure 3. Isoabundance-contoured plots of DBE versus carbon number (top) for O_x classes (O_2−O_{17}) for (−) ESI analysis of the water-soluble fraction from 168 h irradiated asphalt and heteroatom compound class distribution for the O_x classes (O_1−O_{18}) (bottom).

panel). The O_x heteroatom compound class distribution (Figure 3, bottom panel) exhibits a pseudo-Gaussian envelope with a relative maximum at O_8 (~8% relative abundance). The O_x compounds comprise most of the total relative abundance for the (−) ESI FT-ICR MS analysis of the 168 h irradiated asphalt water-soluble extract; more than 58% of species belong to an O_x class. The DBE versus carbon number distribution (top panel) highlights the shift from a low carbon number and DBE (e.g., for O_2, compounds contain 9−21 carbons, DBE = 1−11) to a higher carbon number and aromaticity as more oxygen atoms are incorporated (e.g., for O_{17}, DBE = 8−18, and 23−39 carbons), in agreement with trends seen for O_xS_1 species (Figure 2).

Photooxidation of Nitrogen-Containing Species. Nitrogen-containing species (N_1 and N_1O_1) were identified in virgin asphalt and oil-soluble photooxidation products by (+) APPI, and therefore are expected to be a source for nitrogen-containing water-soluble species upon photoirradiation. Figure 4 presents the suspected starting material [(+)

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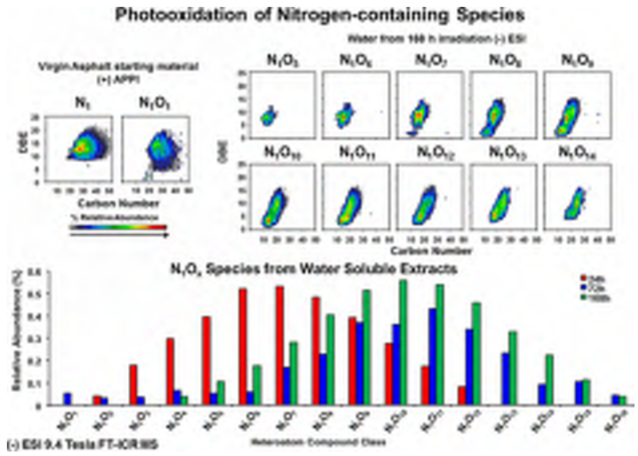

Figure 4. DBE versus carbon number plots (top) for nitrogen-containing species based on (+) APPI FT-ICR MS of virgin asphalt starting material (left) and (−) ESI FT-ICR MS of water-soluble material (right). Heteroatom compound class distribution (bottom) for nitrogen-containing oxygenated photoproducts from water-soluble extracts for 24, 72, and 168 h irradiated asphalt.

APPI, top left panel] as well as water-soluble photoproducts. Isoabundance plots of DBE versus carbon number are displayed for water-soluble photoproducts from the 168 h irradiated asphalt (top right panel) and reveal a unique compositional range (in DBE and carbon number) compared to the starting material (top, left panel). The lower-order oxygenated N_1O_x species (e.g., N_1O_5) occupy a compositional range of lower carbon number (10−20) and DBE (5−12) than the nitrogen-containing starting material (left panel), for which most species have greater than 20 carbons. Again, this trend suggests the presence of photofragmentation reactions, as previously reported for multicore asphaltenes.[8] Moreover, as more oxygen atoms are incorporated to produce higher-order oxygenated N_1O_x compounds (e.g., N_1O_9), a bimodal distribution (at DBE ∼3 and DBE ∼10) is observed. The discrepancy between the DBE range of the N_1 class (9 < DBE < 22) and the water-soluble NO_x species (1 < DBE < 17) again strongly suggests that photofragmentation reactions are responsible.[8] The presence of these two distributions at different DBE ranges (centered at DBE ∼3 and DBE ∼10) and their number of oxygen dependence on water solubility suggests structural and/or nitrogen chemical functionality differences between these photoproducts. This finding could be explained by potential differences in photoreactivity/photoproducts for the two predominant structures of nitrogen-containing molecules in petroleum: five-membered ring (pyrrolic, DBE = 3) and six-membered ring (pyridinic, DBE = 4); however, standards will be employed to confirm that hypothesis in a future study.

The bottom panel of Figure 4 shows the class relative abundance of N_1O_x species in water-soluble extracts from irradiation of asphalt after each of three time periods (24, 72, 168 h). Although the N_1O_x species exhibit a much lower relative abundance than their O_x and O_xS_1 counterparts, the class distribution of N_1O_x compounds is similar to the oxygen continuum observed for the other two. Longer irradiation periods (72 and 168 h) yielded higher abundances of higher-order N_1O_x compounds and greater mass yields in the water-soluble extract. However, compositional differences between 72 and 168 h are minimal.

Photooxidation as a Function of Irradiation Period. The asphalt samples were each irradiated for different periods and produced increasing amounts of dissolved organic species as a function of increasing irradiation time periods (Table 1). Mass analysis of each water-soluble extract revealed only slight differences in terms of molecular composition, illustrated in Figure 5, which displays the isoabundance-contoured plots of

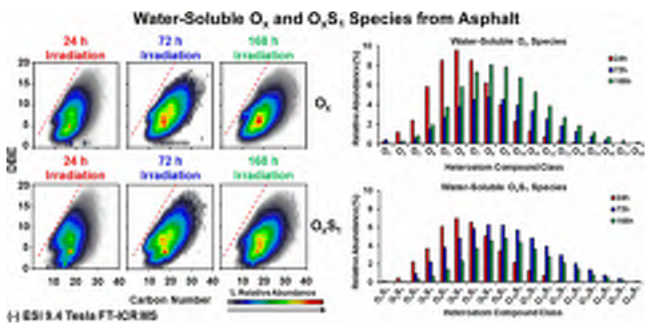

Figure 5. DBE versus carbon number plots (left) for O_x (top) and O_xS_1 (bottom) compound classes for water-soluble extracts from 24, 72, and 168 h irradiated asphalt and their corresponding heteroatom compound class distributions (right).

DBE versus carbon number for all O_x and O_xS_1 species plotted together for each period (left panel) and the corresponding heteroatom compound class distribution for these classes (right panel). The DBE versus carbon number plots reveal only slight differences in the compositional range between each irradiation period for a given class; however, longer irradiation periods were shown to shift away from the polyaromatic hydrocarbon (PAH) limit (red dotted line). The PAH limit is defined as the highest possible degree of aromaticity (DBE value) for a given carbon number, while remaining planar; molecules with DBE values above this PAH limit correspond to buckybowls and buckyballs.[31] Samples with compounds near the PAH limit contain a high concentration of pericondensed aromatic structures, which are characteristic of asphaltenes. The heteroatom compound class distributions for O_x (top right panel) and O_xS_1 (bottom right panel) show that increased irradiation periods produce higher-order oxygenated compounds (e.g., up to O_{18} for 168 h); however, there are not large differences between the 72 and 168 h time points, in agreement with the trends seen for N_1O_x species (Figure 4, bottom panel).

This study confirms that the asphalt binder exhibits a composition typical of heavy petroleum fractions and is enriched in sulfur-containing aromatic species. The asphalt binder readily produces abundant oil- and water-soluble photooxidized transformation products upon photoirradiation. The water- and oil-soluble photoproducts reveal the presence of abundant SO_x and O_x species and notable amounts of NO_x products. NPOC analysis of the water that washed asphalt binder films during irradiation suggests that longer irradiation periods increase the mass of leachable material from the asphalt binder. Compared to other work that involved dry UV-irradiation or asphalt binders prior to leaching in water, the present experiments (asphalt irradiation while submerged in water) yielded higher amounts of dissolved carbon (NPOC values) for similar periods of irradiation (e.g., for 7-day irradiation periods, their samples produced ∼10 and ∼15 mg/mL DOC for two asphalt binders compared to 52.9 mg/mL NPOC for our asphalt binder irradiated in water).[13] However,

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there are notable differences in the experimental design, especially the presence of water and in the type/output of the lamps employed. The irradiation experimental design described herein was chosen intentionally to promote the rapid production/removal of water-soluble photoproducts to characterize longer-term photoproducts that may form in the environment. We also confirm the abundant production of high-order oxygen-containing dissolved organic sulfur and nitrogen, with up to 18 oxygen atoms. The compositional range of the starting asphalt binder material and the photooxidation oil- and water-soluble products demonstrates the occurrence of photo-induced oxidation, fragmentation, and potential polymerization of transformation products in the production of water-soluble contaminants. Because the asphalt binder is comprised of about ∼17 wt % of asphaltenes (toluene-soluble/heptane-insoluble) and ∼83 wt % of maltenes (toluene- and heptane-soluble), individual contributions from each solubility fraction to the production of water-soluble oxidized transformation products will be addressed in a future study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c02263.

Heteroatom compound class distributions for (+) APPI FT-ICR MS analysis of virgin asphalt (Figure S1) as well as for irradiated asphalt with comparison to a dark control and virgin asphalt (Figure S2); DBE versus carbon number plots for (+) APPI FT-ICR MS analysis of the virgin asphalt, dark control, and 168 h irradiated asphalt (Figure S3); DBE versus carbon number plots to enable comparison of (+) APPI FT-ICR MS analysis of virgin asphalt and the 168 h irradiation photoproducts (Figure S4) (PDF)

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Notes

The authors declare no competing financial interest.

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ADDENDUM 33-2

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Research article

Assessing the effects of sunlight and water on asphalt binder and pavement leachability related to the environment

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ABSTRACT

Extensive global research conducted over 30 years explores asphalt leachability and stormwater runoff. Asphalt's widespread usage in construction materials underscores the importance of understanding its environmental consequences. This study aims to assess the influence of sunlight exposure on water quality, particularly regarding the release of hazardous organic compounds such as polycyclic aromatic compounds. We investigated the effect of concurrent versus sequential exposure to water and sunlight, and dark versus light trials utilizing thin films of asphalt binder as well as old and freshly prepared pavement cores for analysis. Initial laboratory experiments reveal significant water-soluble species when thin asphalt films are exposed to solar simulation while underwater. However, simulating environmental conditions found in roadways by exposing the asphalt binder to solar simulation followed by water immersion leads to a substantial decrease in compound formation. Leachate water from 17-year-old asphalt and 15-year-old concrete pavements exhibits complex compound compositions associated with atmospheric and/or vehicular deposition, posing challenges in deconvoluting their origins. Light and dark trials conducted on freshly prepared asphalt pavement under environmental conditions of sunlight and rain demonstrate minimal runoff variation, with semi-volatile organic compound levels resembling the background. Future investigations will focus on applying insights gained from this study to analyze larger sample sets, with an emphasis on inherent hazardous compound variations.

1. Introduction

There are 2.6 million miles of compacted asphalt pavements in the US, typically composed of 4–6 wt.% of asphalt binder (bitumen) coated on mineral aggregate (U.S. DOT, 2018). Therefore, understanding the environmental impact of the product is of great importance. Here we focus on asphalt pavement leachability and stormwater runoff (Azadgoleh et al., 2022, Kriech and Osborn, 2022) while introducing the influence of exposure to sunlight. Asphalt binder, the non-distillable "heavy" fraction from refining crude oil, is composed of a chemically complex array of hydrocarbons (Kurek et al., 1999, ISO 230 2015, Le Guern et al., 2010). To simulate environmental impacts, various laboratory methods have been developed to extract and characterize leachate and stormwater runoff from materials found in the environment. Column leaching studies (U.S. EPA, 2013a), EPA's toxicity characteristic leachability procedure (TCLP) (U.S. EPA, 1992), and monolithic leaching (U.S. EPA, 2013b) are three commonly referenced procedures, but many variations of these techniques are employed (Spreadbury et al., 2021; Kalbe et al., 2014; Azadgoleh et al., 2022). These procedures are commonly used to produce leachate or runoff to test the leachability of known hazardous components such as metals and/or polycyclic aromatic compounds (PACs) or more specifically a subset of compounds called polycyclic aromatic hydrocarbons (PAHs) (Birgisdottir et al., 2007). However, these standard methods do not include specifications about sample exposure to sunlight.

In the wake of crude oil spills into seawater, such as the Exxon Valdez (1989), Deepwater Horizon (2010), and the Refugio oil spill (2015) partial photochemical oxidation has been found to be a reaction pathway for the conversion of hydrocarbons to oxygenated species in the seawater (Freeman and Ward, 2022; Dutta and Harayama, 2000; Payne and Phillips, 1985; Ward et al., 2018). Multiple studies have investigated this reaction pathway by floating a layer of crude oil on

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water and exposing it to simulated sunlight (Bobra and Tennyson, 1989; Bobra, 1992; Niles et al., 2019; Ray et al., 2014; Zito et al., 2020). Under these conditions, crude oil can increase in viscosity, form a film that tends to produce a crust, increase in asphaltene and polar aromatic content (Bobra and Tennyson, 1989; Bobra, 1992; Snyder et al., 2021), as well as produce oxygenated species (Ray et al., 2014; Aeppli et al., 2012). Some heavy bitumen crudes have produced a nontransparent crust, showing limited chemical transformations, and increased density, eventually causing the settling of the residue (Bobra, 1992; Ward et al., 2018). Research has also shown that the concentration of water-soluble compounds can be higher when using light crude oil versus heavy bitumen crude (Bacosa et al., 2015, Hounjet and Stoyanov, 2018), demonstrating that the source and the composition of crude oil can influence the reaction pathways.

Recent studies have reported on the production of water-soluble compounds from thin films of asphalt binder submerged under water while exposed to simulated sunlight (Niles et al., 2020). Extensive chemical analyses revealed that photo-induced oxidation, fragmentation, and potential polymerization are all processes involved in the production of water-soluble oxygenated hydrocarbons. A follow-up study investigated the difference in the biotoxicity of water-soluble compounds produced from asphalt binder and coal tar sealers (Glattke et al., 2022). This study determined that asphalt produced lower levels of toxic water-soluble species based on a Microtox bioassay and had molecular composition consistent with naturally dissolved organic matter. Coal tar sealant, which had higher inherent levels of PAHs, produced a high abundance of oxygenated PAH-like molecules of high toxicity. These findings are consistent with studies based on the photo-oxidation of PAHs and crude oil (Aeppli et al., 2018).

To date, there have been limited studies that examine the effects of sunlight and rainfall on asphalt binder and have not included more complex pavement-based samples. Asphalt binders are typically not used in applications alone, but rather as a minor component in combination with other materials such as aggregate which is compacted into pavements such as Hot Mix Asphalt (HMA). HMA is typically produced by heating aggregate and coating the aggregate with a thin film (8–15 μm) of liquid asphalt binder (Karim et al., 2021). Pavement construction involves heated HMA being transported to the paving site in trucks, laid on a prepared base with an asphalt paver to a specified thickness, and compacted with a roller to achieve a density with ~4–6% air voids by volume. Most asphalt pavements are designed to be dense, with little interconnected voids to keep water from entering the pavement structure. These pavements shed water quickly and dry to maintain friction and minimize hydroplaning of vehicles during rainfall events. The top layer of the pavement wears over time due to freeze-thaw cycles, traffic, de-icing/plowing, and ultraviolet (UV) radiation. However, due to the limited penetration depth of UV into bitumen (Hu et al., 2018) the UV effects are constrained to the surface of the pavement and cannot penetrate the aggregate.

The aim of this study is to investigate how sunlight and water influence the quantity and composition of leachate and stormwater runoff from compacted HMA pavements. The influence of experimental conditions on leachability was investigated using thin films of asphalt binder and the results were applied in the design of environmental simulations to produce pavement water runoff. The study compares runoff from freshly prepared HMA (HMA_0) and 17-year-old HMA (HMA_{17}) pavements produced with and without exposure to simulated sunlight and uses results from 15-year-old Portland Cement Concrete (PCC_{15}) pavement and unbound aggregate (stone base) as non-asphalt based environmental controls.

2. Materials and methods

2.1. Materials

Three asphalt binders from different regions in the US were selected: AB1 (ASTM PG 64–22) from Indiana, AB2 (ASTM PG 67–22) from Florida, and AB3 (ASTM PG 64–22) from Alabama. These binders were classified using Superpave specifications adopted by the US Department of Transportation (NCSC at Purdue University, 2007).

Continuous films of asphalt binder were created by cutting and cleaning glass surfaces, followed by applying a thin film (50–100 μm) of asphalt at 140 °C using a stainless-steel film applicator. The asphalt binder films were stored in the dark for up to one month before use.

Freshly compacted pavement samples (HMA_0) were prepared to replicate the mix design of a 17-year-old asphalt pavement. The samples consisted of Superpave 9.5 mm mixture, SBS polymer, 0.1% polymer crosslinker, and AB1. The samples were compacted at Milestone Contractors LP in Indianapolis, IN, targeting 5.0% air voids. The HMA_0 samples simulated cylindrical pavement specimens and 6″ × 6″ squares based on historical records of roadway cutouts.

Twelve samples of HMA_{17} were collected in January 2021 from a frontage road adjacent to I-65 in Indianapolis, IN. The samples were taken from a pavement paved in 2004 and were approximately 7″ × 7″ in dimension with a thickness ranging from 1″ to 1.5". The surface mix was removed from the underlying asphalt pavement for testing. Additionally, 2 kg of loose stone base (limestone) near the edge of HMA_{17} were collected as environmental controls.

Three core samples of PCC15 were obtained from the slow lane of State Route 37 near I-465 South. The pavement was paved in 2006/2007, and the core samples were 6″ in diameter. The cores were later trimmed to a 2″ thickness before analysis. The reported results represent the average of three measurements taken from the left and right wheel tracks and center lane.

2.2. Methods

2.2.1. Advanced weathering chamber

An advanced weathering chamber (Q-Sun Model Xe-3) with three xenon arc lamps, a daylight Q filter, water spray, and a programmable controller was used for simulated sunlight and rainfall exposure. Irradiance levels ranged from 0.35 to 1.36 $W \cdot m^{-2}$ at 340 nm, representing various sunlight conditions. The exposure duration spanned from 0 to over 50 days of sunlight exposure, simulating a reasonable range of pavement exposure.

Thin films of asphalt binder on glass slides were exposed to simulated sunlight either in a water-submerged or open atmosphere configuration. The water-submerged configuration involved a beaker with ultrapure water and a glass spacer, while the open atmosphere configuration directly exposed the slides to sunlight (Fig. S2). After exposure, samples were submerged in ultrapure water for 18 h, followed by drying and immediate analysis.

Pavements were exposed to simulated sunlight. Cylindrical pavement samples of HMA_0, HMA_{17}, and PCC15 measuring 6″ in diameter were exposed to energy in the open atmosphere of the Q-Sun chamber. The top portion of the core was submerged in water for 18 h, with a stir bar.

HMA_0 and HMA_{17} Pavement Exposed to Simulated Sunlight According to ASTM G155 (ASTM G155, 2021). ASTM G155 and modified ASTM G155 methods were employed to compare water-soluble compounds in runoff from a blank, HMA_0, and HMA_{17} specimens. Light-exposed samples followed the ASTM G155 cycle, alternating simulated sunlight exposure and water spray. Dark experiments were conducted with the xenon arc lamps turned off. Five sets of samples were conditioned to simulate environmental exposure, including a blank, HMA_0 dark, HMA_0 light, HMA_{17} dark, and HMA_{17} light. Water runoff was collected at five specific time intervals for analysis.

2.2.2. Analytical

Prior to analysis, water samples and stone base samples required extraction. Aqueous leachate samples were concentrated using a dichloromethane (DCM) liquid-liquid extraction following US EPA

SW846–3510C. A 1 L aliquot of the sample was sequentially extracted with DCM, and an acid extraction was performed by adjusting the pH (<2) with sulfuric acid. The resulting extracts were combined and concentrated to a final volume of 1.0 mL. Alternative extraction techniques are described in Supplemental S1. Stone base samples were extracted to examine organic environmental deposits using a modified EPA SW846–3550 B method. The samples were not crushed to meet particle size requirements, and no drying agent was used. In summary, 250 g of the stone sample was sonicated with DCM:acetone (80:20) in a glass jar for 1 h. After decanting the initial DCM aliquot, the stone sample was rinsed twice with DCM, and the combined extracts were concentrated to 1.0 mL.

Sievers InnovOx ES Laboratory total organic carbon (TOC) analyzer was used to determine the non-purgeable organic compounds (NPOC). All samples were prefiltered with a 0.7 μm acid-free syringe filter. In NPOC mode, inorganic carbon is sparged from an acidified sample with purified N_2(g) open to the atmosphere before the sample enters the supercritical water oxidation chamber.

Gas Chromatography (GC)/Flame Ionization Detection (FID) was used to determine the TOC based on calibration with a certified diesel oil standard. A GC-quadrupole time of flight-mass spectrometer (GC-QTOF-MS) was used for semi-quantitative detection of oxygenated compounds ($C_xH_yO_z$) and semi-volatile organic compounds (SVOCs) with identification based on the NIST Spectral Library. Two-dimensional GCxGC/TOF-MS with NIST Spectral Library was used for non-quantitative compound identification. Finally, the GC-QTOF-MS was used to quantify 33 PACs via internal standard after calibration. Additional GC method details are available in supplemental section S2.

Table 1 provides a concise summary of the experimental design, including simulated sunlight and water exposures, sample preparation, and analysis for leachate and runoff samples. It outlines the parameters measured and the types of samples analyzed. Experimental conditions related to simulated sunlight and water exposure are explained in the table footnotes.

The Iatroscan TLC-FID method, following IP 469/01 (Energy Institute, 2006) protocol, was used to analyze asphalt binder for saturates, aromatics, resins, and asphaltenes (SARA). Before and after treatment, the asphalt binder samples were dissolved in 10.0 mL DCM to prepare a thin film for SARA analysis. While there are challenges associated with SARA analysis, samples were run together under the same conditions to optimize side-by-side data comparisons.

2.2.3. Data analysis

Equation (1) calculates the energy exposure of each sample, reported in joules (J), at a wavelength of 340 nm. The equation is defined as follows:

$$J(340\ \text{nm}) = P \cdot t \cdot SA \tag{1}$$

Here, P represents the irradiance power of simulated sunlight measured in $W \cdot m^{-2}$ at 340 nm, t denotes the duration of exposure in seconds, and SA represents the surface area of the thin film sample in square meters. To determine the surface area of the asphalt binder thin film, measurements of the width at the top and bottom of both sides of the underlying substrate were taken using a caliper. Expressing the energy as $J_{340\ nm}$ allows for the normalization of irradiance across different experimental setups.

To quantify the leached organic material in asphalt runoff, total organic carbon (TOC). The amount of TOC in $mg \cdot L^{-1}$ is reported as dissolved organic matter (DOM) in $mg \cdot m^{-2}$. DOM is used to present results from both non-purgeable organic carbon (NPOC) via direct injection and gas chromatography flame ionization detector (GC-FID) from a liquid/liquid extracted sample into DCM. This method normalizes the values across several different experimental designs where the asphalt binder (SA) surface area in m^2 and the volume of water (V) in L used in each experiment varied. The conversion of TOC to DOM is shown in Equation (2).

$$DOM = TOC \cdot V/SA \tag{2}$$

To measure the amount of leached organic material in asphalt water runoff, total organic carbon (TOC) is utilized. The quantity of TOC is expressed in milligrams per liter ($mg \cdot L^{-1}$) and is reported as dissolved organic matter (DOM) in milligrams per square meter ($mg \cdot m^{-2}$). DOM is employed to present the findings obtained through two methods: direct injection of non-purgeable organic carbon (NPOC) and gas chromatography flame ionization detector (GC-FID) analysis of a liquid/liquid extracted sample using dichloromethane (DCM). The concentration of the water-soluble compounds is inherently dependent on the surface area of the asphalt binder and the volume of water used in various experiments. This approach standardizes the values across various experimental designs where the surface area of the asphalt binder (SA) in square meters (m^2) and the volume of water (V) in liters (L) utilized in each experiment may vary. This test was used to look for trends in the data. To ensure the quality of the data, control groups and background corrections were used. The conversion of TOC to DOM is illustrated in Equation (2).

3. Results

3.1. Exposing continuous films of asphalt binder to simulated sunlight and water

In the underwater experiments, the photooxidation of the asphalt binder caused the production of water-soluble compounds that were quantified by measuring NPOC and reported as DOM in $mg \cdot m^{-2}$. DOM values ranged from 290 to 4900 $mg \cdot m^{-2}$ for these experiments that

Table 1
Outline of experimental design, analysis, and various leachate and runoff samples.

Experimental design	Simulated Sunlight and Water Exposure	Single Exposure[a]		ASTM G155 Cycles[b]					No Simulated Exposure[c]
	Analysis	NPOC DOM, $mg \cdot m^{-2}$		GC-FID DOM, $mg \cdot m^{-2}$	$C_xH_yO_z$, ppm	SVOC, ppm	GC/GC, ID	PACs, ppb	PACs, ppb
Samples	thin films of asphalt binder	W–S	OA						
	PCC_{15}		OA						
	blank	W–S	OA	L	L	L	L	L	
	HMA_0		OA	L&D	L&D	L&D	L&D	L&D	
	HMA_{17}		OA	L&D	L&D	L&D	L&D	L&D	
	stone base								NE

[a] Aqueous samples were passed through a 0.7 μm syringe filter in preparation for analysis.
[b] Aqueous sample preparation for analysis EPA SW846–3510C (U.S. EPA, 1996).
[c] Aqueous sample preparation by modified EPA SW846–3550 B (section 3.3.2) (U.S. EPA, 2015), W–S – water-submerged, OA – open atmosphere, L – light, D – dark, and NE – no simulated exposure.

spanned from 0 to 2.5 × 10^3 $J_{340\ nm}$ of continuous illumination (Fig. 1). Data from the submerged AB1 experiments revealed a direct correlation between the concentration of dissolved organic carbon in the water and the energy of simulated sunlight exposure ($J_{340\ nm}$). Furthermore, longer irradiation periods were observed to result in higher amounts of leachable materials from the asphalt binder. In addition to AB1, two other asphalt binders, AB2 and AB3, were investigated. Results for the three selected asphalt binders demonstrated similar trends suggesting limited impact from crude source and processing on the behavior between the three asphalt binders. However, notable inconsistencies in the trends can be observed, particularly at ~730 J in the underwater configuration. These variations were attributed to minor changes in sample preparation requiring further experimentation to define the true variance in the production of water-soluble compounds while asphalt is exposed to sunlight while underwater.

The open atmosphere configuration was selected to better represent weather patterns in the natural environment, where full sunlight and rainfall do not generally occur at the same time. This configuration shows significantly less DOM ranging from 25 to 190 mg·m^{-2} and does not increase with $J_{340\ nm}$ (Fig. 1). The decrease in the amount of DOM produced and the change in the relationship between the production of DOM and exposure to simulated sunlight away from a linear increase suggests that there is a change in the mechanism of production.

3.2. *Characterization of asphalt binder in thin films after exposure to simulated sunlight underwater or in open atmosphere*

Representative images of the water-submerged and open atmosphere asphalt binder thin films after simulated sunlight exposure at 2.5 × 10^3 $J_{340\ nm}$ are shown in Fig. 2. Dramatic differences in the appearance of the asphalt binder were observed; the underwater exposed asphalt binder thin films exhibit lightening of color, partial delamination from the glass slide, and increased brittleness. It was observed that the underwater exposed asphalt binder exhibited atypical rheological behavior and shows evidence of deeper penetration throughout the thickness of the thin film observed on the back of the slide. In contrast, the thin film of asphalt binder exposed to the open atmosphere retained the original

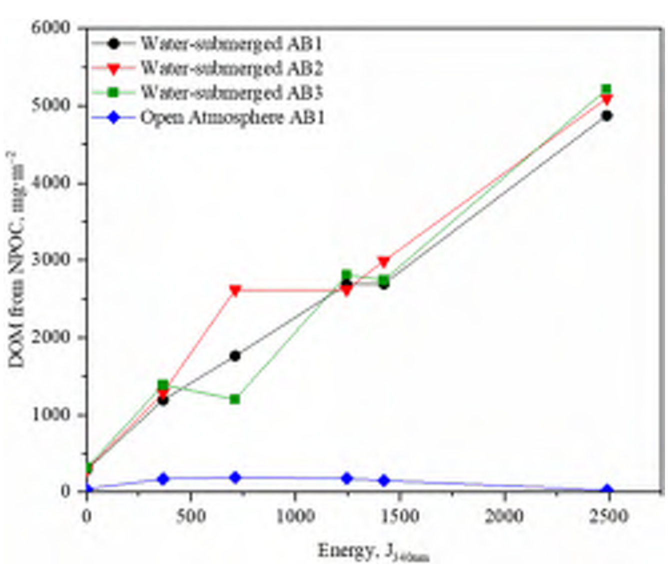

Fig. 1. DOM calculated from NPOC in mg·m^{-2} as a function of energy exposure in $J_{340\ nm}$, in the water-submerged experiments for AB1, AB2, and AB3 as well as open atmosphere configuration for AB1. Exposing the asphalt binder surface to sunlight and water had a significant impact on the quantity of material produced as did the energy levels ($J_{340\ nm}$). Three different asphalt binders show similar trends with relatively minimal variations. Conversely, the open-air results show minimal levels of DOM and did not show an increase with increased energy ($J_{340\ nm}$).

dark surface color, remained adhered to the glass surface, and retained tackiness at the end of the experiment.

To further our understanding of the impact of experimental design the composition of the resulting asphalt binder was assessed via Iatroscan SARA analysis and compared to the starting material (unmodified asphalt binder). Separation of the asphalt binder into four fractions namely saturates (S), naphthenic or aromatics (A), polar aromatics or resins (R), and asphaltenes (A) occurs based on solubility (increasing polarity) and adsorption properties. Results from unmodified AB1 as well as water-submerged AB1 and open atmosphere AB1 both exposed to 1.2 × 10^2 $J_{340\ nm}$ of simulated sunlight were compared (Fig. 3). Unmodified and open atmosphere experiments show similar results, whereas the water-submerged asphalt binder shows a significant increase in polar aromatics and respective decreases in the other fractions. The slight variations observed in the open atmosphere sample were ascribed to the limited depth to which simulated sunlight could penetrate the majority of the asphalt binder. Based on results from thin film trials and the deviation from historical data on typical asphalt aging when asphalt binder is exposed to sunlight underwater, the open atmosphere experimental configuration was more predictive of environmental conditions.

3.3. *Impact of atmospheric and vehicular deposition on runoff from pavements*

To determine how potential surface deposition influences DOM, several pavement types with varying degrees of exposure to the environment were compared. HMA_0 pavement was never exposed to the outdoor environment (no atmospheric or vehicular deposition), HMA_{17} pavement was subjected to both types of environmental deposition over its lifetime, and PCC_{15} had no initial inherent organic compounds but did have environmental exposure. All samples were exposed to 5.5 × 10^2 J_{340nm} in the open atmosphere configuration and DOM analysis showed that HMA_0, HMA_{17}, and PCC_{15} produced 26.3, 151, and 131 mg·m^{-2}, respectively (Fig. S3). HMA_{17} had 5.7 times higher levels of DOM compared to HMA_0 but was relatively close in value to PCC_{15}. These results indicate that atmospheric and/or vehicular deposition on HMA_{17} can influence the amount of DOM found in leachate or stormwater runoff.

3.4. *Using standardized methods for the production, identification, and quantification of organic compounds in HMA runoff after exposure to simulated sunlight*

Simulated sunlight and rainfall exposure of asphalt pavement was used to produce 25 runoff samples following ASTM method G155. ASTM G155 for accelerated weathering was chosen to produce pavement runoff samples based on results from laboratory studies presented above. This method allowed for the use of a standardized method that separates the exposure to simulated sunlight and rainfall in time. There are five time-related samples for each sample category shown in Fig. 4. Initial NPOC analysis indicated results below background, so the experimental techniques shifted to liquid/liquid extraction followed by GC-FID analysis. With the calculated DOM, values for runoff samples ranged from 0.38 to 200 mg·m^{-2} (Fig. 4A). The least amount of extracted DOM was observed in the HMA_{17} light samples. Low DOM values indicate little production of water-soluble compounds on older pavement due to exposure to sunlight. Lower levels of DOM are consistent with the wearing of the thin asphalt binder layer on the surface of the pavement over time due to the reduction in the amount of organic material available. Another notable trend observed in the DOM data is that the highest concentrations were found in the initial 2-h samples, followed by a rapid decline.

Oxygenated compounds ($C_xH_yO_z$) and semi-volatile organic compounds (SVOCs) in the extracted samples are shown in Fig. 4B. In all cases, the level of detected oxygenated compounds was similar. SVOC

Fig. 2. Pictures of asphalt binder (AB1) after 2.5×10^3 $J_{340\ nm}$ of simulated sunlight exposure in the water-submerged (left) and open atmosphere configurations (right).

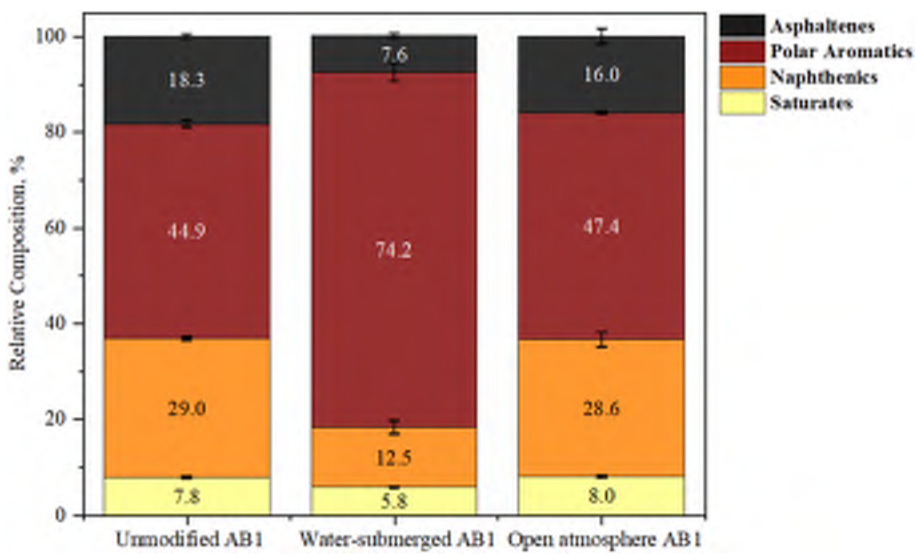

Fig. 3. Results of SARA analysis namely saturates (S), naphthenic or aromatics (A), polar aromatics or resins (R), and asphaltenes (A).

and oxygenated compounds data indicate similar trends, with the highest concentrations observed in the initial 2 h samples and lower concentrations for subsequent samples. Sub ppm quantities of SVOCs and oxygenated compounds were found in the extracted samples, except for the SVOCs in the initial, 2 h HMA_{17} dark sample. The primary organic compounds such as paraffins, isoparaffins, olefins, naphthenes, aromatics, and thiols typical of petroleum/asphalt samples were most abundant in the initial 2 h, HMA_{17} dark sample. Higher levels in the HMA_{17} dark sample suggest the presence of atmospheric or vehicular deposition and lower levels in the HMA_{17} light indicate the potential breakdown of those compounds with exposure to sunlight. System contaminants that were identified are described in S3.

A targeted group of 33 PACs, listed in Table S1, were investigated in these samples. Results are reported at ppb levels (several orders of magnitude lower than oxygenated compounds and SVOCs). Once more, the general trend shows the highest levels of PACs detected in the 2 h samples, followed by a decrease in concentration over time, with HMA_{17} dark displaying the highest concentrations. Fig. 4C displays the 11 highest individual PAC concentrations and the sum of the remaining 22 compounds in the leachate water samples. Phenanthrene, fluoranthene, and pyrene were detected at the highest concentrations in the HMA_{17} pavement samples. The highest concentrations of PACs (2-h HMA_{17} dark) were 0.38, 0.33, and 0.23 ppb of phenanthrene, fluoranthene, and pyrene detected respectively, and a total of 1.5 ppb of the sum of 33 PACs. For reference, the California Office of Environmental Health Hazard Assessment (OEHHA) set the notification level for naphthalene as 170 ppb.

4. Discussion

Thin films of asphalt binder were exposed to sunlight while submerged underwater, causing a linear increase in the production of DOM as energy ($J_{340\ nm}$) is increased. These findings corroborate the previously published data (Niles et al., 2020) and provide further evidence that when asphalt binder is exposed to sunlight underwater, it results in an increase in water-soluble products. Exposure of water to sunlight leads to the production of highly reactive hydroxyl radicals, which likely contribute to the generation of DOM and can influence the characteristics of water-soluble compounds (Mill et al., 1980; Tai et al., 2004).

The significant shift towards the polar aromatic fraction observed in the underwater configuration indicates above-average oxidation of the sample produced by the experimental conditions of water submersion, which is not typical of most aged asphalt binders (Li et al., 2009). Comparative data from asphalt subjected to accelerated aging

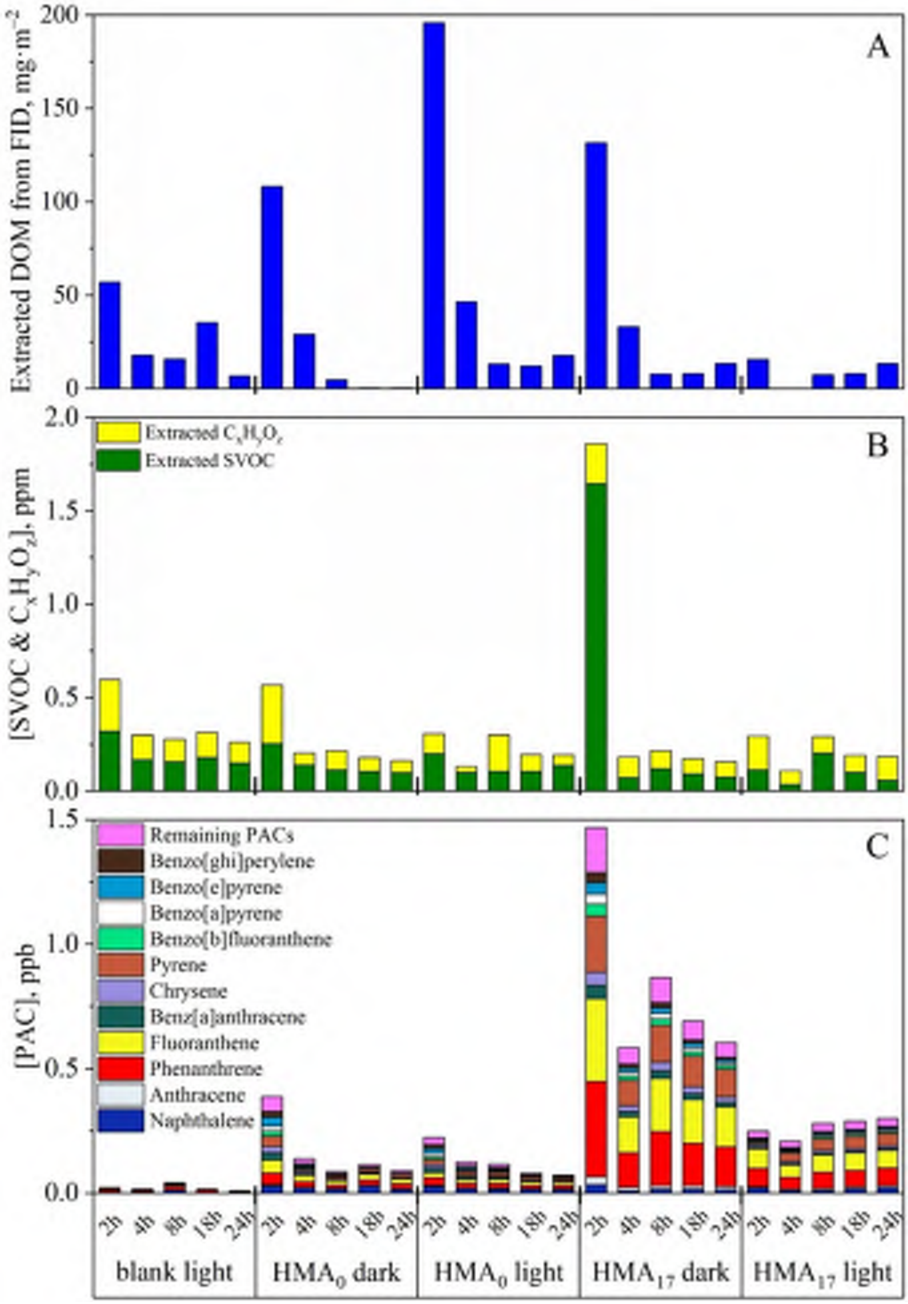

Fig. 4. A) GC/FID results of extracted concentrate given in DOM ($mg \cdot m^{-2}$), from equation (2), for the blank trial light, HMA_0 dark, HMA_0 light, HMA_{17} dark, and HMA_{17} light and B) Semi-quantitative analysis of SVOCs and oxygenated compounds from extracted runoff samples and C) quantified PACs in the extracted runoff.

procedures, traditionally matched to 8-10-year-old pavements using methods like rolling thin film ovens and 20-h pressure aging vessels, show less pronounced shifts in the SARA (Saturates, Aromatics, Resins, and Asphaltenes) fractions (US DOT FHWA, 2021).

Importantly, the resulting thin films of asphalt were determined to be atypical and not representative of field-weathered asphalt surfaces. The unrepresentative asphalt binder suggests the water-soluble compounds produced may undergo a different mechanism of production and thus may represent a different concentration and array of compounds in the leachate.

Conversely, open atmosphere exposure of asphalt binder thin films to simulated sunlight followed by submersion in water produced more representative results, as the asphalt binder maintained its black color and remained tacky to the touch similar to those of asphalt exposed to environmental weathering. This sequential exposure of sunlight and water was determined to better represent the natural environment and allow for more representative production of asphalt pavement leachate/ runoff after exposure to sunlight.

Advanced weathering trials were performed to simulate the production of real-world pavement runoff through a series of simulated sunlight and rainfall events. The trials revealed evidence of the first flush phenomenon, the potential breakdown of hazardous materials with sunlight, the indication of vehicular deposition, and low levels of identifiable compounds. This observed pattern aligns with historical data from Lee et al. (2004) and Todeschini et al. (2019), which demonstrate the presence of a “first flush” phenomenon characterized by significantly higher concentrations of pollutants. These findings emphasize the potential in prioritizing the first flush phenomenon to implement cost-effective stormwater quality control practices.

This work provides insights on how to design future studies related to sunlight exposure on asphalt and the production of water-soluble compounds.

5. Conclusions

Our laboratory experiments assessed the impact of sunlight and water exposure on asphalt binder and pavement surfaces in generating water-soluble compounds found in runoff. We found that the method of exposure (simultaneous or sequential) significantly influenced asphalt binder properties and compound production. Advanced weathering trials demonstrated that the open atmosphere setup yielded results more consistent with real-world pavement runoff samples, highlighting the presence of the first flush phenomenon, potential breakdown of hazardous materials with sunlight exposure, vehicular deposition indications, and low levels of identified compounds. This research provides valuable insights for future studies, emphasizing the importance of investigating the effects of sunlight on water-soluble compounds in runoff using the open atmosphere configuration. To enhance our understanding of the environmental impact of asphalt runoff, larger sample sets are recommended to account for inherent variations in hazardous compounds.

Author contributions

Crawford, Alexis: Methodology, Validation, Formal Analysis, Data Curation, Review, Visualization, Writing, Supervision. Kriech, Douglas: Conceptualization, Methodology, Validation, Analysis, Investigation, Data Curation, Visualization, Writing. Smith, Lisa: Formal Analysis, Data Curation, Review, Writing. Osborn, Linda: Methodology, Validation, Formal Analysis, Review, Writing. Kriech, Anthony: Conceptualization, Methodology, Writing, Review.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2023.118638.

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Review

Review of the impact of stormwater and leaching from pavements on the environment

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ABSTRACT

The intensive growth of roadway infrastructure worldwide leads to growing concerns over the health impacts of stormwater runoff and leachate from roadway materials. This comprehensive review combines various sources of information from the last 30 years of research on the impact of pavement stormwater runoff and leaching on the environment. Of the 95 papers found in library searches, 42 papers add significantly to the body of literature around this subject after review of content and quality.

Normally constructed asphalt and concrete pavements were found to release low levels of contaminants during their life. However, deposition from atmospheric pollutants and materials dispersed by vehicles on pavements do have a measurable impact on the quality of stormwater runoff. These tend to be expressed in initial flush from stormwater events. Reuse of old pavements at end of life tend to have little environmental impact when recycled. However, because of deposition of pollutants over their life these materials can have an impact when used in unbound layers of the pavement or in storage before reuse. Water quality can be improved by porous pavements, which allow infiltration of water and drainage to lower layers, thereby filtering many pollutants in stormwater runoff. The challenge is preventing the high initial pavement porosity from plugging over time. Pavement sealers containing coal tar pitch have high levels of polycyclic aromatic compounds and have been shown to impact aquatic life negatively and produce sediment buildup in ponds and streams. Recent studies have investigated photooxidation of pavements and its influence on leaching, but these remain as laboratory-scale studies. Tables outline materials tested, analytical parameters measured, and methodologies to allow readers to easily identify studies most relevant to their focus on impact of stormwater and leaching from pavements on the environment.

1. Introduction

Society's extensive infrastructure developments have significantly impacted natural drainage and water quality, introducing more pollutants into waterways and groundwater during flooding. Structural and nonstructural approaches have been put into place to mitigate flooding from stormwater including the creation of stormwater runoff ponds, separation of sewage from stormwater collection, and underground storage tunnels which relieve the loading on wastewater treatment facilities during heavy rainfall events. Pavement roadways, runways, and parking areas are significant sources of rapid release stormwater events in urban areas because most are relatively impervious to water. Here, we review the last 30 years of research to understand how various pavement materials impact water quantity and quality entering our waterways and groundwater.

Since the 1970's, with the growing recognition of the environmental movement in the United States, the paving industry looked for ways to reduce, reuse, and recycle materials at the end of their life cycle. Today, asphalt pavements are the largest recycled product in North America by source quantity. These end-of-life materials are both recycled and reused in various ways within the pavement structure. Evaluating the environmental impact of pavements at different stages of their life cycle is a focus of this review.

With a strong impetus to develop a circular economy, many industries outside the usual material suppliers such as construction and demolition (C&D) waste, coal fly ash, plastic, and tires see their byproducts and end-of-life wastes as potential viable alternative components for pavements. We discuss the environmental impacts of these byproducts and waste materials included in pavements at the time of construction and when the pavements containing these materials are

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recycled or reused at the end of their life.

Finally, we examine the source of pollutants; those that come from the pavement systems themselves and contaminants that fall and collect on the pavements over time, which are washed away during rainfall.

2. Methods

Peer-reviewed and widely referenced articles within the literature between 1990 and 2021 were assessed for relevance and quality on the topic of *environmental impact of stormwater runoff and leaching from pavements*. Studies were organized into two categories: pavement stormwater runoff, and pavement leachate. These studies were evaluated separately because they are measured under different conditions and give insight into different endpoints of environmental impact. Other reviews have synthesized historical water quality trends related to highways (Kayhanian et al., 2012) and RAP (Spreadbury et al., 2021). Here we itemize a vast array of materials, analytical parameters, methods used and comments such that users can select those publications that best relate to their specific circumstances related to environmental impacts.

2.1. Pavement stormwater runoff studies

Because of water scarcity in many parts of the world, stormwater is often collected and can be used for potable water when properly purified through desalination (Panagopoulos, 2021a, 2021b) and other techniques. It can also be used in industrial applications. Studies that evaluate stormwater runoff events on roads focus on dissolution of adsorbed compounds off the pavement surface in the event of rainfall. Contaminants that build up on pavement surfaces during dry periods are mobilized and carried away with water runoff. Examples include dust and airborne pollutants, materials dropped from vehicles such as lubricants, tire abrasion or spills from trucks carrying chemicals, sealers, and road debris. These studies are important because stormwater events can lead to flooding and can overwhelm the collection and treatment of pollutants before they enter ditches, sewers, streams, lakes, rivers, oceans, and subsurface groundwater.

Porous pavements (sometimes called permeable pavements) are a relatively recent alternative for stormwater management; these studies are included in this review to glean additional information on the benefits and challenges of these systems (Kayhanian et al., 2019). In 2019, Congress enacted the "Water Infrastructure Improvement Act" encouraging practices that catch water where it falls. Porous pavement is a good example of this, allowing water to quickly pass through and get stored below where it is filtered through soil and slowly released to the environment. The rapid drainage of water through porous pavement also enhances contact between the tire and the pavement during rainfall events, which prevents hydroplaning and improves wet friction stopping distance. As the tire rolls over these wet pavements, a suction is created on the back side of the tire that helps to clean particles out of the pores and maintain porosity.

Stormwater runoff studies generally involve runoff simulations from the field, or laboratory, by running water over a material. These studies investigate desorption of materials off pavement surfaces rather than leaching through dissolution mechanisms. Laboratory studies consist of elution of water through a column loosely packed with a sample, then collection and analysis of the eluate, including suspended particulate. Alternatively, field studies involve collection of water runoff from a pavement, or stockpiles of old recovered pavement materials, including construction debris.

2.2. Pavement leachate studies

Leachate studies focus on extractable compounds into water as it passes through materials (e.g., pavement) under various conditions. Landfills were an early area of concern to the Environmental Protection Agency (EPA) because they released significant pollutants back into the environment over time. As a result, the EPA developed tests that simulate and assess the release of compounds through leaching into the environment, one of which is the toxic characteristic leachability procedure (TCLP). These evaluation concepts came from the Resource Conservation Recovery Act (RCRA) of 1976.

Leachate batch studies discussed herein utilized the standardized TCLP EPA method (instrument shown in Fig. 1) or slight variations of this test. Additionally, several studies compared monolithic leachate to standard TCLP leachate. In a standard EPA TCLP, the sample is crushed to less than 9.5 mm to increase the surface area contact, then tumbled in a 20:1 water-to-sample ratio for 18 h. The water is buffered either slightly acidic, neutral, or basic to assess the impact of pH on the leachability of compounds into the water. Conversely, monolithic leachate testing does not involve crushing the sample, therefore only the sample's outer surface is exposed to water. In this case, if the material tested is impermeable to water, there is a reduced opportunity to extract and solubilize compounds into the water. One important aspect of the TCLP EPA method leachate testing is that the water is filtered to remove particulate, and only compounds that are solubilized into the water are measured.

Lastly, column leachate testing, often measured in bed volumes of water passed through the sample, describes a third type of leachate study. Column leachate testing is employed to analyze water soluble materials within the material, rather than simply removing surface contaminants. Like TCLP, this method also involves water filtration such that only water-soluble compounds are evaluated. Together, these procedures consider dissolution and diffusion processes that contribute to pollution. All three methods of leaching, and the distinctions they raise, are important in understanding potential sources of pollution and mechanisms for entering the water.

2.3. Challenges associated with stormwater runoff and leachate studies

Challenges related to stormwater runoff and leachate studies include *what* to measure and *how* to measure it. Generally, regulatory agencies focus on harmful compounds that may be released into the environment. Quantitative analysis of hazardous substances, such as heavy metals and known toxic compounds, is conducted to determine their concentrations, if present. Comparison to regulatory limits for drinking water, or typical background levels found in residential or industrial settings, determine compliance status. While other materials may be released, only those which are regulated are analyzed. Nonetheless, some studies discussed herein consider non-regulated compounds, and raise questions about their environmental impact. Often, these are emerging pollutants that are found at low levels in the environment, that do not have regulatory limits currently, or known health effects. Examples of such emerging pollutants include antioxidants, such as butylated hydroxytoluene (BHT), and endocrine disruptors (e.g., phthalates). While

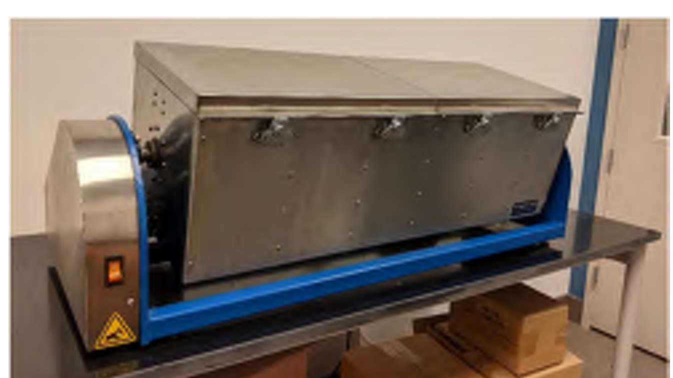

Fig. 1. TCLP instrument used for EPA method.

interpretation of health effects of these non-regulated compounds, if present, may yield more questions than answers, these studies help to direct future research and potential regulations.

Decisions to conduct laboratory versus field testing is another challenge facing researchers. In laboratory settings, variables can be tightly controlled to minimize the impact of confounders present in field studies. However, lack of understanding about potential confounders in the field can lead to misassumptions about the source of the pollutants found. Therefore, well-designed, and well-conducted field studies are invaluable to understanding the impact of confounders on water quality. Validation of laboratory versus field data is ultimately an important and necessary component in understanding water quality issues in the environment.

Over the past 30 years, major strides have been made in analytical instrumentation. Innovation has allowed for better selectivity and sensitivity, therefore improving qualitative and quantitative measurements, greatly advancing our understanding of potential pollutants at low levels in water. Moreover, analysis of complex mixtures, such as asphalt pavements, has been facilitated by advancements in chromatographic separation and mass spectrometry. Altogether, this advancement helps ascertain potential health impacts on plants, animals, and humans. With that in mind, the year these studies were conducted, and the tools used were considered in this review. Studies were evaluated from oldest to most recent within the stormwater runoff and leachate categories.

Strengths and weaknesses in experimental design of the 42 selected studies are critical to determine the importance that individual studies should carry in the literature. Herein, we contemplated the following: Did the study consider confounders or were there validation steps conducted during the research? Are the conclusions reached in agreement with previous published work? If the outcomes run counter to the preexisting body of evidence, were there explanations for the discrepancies? Finally, our conclusions are drawn based on the science presented in these studies, and scientific data gaps identified.

3. Review

3.1. Pavement stormwater studies

Water quality runoff was investigated from stockpiles of salvaged concrete and bituminous paving (Sadecki, 1996). Conducted on behalf of the Minnesota Department of Transportation (DOT) by the Office of Environmental Services, the study investigated stormwater runoff from three stockpiles of reclaimed pavement materials. One was a stockpile of crushed concrete pavement between 4.75 and 19.0 mm. The second contained crushed concrete less than 4.75 mm in size and the third pile was salvaged reclaimed asphalt pavement (RAP). All were placed on a pad with a lined trench collection system for runoff. Metals, total suspended solids (TSS), pH, alkalinity, and chlorides were tested as well as polycyclic aromatic hydrocarbons (PAHs) from the RAP stockpile. The authors conclude that, although there are sediments and leachates emanating from the three stockpiles, the primary concerns were related to TSS, pH, and possible chromium in the concrete runoff. In the RAP stockpiles, no PAHs were detected, alkalinity was neutral, and TSS and metals were lower. The authors recommend that those stockpiles be kept away from environmentally sensitive areas.

Permeable pavements were studied after six years of use (Brattebo and Booth, 2003). Water collected under the permeable pavements showed appreciably improved quality compared to runoff water collected from non-permeable pavements. Concentration of metals, such as copper and zinc, in water were much lower in the filtered underdrain pavements than the nonpermeable pavements. Motor oil was also 89% lower in the permeable sections compared to the impermeable sections in stormwater runoff samples. These results were supported by later studies, which showed the ability of underlying soils to remove pollutants (in porous pavements), through filtration processes or by absorption. These results also suggest that metals released in the stormwater runoff were either in the form of particulate or absorbed onto particulate matter and not water soluble.

Release of organic contaminants from storage of stockpiled RAP in Sweden, were explored both in the field and in the laboratory (Norin and Strömvall, 2004). Drains under the RAP piles allowed water collection at four locations, in concentric rings radiating from the center. Collection closest to the center of the pile had the highest amount of RAP sitting above it, with the lowest liquid-to-solids ratio. Tests were conducted immediately after making the pile, then a year later after collecting water over time. Laboratory studies involved column leaching tests with these same RAP materials. Water was tested for semi-volatile organics, PAHs, and other compounds of interest. Results showed that naphthalene, BHT, and dibutyl phthalate (DBP) an environmentally persistent chemical (Jobling et al., 1995) were the dominant compounds released from the RAP. BHT is a synthetic antioxidant and DBP is a very water-soluble plasticizer; both ubiquitous in the environment, but neither are added to asphalt. Other compounds were detected but could not be identified. Samples taken over time showed larger molecular weight PAHs collected in the water. Laboratory column studies showed lower concentrations of pollutants in the recovered water. The authors conclude that the lower liquid-to-solids ratio for stockpiles collection leads to concentrating the pollutants in the water. Additionally, column studies revealed that the concentration of pollutants decreased significantly after the initial flush, suggesting dissolution rather than diffusion mechanism. The authors conclude that compounds on the surface of the asphalt, including traffic pollution (car and diesel exhaust particulate), crankcase drippings, grease, and spills are the most probable sources of pollutants. Overall, this study emphasizes the importance of conducting more than just laboratory studies and the need for validation with field studies. The best management practices in use today involve constructing RAP piles on impervious paved surfaces with a slope, so that water can be collected and filtered through sand and soil before discharge.

Parking lot sealcoats were studied, and researchers found that the use of coal tar sealants resulted in significant PAH contamination (Mahler et al., 2005). PAH levels in the sediment from stormwater runoff, into ditches and streams, were 65 times higher than unsealed asphalt parking lots. This early study was supported by subsequent studies and has led the ban of coal tar sealants by many municipalities. Coal tar sealers were used widely in military air bases where planes are fueled, primarily to protect asphalt pavements from crankcase drippings and fuel spills. Because coal tar retains its dark color over time, it also was used in parking lots and driveways for aesthetic purposes. Most roads are not sealed with coal tar, so it was limited to special uses and not on streets or highways. One important point is that most of the PAHs are in the form of particulate flaking and have limited solubility in water. However, the particulate PAHs can build up over time in the sediment. Ingestion of these materials cause genotoxic effects to bottom feeding fish and other species, harming them and individuals eating fish taken from these waters.

Stormwater runoff from asphalt, concrete paving bricks (pavers), and crushed stone driveways were studied and evaluated for the amount and quality of runoff through measurement of total particulate, nitrates, and heavy metals (Gilbert and Clausen, 2006). Impermeable asphalt pavement released water the quickest and the source of most pollutants was attributed to materials that collect on their surface during dry periods. Concrete paver bricks collected more water within the lower layers, allowing water to flow between the bricks into the underlying layers of the pavement, instead of quickly shedding the water and pollutants. This water was effectively filtered and was cleaner (less particulates, nitrates, and metals). This study supported the value of using permeable pavers for driveways to improve runoff water quality.

In New Zealand, studies were conducted to better understand stormwater runoff contamination from chip seal asphalt (bitumen) emulsions (Ball et al., 2008). Chip seals are a common and economical pavement type used on rural and low volume roads throughout the world. It involves spraying the asphalt emulsion on the prepared road (Fig. 2) and then quickly dropping stone chips (Fig. 3) over the asphalt emulsion. The emulsion quickly sets through chemical attraction to the aggregate. Evaporation produces an impervious roadway (Fig. 4) with aggregate chips providing friction for traffic. Cationic emulsifiers used to make these asphalt emulsions were determined to be ecotoxic to fish and biodegrade slowly. The study references other works that suggest that many of these emulsifiers are quickly absorbed by soil and do not migrate far from the roadway. Therefore, these emulsions may be safer for rural use than in cities, where there is little soil along the roadway. The study also showed that cured asphalt (after 20 min) was not generally bioavailable and had low water solubility.

An extensive runoff study on Portland cement concrete (PCC) and asphalt pavements, both in laboratory and field settings, was conducted in California (Kayhanian et al., 2009). Ten laboratory-produced pavement types were evaluated that included a variety of compositions used widely in California roads. Additionally, 30 actual pavement sites, in urban and non-urban areas, were monitored for runoff over a three-year period. Both particulate and soluble compounds found in the pavement runoff were tested for metals. The laboratory pavements were artificially aged to simulate 15–18 years in service. Water was passed over the pavement, or through it, as in the case of permeable pavements, to simulate rainfall typical of California. The runoff was collected over an 8-h period, in stainless steel carboys, and tested via inductively coupled plasma-mass spectrometry (ICP-MS). The pH was adjusted at four different pH levels between 4 and 7. The study was also conducted over three different air temperatures of 4, 20 and 45 °C. In laboratory studies, most of the metals originated from corrosion of the metal trays and not from the pavement samples. Nonetheless, chromium was observed in concrete pavements runoff and was determined to come from the Portland cement used, not the aggregate. The authors conclude that chromium in the concrete leaches early in the pavements life and then remains low. Studies like this one are important because the researchers investigated the causes of the anomalies and determined the sources of the metals.

In New Zealand, concentrations in adjacent stream sediments were studied from coal tar and asphalt binders in street pavements to develop a concentration-weighted mixing model to apportion PAHs (Ahrens and Depree, 2010). Based on chemical differences between asphalt and coal tar, the likely sources of PAHs found in aquatics sediments were determined. The challenge is that both asphalt and coal tar look similar physically (viscous black binder) but are very different chemically. Coal tar is produced from pyrolysis tars generated from coal at high temperatures and has significant PAH concentrations. Asphalt binders are produced from the vacuum distillation of crude petroleum and have trace levels of PAHs. Through quantitative analysis of individual PAHs, Ahrens et al. demonstrated that coal tar is the principal source of aquatic PAH pollutants in New Zealand stormwater runoff from pavements.

Fig. 2. Asphalt emulsion sprayed on the prepared road during chip seal process.

Fig. 3. Aggregate stone chips are spread on the freshly sprayed road.

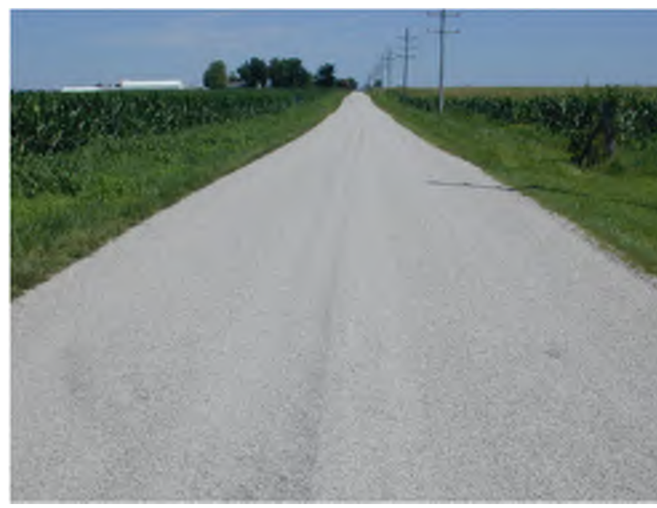

Fig. 4. Newly finished chip seal impervious roadway.

Utilizing stakeholder input and field assessments to select appropriate sampling locations, a study reporting on the sediment of 15 urban stormwater ponds in Minnesota focused on PAHs (Crane, 2014). A suite of 34 PAHs were tested on each sample using US EPA SW-846 method 3550 for an ultrasonic extraction. Forensic analysis was performed to determine the most likely source of PAHs present in the sediment, based on specific ratios of PAHs detected. The study concluded that most of the PAHs present in ponds (67.1%) were the result of particulate from coal tar sealants, used on driveways and parking lots, flaking into runoff. Another 29.5% were attributed to vehicle related sources, and 3.4% from wood combustion particles. Furthermore, differences based on land use, such as industrial versus residential, could not be determined. PAH levels were high enough in three ponds to present risk to benthic invertebrates. Nine ponds exceeded human health risks-based benchmarks that would prompt more expensive disposal of dredging's. The authors recommended banning coal tar sealants.

Permeable pavements' ability to absorb metals and other pollutants was investigated, both in a laboratory setting as well as field pavement, in Xi'an, China (Jiang et al., 2015). The laboratory apparatus was very similar to a column leach study. A porous asphalt pavement (PAP) was used in the study, with a 20% air void mixture to allow water to flow quickly through the permeable pavement. Natural sand was below the PAP to act as a storage and collection zone for water infiltrating into the pavement. Contaminants that buildup on roadways after a 15-day dry spell were collected from three collection sites during a rainfall event. The three sites were selected based on the surrounding businesses that were located along the roadway. All sites were in urban environments where either heavy traffic existed (100,000 vehicles/day), pet and plant markets were along the roadway, or chop houses existed. The runoff water was collected in dust pans and then all three sites were comingled to form a 60-liter sample. Only large debris were filtered out of the samples. Water samples from each site passed through the laboratory produced PAP, then analyzed before entering and after exiting the underlying sand layer. Testing included pH, turbidity, suspended solids (SS), chemical oxygen demand (COD), biological oxygen demand (BOD), ammonia, total nitrogen (TN), hexavalent chromium (Cr(VI)), chloride, zinc, lead, and cadmium. As expected, results showed significant reduction in turbidity and SS due to filtration through the PAP and sand layer. Copper, zinc, and lead were reduced to below limits of detection. Cadmium was reduced some through the filtration and possibly sorption processes. Predictably, pH, COD, BOD, and chlorides were essentially unchanged; this is because there is no mechanism for reducing these organics, except through absorption in the soil layers, which were not evaluated in the study. It was concluded that PAPs can reduce pollutants through filtration and absorption mechanisms in the pavement structure. Nevertheless, long term performance of PAP roadways, from the standpoint of plugging from debris getting carried onto the roadway, was not evaluated. Finally, the actual capacity to absorb heavy metals, and keep them stabilized long-term, was not determined.

Examination of runoff from coal tar sealants determined that particulate from coal tar in runoff induced genotoxicity in fish liver cells and impaired DNA repair capacity a month after placement of the coal tar sealer (Kienzler et al., 2015). Exposure to PAHs and methylated derivatives, N-heterocycles, and other compounds in combination with UVA exposure caused DNA damage even with a 1:100 dilution of runoff. Similar results were found in a follow up study on acute toxicity from coal tar sealed parking lots (Mahler et al., 2015). Ceriodaphnia dubia (cladocerans) and Pimephales promelas (fathead minnows) were used for toxicological tests. This work found a 100% mortality rate from runoff up to 36 days after placement.

Near Gothenburg, Sweden researcher looked at how PAHs partitioned in stormwater runoff collected during a rainfall event from roadway catch basins from two locations (Nielsen et al., 2015). One was on a heavily trafficked roadway and one near a more residential roadway. Samples with the highest TSS contained the highest concentration of PAHs. The filtrated particles (>0.7 μm) contained the highest molecular weight PAHs. Colloidal fractions retained the most PAHs in the 10-nm fraction (smaller particles). The solubilized fraction contained the lowest molecular weight PAHs as hypothesized. This paper conveys the importance of understanding how different PAHs, which have limited solubility in water, can migrate in water and soil. Low molecular weight PAHs are far more mobile than large molecular weight PAHs, which are bound on particles. This study helps determine the most effective mitigation methods for eliminating PAHs in stormwater runoff.

Conducted on Milwaukee streambeds and parking lots, samples of 30 different streambed sediments and six parking lot dusts were analyzed for PAHs (Baldwin et al., 2017). Most observed PAHs (77%) were attributed to be from coal tar sealants. The study found 78% of the streambed samples would cause adverse effects on benthic organisms.

An extensive laboratory study of permeable pavements, and their role on reducing pollutants in stormwater runoff was conducted in Spain (Hernandez-Crespo et al., 2019). Authors investigated potential clogging of these pavements over time, with dust and dirt building up on pavements, and the resulting impact on permeability and filtration capacity of these pavement systems. Consistent with other studies (Brattebo and Booth, 2003; Jiang et al., 2015), permeable pavements were found reduce the quantity of pollutants and improve the quality of water entering the receiving bodies of water. The study recommends improvement to the underlying layers that store and filter the water before releasing it and stresses the importance of cleaning porous pavements to avoid plugging and to maintain high infiltration (porosity) rates.

In California, asphalt, and concrete permeable pavement systems, as well as underdrain designs, were explored in terms of controlling and maintaining good permeability (Kayhanian et al., 2019). It was found, through study of both actual pavements and laboratory simulations, that there is a great potential for permeable pavements in improving stormwater runoff quality. Maintaining these systems, including clogging prevention, which reduces permeability over time, is the main challenge. Regarding water quality, chromium was the only pollutant observed. Variable levels of chromium were detected in concrete pavements shown to come from the cement itself. The source of other pollutants present in pavement runoffs was determined to be from deposition of materials during use, not from the pavement materials themselves.

A field study was conducted in Madison, Wisconsin, to measure stormwater quality performance on lined permeable pavements and included concrete pavers, pervious concrete, and porous asphalt pavements (Selbig et al., 2019). Water, collected from each pavement type, was analyzed for its quantity and quality. The study found that the infiltrated water contained less particulate but soluble compounds, such as deicing salt, generally moved through these systems quickly. Clogging was a significant problem for all pavements evaluated over the 22-month study.

Within the state of Maryland, seven RAP materials were studies to determine if they could be safely used for highway shoulder edge drop-offs (Mijic et al., 2020). The study looked at constant head and batch leaching for metals. This laboratory study revealed that different metals in the RAP are controlled by different mechanisms within the RAP. Calcium, barium, and magnesium are controlled by carbonate content. Aluminum and iron are controlled by oxide and hydroxides present, as well as the pH of the aggregate. Measurable levels of copper and zinc were released early, after a few bed volumes (first flush) of water, then remained low. Under acidic conditions, arsenic is released in its less toxic, pentavalent form (As(V)). The concentrations of all metals released during the water leach tests were below quality limits, except for copper. An explanation was given for the lack of metal leaching from RAP, however, no account for the sources of copper was presented. Finally, low concentrations of PAHs were detected in stormwater. Although this was a laboratory study exclusively, recommendations were made for additional future studies.

Table 1 summarizes the stormwater runoff studies reviewed.

3.2. Pavement leachate studies

Leachability of a new standard Hot Mix Asphalt (HMA) Surface Mixture, used by the Indiana DOT, was determined in accordance with EPA Method SW846-351 TCLP leaching (Kriech, 1990). Heavy metals, volatiles, semi-volatiles, and PAHs on EPA's list of hazardous compounds were analyzed by a US EPA accredited laboratory. Because the aggregate used was a blast furnace slag byproduct from the iron making process, there were concerns about heavy metal leaching. Low levels of chromium (0.1 mg/L) were observed in the leachate water. No volatile or semi-volatile compounds tested were found above the limit of detection, except for trace levels of naphthalene (est. 0.25 μg/L). At the time, these were below regulatory levels.

In 1991, the Illinois EPA (IEPA) investigated the use of old asphalt pavement materials for use as Clean Fill in highway embankments for the Illinois DOT. The primary goal was to determine the safety of these

Table 1
Summary of storm water runoff studies.

References	Material/Location	Testing	Lab	Field	Batch	Other	Column	Comments	Findings/Conclusions
Sadecki (1996)	Crushed concrete pavement and RAP MN, US	Metals, total suspended solids (TSS), pH, alkalinity, and chlorides, PAHs (RAP)	✓					Extensive data collected and statistical summaries provided. Valence of chromium leaching from crushed concrete would allow better estimate of toxicity	Results lead to best practices for managing recycled pavement stockpiles, which are varied and dynamic
Brattebo and Booth, 2003	Permeable pavements - nine test parking stalls WA, US	Tested surface runoff and subsurface infiltrate for metals and organics, Cu, Zn, Motor oil		✓		✓		PP voids allow stormwater to filter through pavement into soil, which helps reduce contaminants in stormwater	Show favorable value using PP although Zn increased compared to 5-yrs earlier. Limitations: not all climate zones included, and dry conditions not studied
Norin and Strömvall (2004)	RAP from two stockpiles, 4 sections each. Stormwater pond and the groundwater samples Sweden	Sixteen PAH by GC/MS	✓	✓			✓	Naphthalene, butylated hydroxytoluene, and dibutyl phthalate were dominant SVOCs	Results demonstrated the importance in following lab studies with real field measurements. SVOCs emitted likely from traffic, with residues of rubber from tires, unburned fuels, or vehicle exhaust
Mahler et al. (2005)	Sealers; Coal tar-based emulsion, asphalt-based emulsion, unsealed asphalt pavement, and unsealed concrete pavement TX, US	13 PAHs by GC/MS, SVOCs		✓		✓		Best indicator of coal tar is PAH ratios - fluoranthene/pyrene, indeno[1,2,3cd] pyrene/benzo[ghi] perylene, benzo[a] pyrene/benzo[e] pyrene	Evidence provided -parking lot sealcoat could be dominant source of PAHs to watersheds
Gilbert and Clausen (2006)	Asphalt, paver, and crushed stone driveways CT, US	TSS, TKN, nitrate-nitrogen, ammonia–nitrogen, total phosphorus (TP), Zn, Pb, Cu		✓		✓		Runoff from asphalt driveways > paver driveways > crushed stone driveways	Runoff from crushed stone driveways were similar in pollutant concentration to runoff from asphalt driveways. Runoff volume higher in asphalt driveways. Paver driveways = lowest concentrations
Ball et al. (2008)	Cationic asphalt emulsions (4) used for chip sealing New Zealand	Daphnia magna acute studies, Algal growth inhibition, Crustacea. pH and dissolved oxygen of each of the test dilutions	✓		✓			Emulsifier - major contributor to the ecotoxicity. ~ 7-fold variation in ecotoxicity observed in 4 emulsions tested	Most ecotoxic component is the emulsifying agent. Different types have varying degrees of biodegradability. Variation in results suggest that a more complete range of chipseal emulsions needs to be assessed
Kayhanian et al. (2009)	Portland cement and asphalt binder materials - 10 specimens with various mix type and binder materials. 30 field runoff samples California	ICP-MS for chromium	✓	✓		✓		Dissolved Cr in leachate- all pavements; variability of Cr based on time (e.g., first flush); impact of pH on Cr leachability	Based on Cr only, pavement materials are not the source in roadway runoff. Results indicate that sources include road-use, land-use sources, or atmospheric deposition
Ahrens and Depree, 2010	nine residential streets situated within the urbanized catchment New Zealand	28 PAHs by GC/MS		✓		✓		Source identification by ratioing PAH signature source; mixing model used to estimate the fraction of coal tar	PAHs from old coal tar pavements are still ongoing and contribute significantly to aquatic environments. Isomer ratios were used to determine if the source of PAHs was asphalt or coal tar. Parking lot

(*continued on next page*)

Table 1 (*continued*)

References	Material/Location	Testing	Lab	Field	Batch	Other	Column	Comments	Findings/Conclusions
									sealcoats and other products that contain coal tar continue to contribute to waterway PAH contamination
Crane (2014)	Sediment from 15 stormwater ponds in the Twin Cities MN, US	carcinogenic PAHs, TOC, black carbon, sum PAH_{34} by GC/MS, TOC, % Moisture		✓		✓		In MN, a statewide CT-sealant ban was enacted 1/1/2014 due to accumulation of PAHs in many urban stormwater ponds. B[a]P equivalents calculated. CMB modeling performed better than source ratios for source apportionment.	CMB8.2 model was used to determine source based on Σ PAH_{34}. Did not correlate with TOC but log did with black carbon, (sorbs PAHs -making them potentially more bioavailable & toxic). CT-sealants - major source of PAHs (67.1%), followed by vehicle emissions (29.5%) and wood combustion (3.4%). Ban of CT-sealants encouraged based on results of study
Jiang et al. (2015)	Permeable asphalt pavement (PAP), Porous asphalt concrete, Open-graded gravel, natural sand, Geotextiles China	Cu, Zn, Pb, Cd, petroleum pollutants (PP), animal & vegetable oil, BOD, COD, ammonia nitrogen, total phosphorus, chloride, and total nitrogen, pH, SS, Turbidity	✓				✓	Lab simulation materials not fully compacted, but real-world samples with smaller air voids would have better filtration effect Decrease in environmental load based on physisorption & porosity of PAP.	Influent and effluent samples tested. PAP is good at removing Cu, Zn, Pb, and Cd. Not as good on petroleum removal, animal & vegetable oil, BOD, COD and NH_4–N. Marginal reduction on total phosphorus, chloride, and total nitrogen. Increased sampling time
Kienzler et al. (2015)	Coal-tar-based (CTB) sealcoat TX, US/France	ΣPAH16, DNA repair—base excision repair activity		✓		✓		Formamido pyrimidine glycosylase (Fpg)-modified comet assay used to assess genotoxicity, which shows CTB sealcoat to have a greater genotoxic potential when combined with UVA.	Exposure to runoff from CTB-sealed pavement & co-exposure to UVA can damage DNA and impair DNA repair capacity, even 36 days after application. Photo-reactivity of PAHs include oxygenated analogues which likely causes increased genotoxicity
Nielsen et al. (2015)	Multiple stormwater grab sampling at 2 Swedish sedimentation facilities and synthetic colloids and nano-sized particles Sweden	Low, medium, and high-molecular weight PAHs, 14 specific PAHs by GC/MS-SIM, TOC, particle size distribution on the Filtrated and Colloidal fractions		✓		✓		Synthetic suspensions and stormwater samples. Looks at how PAHs partitioned in stormwater runoff Need to complement treatment technologies with techniques that reduce dissolved PAHs.	Stormwater highway runoff contained PAHs that were higher in concentration & MW in Filtrated fraction. TSS was implicated and play an important role in mobility. Risks of secondary pollution from the sedimentation -based systems was highlighted.
Baldwin et al. (2017)	stream bed sediment—composed mostly of silt, but also clay and sand and parking lot dust and particulates WI, US	38 parent PAHs and 25 alkylated PAHs, TOC, toxicity tests	✓			✓		Coal tar–based pavement sealant was the primary source of PAHs. Biological endpoints showed adverse effects Toxicity tests showed that if coal tar-sealants were eliminated, significant improvement of	Ratios of parent and alkylated PAHs were used to differentiate between petrogenic (alkylated & low MW) compounds and pyrogenic (parent & high MW) PAHs. Total PAH_{16} concentrations in streambed sediment

(*continued on next page*)

Table 1 (*continued*)

References	Material/Location	Testing	Lab	Field	Batch	Other	Column	Comments	Findings/Conclusions
								stream health would occur. PAH UV-induced toxicity was also shown in this study	was 55.1 mg/kg (0.6–208 mg/kg).
Hernandez-Crespo et al. (2019)	Permeable Pavements (PP) Spain	Suspended solids, organic matter and nutrients, COD, Total N and Total P, pH, TP, COD, TSS, ammonia, nitrates, nitrite	✓			✓		Adequate cleaning of PP in dry conditions is essential	PP have reduced surface runoff, better infiltration and water quality compared to impermeable pavements. Nitrogen infiltrated the most.
Kayhanian et al. (2019)	PP; Rubberized asphalt concrete (AC) open-graded (OG), rubberized AC gap-graded, OGAC and polymer-modified OGAC, terminal-blend modified binder gap-graded, dense-graded AC, & Portland cement concrete CA, US	pH, conductivity, turbidity, hardness as $CaCO_3$, TSS, TDS, PAHs, O&G, COD, TOC, and toxicity	✓			✓		PP discharged overflow is cleaner than surface runoff generated from impermeable pavement A complete configuration in PP was recommended for this Mediterranean climate to retain larger water volumes, the greater the thickness of the gravel layer, the greater the reduction of effluent volume and the lower the environmental load	Hydrographs of high intensity events (22 mm/10 min) under different pollution build-up levels were determined: 1-month (140 g/m_2) and 6-month (840 g/m_2). Reactive barriers in the gravel layers would improve the quality of infiltrated water even more. Nitrates could be reduced by regulating outflows.
Selbig et al. (2019)	3 permeable pavements: permeable interlocking concrete pavers, pervious concrete, and porous asphalt WI, US	TSS, Total & dissolved Phosphorus, *E. coli*, chloride, and metals		✓		✓		Parking lot runoff from the underdrain toward the monitoring chamber Their configuration allowed direct measurement of the quantity and quality of runoff sent from the parking lot to each permeable pavement.	Part III of a 3-phased 22-month study. 84 of 95 runoff events were sampled for water-quality. Seasonal influx of sediment & high chloride from de-icing agents observed. Elevated levels of pH in PC could have fostered metal precipitation. A PP system with impermeable liner successfully removed sediment (~60% efficiency for TSS) and sediment-bound pollutants from runoff from an asphalt parking lot
Mijic et al. (2020)	RAP from 7 roadways MD, US	pH, EC, hydraulic conductivity, Br tracer tests, Al, As, B, Ba, Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, V, Mg, and Zn	✓		✓		✓	Data modeled to simulate effect of natural formation & distance on trace metal conc. within surface waters Variables included fines content, sand-to-gravel ratio, and coefficient of uniformity. CaO and higher asphalt content showed lower dry unit wt and higher HC. Chapuis equation was better predictor of HC values. pH of the leachates varied between 6.69 and 8.50.	RAP & natural aggregates from shoulders showed similar hydraulic conductivity (HC) (varied between 6.9 × 10-3 - 1.1 × 10-3 cm/s). Cu and Zn in 2 RAPs were above EPA WQLs in first flush but quickly fell below. Transport model showed decreased metal concentrations for all RAP samples (<WQLs) after passing through natural formation and decrease more with horizontal distance

TKN = Total Kjeldahl nitrogen, TSS = Total Suspended Solids, TDS = Total Dissolved Solids, PAHs = Polycyclic Aromatic Hydrocarbons, O&G = Oil and Grease, BOD=Biological Oxygen Demand, COD=Chemical Oxygen Demand, TOC = Total Organic Carbon, ICP-MS=Inductively Coupled Plasma-Mass Spectrometry, GC/MS = Gas Chromatography/MS, RAP = Recycled Asphalt Pavement, SVOCs=Semivolatile Organic Compounds, PAP= Permeable Asphalt Pavements PP= Permeable Pavements, CTB=Coal-tar-based sealcoat. WQL = Water Quality Limit.

materials and their potential impact on groundwater. Collaborative efforts between the Illinois Asphalt Pavement Association (IAPA), the Illinois DOT, and HRG allowed collection and testing of six old pavement millings from around the State of Illinois. Leachability was conducted in accordance with EPA TCLP methods. Kriech (1991) conducted the study and reported the finding to IEPA. Leachates were analyzed for heavy metals, semi-volatiles, PAHs, and polychlorinated biphenyls (PCBs). Metals were determined via ICP-AES. Gas chromatography-mass spectrometry (GC-MS) was employed for analysis of organic compounds. Low levels of barium (<0.5 mg/L) in three samples, and 0.52 mg/L of chromium in one sample, were detected. Low levels of a few PAHs (<1 μg/L) were observed, but no semi-volatiles or PCBs were found above the detection limit.

A larger follow-up study ensued after IEPA reviewed the results. In December 1991, IDOT collected samples from two roads in Illinois. One was a PCC pavement and the other was HMA pavement of similar age (1976) built on the same state highway route, receiving the same traffic. Samples were taken transversely across each pavement, as well as longitudinally. This included outside the wheel path, in the wheel path, between the wheel path and from the shoulder of the road. Per IEPA request, leachates were analyzed for PAH and metals only, as previous results showed no evidence for other compounds of concern. Findings were reported to IEPA (Kriech, 1992a). Low levels of barium (mg/kg range) were detected in the HMA pavements (5 out of 6 samples) taken across the pavement; these were below regulatory limits. Through component source testing, barium was determined to originate from the natural limestone aggregates. Trace levels of a few PAHs were detected, with naphthalene present at the highest concentration, but less than 1 μg/L. Interestingly, the concrete pavements also showed low levels of naphthalene (4 out of 6 samples) taken across the pavement. This suggests other sources of confounding materials, dropped on the pavement from traffic, and not related to asphalt which was originally assumed. After this second study, IEPA determined that asphalt and concrete materials from old pavements could be safely used in Clean Fill applications. The State of Illinois enacted this finding into law.

Research was conducted to study leachability of cold mix asphalt used for patch mix and low volume rural roads in the US (Kriech, 1992b). These types of pavements had never previously been studied. Because these asphalts are often made with water-based asphalt emulsions, and sometimes contain solvents such as kerosene or #2 fuel oil at low concentrations, they were evaluated for metals, volatiles, semi-volatiles, and PAHs using EPA's lists for hazardous materials. No metals, volatiles, and semi-volatiles were observed above the limits of detection of 1 mg/L (metals) and 0.1 mg/L (volatiles/semi-volatiles). Low levels (range μg/L) of a few smaller PAHs, up through pyrene, were measured. It was recommended that these cold mix asphalt stockpiles not be stored near bodies of water.

A study for the Texas DOT was conducted to see if any constituents of environmental concern leached from a total of 33 asphalt stockpiles across the state (Southwest Laboratories, 1993). Materials tested included asphalt patch mix for potholes, RAP (Fig. 5) from milling of old roads, asphalt emulsion precoated aggregate for asphalt chip seals, and reclaimed asphalt millings with a rejuvenator added. Testing included TCLP for metals, semi-volatiles, and volatiles including benzene, toluene, ethyl benzene, xylene, and methyl ethyl ketone. Trace metals were detected, including one sample that contained cadmium just above the standard for drinking water of 0.01 mg/L. One sample contained benzene just over the 5 μg/L limit in drinking water. Compounds for all other samples were below the drinking water standards. The study concluded that asphalt materials used in stockpiles in Texas were not a significant environmental concern.

The University of Florida conducted a comprehensive study of leaching characteristics of asphalt road waste assessing RAP from six stockpiles across Florida (Townsend and Brantley, 1998). Leachate samples were tested for volatiles, PAHs, and metals. Both TCLP and column (lysimeter) leaching were conducted. The TCLP leachate water showed no metals above the detection limit. Additionally, no volatiles or PAHs were found above the detection limit. Only one column test showed lead at concentrations above the groundwater guidance of 15 μg/L. Prior use of leaded gasoline was presumed to be the source of lead, as it was observed only in the oldest RAP sample.

Fig. 5. Pile of reclaimed asphalt pavement (RAP).

In Europe, aqueous leaching of PAHs was studied from bitumen and asphalt (Brandt and De Groot, 2001). For clarification, in Europe, a bitumen is equivalent to an asphalt binder in North America, whereas asphalt refers to the pavement type used. Nine different commercially available European asphalt binder samples, and one asphalt pavement made from one of the asphalt binder sources were explored. This Dutch study used a standard Dutch Static 30-h static Leachate Test Method, as well as a Dynamic European Union Leachate, using a Zero Headspace Extraction (ZHE) leachate, which is very similar to US EPA TCLP's ZHE leaching. Both total and leachable testing of PAHs were conducted on all nine neat bitumen samples. Asphalt binders and pavement met all criteria for leachate results that were below potable water standards in European Countries. Leachability within the first 3–6 days was predictive of ultimate total leachability of the samples using the Dutch Standard Method. Brandt's study is important because it considered total PAHs in the asphalt binder as well as the leachable PAHs. Knowing both helps to determine the upper limit of what could potentially be released and the propensity to do so over time. This study found that the total PAHs are low and the propensity to leach are orders of magnitude lower.

Similarly, studies of six paving asphalt binders used widely in North America were investigated. Standard EPA TCLP methods were employed to determine total and leachable PAHs (Kriech et al., 2002). Extraction and analysis of PAHs in a complex material, like asphalt binder, is challenging. Authors considered commonly used methods and determined that the best recoveries were obtained using a micro Dimethylsulfoxide (DMSO) extraction. Total PAHs levels were low, and the leachable levels of PAHs were near or below detectable levels.

Complimentary testing was conducted to explore different analytical methods to quantify metals in neat asphalt binders, as well as leachate from ten different asphalt binders (Kriech et al., 2005). Neutron activation was determined to be the most sensitive for evaluation of neat asphalt binders, however, this instrumentation is not readily available. ICP-MS was the most sensitive for testing leachate water from asphalt. Low concentrations (μg/L) of only aluminum, chromium and titanium were detected in the leachate. Wrapping the sample in foil confounded the aluminum concentration.

Leaching was conducted on RAP, as well as RAP recycled back into new pavements at 10% and 20% levels to investigate both PAHs and heavy metals (Legret et al., 2005). Samples were subjected to standard French leaching procedures and column leaching testing for metals and

PAHs. Results showed that small amounts of RAP materials leached early in contact with water, then decreased quickly to non-detectable levels. New pavements that contained RAP showed very low levels of leachate in water. Because samples were crushed for testing, a correlation between particle size (surface area) and leachable compounds was determined. It was suggested that contaminants collected on the RAP over its life tend to release mostly in the first flush when stored in a stockpile.

Four pavement cores of various ages from Denmark were crushed, extracted for total PAHs, and leached using a 64-day column study (Birgisdottir et al., 2007). A model of determining potential cumulative release was built from comparison of total PAHs to available PAHs leached over time. Three of the four pavements met Danish water quality criteria of less than 1.5 mg/kg of total PAHs. The older pavement was just above the limit at 1.7 mg/kg. It was concluded that leaching is diffusion controlled and only a minor portion of PAHs is released from pavements. Samples for this study were ground to <125 μm, which creates a larger surface area. Compared to the standard EPA TCLP procedure, which crushes the material to less than 9.5 mm, this study presents a significantly more severe process. Results suggest that only the smallest, most water-soluble PAHs, such as naphthalene, follow the diffusion model. Confounding pollutants from a fueling station potentially added to the PAHs but contributions were not determined.

Water quality was investigated of leachate produced from pavement specimens via a controlled laboratory study (Kayhanian et al., 2010). California DOT aimed to determine if pavement materials were contributing sources of pollution in highway runoff. In collaborative efforts with UC Davis, eight asphalt cement and two PCC specimens were tested. A specially designed apparatus and water distribution tray was employed for evaluation of the water quality of the corresponding leachates. Most organic and inorganic chemical constituents were below or near the reporting limit, except for chromium and vanadium from Portland cement in a single cement sample.

Recycled concrete aggregate (RCA) as granular bases under asphalt pavements was studied in Norway (Engelsen et al., 2012). The pavement sections collected water infiltrating through the roadway for four years. Some sections were not covered with asphalt. The collected water was tested for pH and metals. Results showed that asphalt covered sections had a much slower pH change in the granular recycled concrete base than the uncovered section. This suggests that the asphalt covering over the RCA acts as an impermeable barrier, greatly reducing the rate in which leaching occurs in the granular base. The addition of deicing salts may contribute to increased leaching of metals in the granular layers, due to improved diffusion of salts into the surface of RCA. None of the metals which leached exceeded acceptance criteria with groundwater and surface water in Norway at the time of the study.

Similarly, five different RAP samples from five states used as an unbound granular base were studied (Shedivy et al., 2012). TCLP in both deionized water and buffered solution was performed per method protocol. Leachate was analyzed for metals via ICP-OES and PAHs via high performance liquid chromatography (HPLC). Metals were observed below the maximum contaminant level (MCL) for drinking water, whereas PAHs were measured either below or near the level of detection. One note of caution is that the UV/fluorescence HPLC method, required by EPA Method SW-846-8310, has limitations for analysis of complex materials, like asphalt, due to lack of chromatographic resolution. With advances in sensitivity, GC/MS is now preferred due to increased resolution and mass spectral confirmation.

A study was conducted in Spain using a variety of recycled aggregates from construction and demolition wastes (Del Rey et al., 2015). RAP, RCA (Fig. 6), and ceramic materials for use in aggregate applications were studied. European leachate test, consisting of a two-step leaching procedures, as well as column leaching at different solid-to-liquid ratios were conducted. Concentration of metals was determined via ICP-MS. Additionally, atomic absorption (AA) spectroscopy aided in quantitation of total chromium. Hexavalent chromium was also tested via a standard European method. Many of the samples (14 out of 20) tested were classified as non-hazardous. The RAP from asphalt and two RCA concrete samples were considered inert in the testing. However, three out of five samples of the ceramic materials and some of the RCA had high levels of sulfate and chromium. Additional work on the type of chromium, however, found that all the ceramics were Cr(III) not Cr(VI), which is more toxic. It was revealed that at high pH conditions, Cr(VI) is released, but at pH levels below 5, primarily Cr (III) is released. This speciation of the type of leachable chromium is important in assessing environmental risks from C&D waste materials. Chromium entering the environment in any form should be carefully considered in studies.

The effect of carbonation on leaching of RCA in China was reported (Qin and Yang, 2015). Concrete pavements are alkaline; when crushed and used as aggregate, this alkalinity goes through a two-step repeating process. During rainfall cycles the alkali substances are diffused through leaching. During dry spells, the alkali exposed to air is converted to carbonates from absorption of carbon dioxide from the air. Because rainfall is slightly acidic, this carbonated material is dissolved and leached away. It was concluded that when RCA is used as a granular base, the surface layers above the granular base should be impermeable to rainfall to slow this two-step leaching process. This paper aligns with Engelsen (2020) in Norway, which found that covering the RCA with an impermeable pavement slows the process of pH reduction over time, releasing leachable compounds at a slower rate to the environment.

Dynamic leaching of monolithic surface pavements in France were assessed using European CEN/TC 351 standardized tests (Paulus et al., 2016). An evaluation of diffusion of materials mixed with binders used

Fig. 6. Pile of recycled concrete aggregate (RCA).

in pavements was presented. Two surface pavements were evaluated; one a hydraulically (cement) bound material, composed of RCA mixed with limestone aggregate, and 7% hydraulic road binder (cementitious), enriched with activated blast furnace slag, and two, an asphalt surface pavement that met French standards. Pavements were evaluated for permeability to water, with average permeability coefficients (K) of 3.68×10^{-6} m/s and 2.12×10^{-7} m/s, for the cement treated surface and asphalt pavement, respectively. Samples were submerged in a vessel of demineralized water and allowed to soak for various times. After a soak period, the water was drained for testing and replaced over the study period. After 64 days of accumulative testing, leachate water was analyzed for pH, conductivity, sulfate, chloride, and fluoride. It was concluded that asphalt surface pavements have little impact on pH and conductivity and released no elements at the level of detection. Conversely, hydraulically bound (cement stabilized) pavements were alkaline, causing the pH of the water to rise to 10.1. Conductivity was between 150 and 220 μS/cm. Sulfate leached continuously throughout the study at ~40 mg/L, except in the last days. Chloride leached slowly over the first 12 days, then stopped. Fluoride was non-detectable in the samples. No trace metals were detected in the sample. It is surmised that the observed pH change is caused by calcium hydroxide leaching from cement over time. Comparable to studies performed on cement-based materials, sulfate and chloride was determined to leach through a pure diffusion mechanism. Hydraulically bound pavement surface was described as designed to carry 50–150 heavy vehicles per day. In contrast to Qin and Yang (2015), intermediate drying of the pavement, which had been shown to form carbonates, then release in rainwater during wet periods, was not investigated in this study. This highlights the importance of simulating field studies to understand real world conditions. In practice, roads used by vehicles are rarely constantly under water, and investigation of the effects of dry periods is essential for full understanding of leaching from roads.

Batch and column leaching of C&D materials in roadways in Portugal were evaluated from an environmental safety standpoint (Roque et al., 2016). Five recycled materials were used, including crushed concrete (CC), crushed mixed concrete (CMC), reclaimed crushed asphalt pavement millings from asphalt pavement, and a control material of crushed limestone aggregate. Batch leaching was tested via European standards (EN 12457-4 (2002)). Column leaching was performed, as described in the paper, by setting columns outside in the natural environment and collecting the leachate from rainfall events. Analyses included metals testing for cadmium, chromium, lead, copper, nickel by ICP. Sulfate and chloride were tested by ion chromatography (IC). Results of batch leaching found that none of the recycled material had metals detected above the Portuguese Standard as inert materials for a landfill. Levels of sulfate, chloride, and dissolved organic carbon (DOC) were within the regulatory limits for inert materials. The pH of the CC and CMC were 11.99 and 11.29 respectively, which are below the standards for hazardous materials. While Portugal had no requirements for pH, the US limits pH at 12.5 for classifying waste materials that would be hazardous by characteristic. Column leaching studies that evaluated different liquid-to-solid ratios had challenges because rainfall was insufficient to reach the last 10 L/kg sample fraction; it was found to be less aggressive than batch leaching. Metal leaching was determined to be low in all cases, but chloride and sulfate levels were higher in the CC and CMC materials than in batch testing. This may have been caused by limited dilution from low rainfall events during the study.

Recycled aggregate concrete (RAC), which is defined as concrete made from waste materials, was investigated in Spain (Cabrera et al., 2019). RACs can include C&D wastes such as concrete, brick, soil, metal, wood, and glass. Other materials include coal fly ash, biomass bottom ash, plastic, tires, volcanic ash (pozzolanic cement), iron and steel slag, or foundry sand. Aiming towards a circular economy, this study looked at the leaching potential of several waste materials. Percolations tests were determined to be most appropriate for granular unbound materials, whereas diffusion testing is best for monolithic materials. In this comprehensive review of C&D waste materials, the authors advise, based on prior studies, as to when and how to assess each potential waste material. The paper suggests both short- and long-term studies for complete evaluation of these various materials. In one study, C&D wastes from Barcelona were explored where a mixed recycled aggregate was used to make a porous concrete pavement. European Standard NEN 7345 method was employed to assess cumulative leaching emissions. The material was determined to be inert by European Standards, therefore they would be safe for use. The authors recommend performing simulation processes that mimic real world situations. Also, diffusion as well as dissolution studies helps to evaluate the effects of waste materials more fully on the environment. Again, total compounds of concern in the Municipal Solid Waste need to be considered in studies like this one.

Dissolved organic carbon on samples of asphalt binder were explored through different aging tests (Xue et al., 2019). This included thin film oven aging (Fig. 7), which simulates oxidation during the manufacturing of HMA materials through a standard Hot Mix facility. The impact of ultraviolet radiation (for 5 and 10 h) was evaluated also. Finally, some samples were subjected to pressure aging vessel (PAV) aging (Fig. 8) for 20 and 48 h. The PAV test was a simulation of long-term aging in the roadway of 8–10 years. Two leaching procedures were performed on the aged asphalt specimens. An 18-h batch leaching test as well as a 30-, 60-, and 90-day long term leaching was conducted. DOC was determined via GC-MS on the dissolved leachate to look for humic, fulvic, and the remaining hydrophilic compounds. Elemental analysis was also performed to determine carbon, nitrogen, sulfur, and hydrogen. Oxygen was determined by difference. Carbonyl index, which is used often to monitor oxidation of asphalt samples, was determined via Fourier transform infrared (FTIR). The results found that between 3.95 and 23.6 mg/L of DOC was released into the water. Leaching was conducted at different pH levels using acid, base, salt, and demineralized water. It was concluded that aging effects appeared to promote leachability of DOC. This laboratory study looked at the asphalt binder (Fig. 9) alone under simulated aging environment with UV radiation. Follow-up investigations to elucidate aging through UV exposure in field settings are necessary, since that is how these materials are used in practice.

Leachate from an asphalt binder and photoproducts were characterized by Fourier Transform ion cyclotron resonance mass spectrometry, revealing a wide array of highly oxygenated water-soluble hydrocarbons (Niles et al., 2020). Thin films of an asphalt binder were prepared by dissolution in a chlorinated solvent, spread on a glass slide and dried under nitrogen. The dried film was submerged under water (25 °C) and subjected to simulated sunlight or darkness. Concluding that asphalt binders can react with UV light in water to generate oxygenated species, the researchers admit that the study was not necessarily simulative of asphalt in actual use.

This and the study by Xue et al. (2019) reported earlier are the first to

Fig. 7. Thin film oven aging.

Fig. 8. Pressure aging vessel (PAV).

Fig. 9. Samples of asphalt binder.

explore the photooxidation of asphalt on leachability of asphalt.

Samples from three RAP stockpiles in New Jersey were subjected to different conditions with UV radiation and precipitation weathering (Yang et al., 2020). Column leaching tests included a secondary column of soil to evaluate metal attenuation. Trace metal analysis was performed on all the samples and compared to MCL standards for drinking water. One unaged and three different weathering simulations were explored. All samples met MCL standards, however, lead was measurable in two of the samples. The study suggests that the soil type under and around the RAP when used as an unbound granular bases should be considered. Low pH soils (pH < 5) should be avoided beneath unbound RAP that contains trace metals in the leachate such as lead, nickel, and manganese.

In Norway, a review of the leaching performance of recycled aggregates was conducted, including different approaches to evaluating recycled aggregates for various road applications (Engelsen, 2020). This thorough report goes through the appropriate steps in determining the suitability of using recycled aggregates. Starting with leaching properties in relationship to total content chemistry in the neat material, acceptable leachable content, and long-term leaching. By characterizing the recycled material for total chemicals present especially ones that are a concern from a health safety and environmental standpoint a clearer risk determination can be made as to the potential to release compounds over the life of the recycled aggregate.

A review of leaching and total concentration data for RAP was analyzed to estimate the risk (Spreadbury et al., 2021). Trace metals and PAH compounds exist in RAP, from both the primary asphalt pavement binder and aggregate, but external sources appeared to dominate with evidence of leachable contaminants from emissions and wear from vehicles. Except for elevated naphthalene concentrations (Norin and Strömvall, 2004), potential leaching risks cited by authors of the reviewed literature were limited aside from elevated naphthalene concentrations (Norin and Strömvall, 2004). The authors aggregated the existing data as much as possible and modeled these data to estimate the risk. A better understanding of factors that affect RAP leaching (e.g., aggregate/asphalt type, traffic exposure), reflective testing protocols, and robust risk assessment approaches can result in reevaluating best management practices to maximize RAP reuse and ensure the protection of human health and the environment.

4. Discussion

The most often studied compounds of environmental concern by researchers were toxic heavy metals and PAHs due to carcinogenic and genotoxic potential. Findings show that neither metals nor PAHs are released by asphalt or concrete pavements at regulatory levels in stormwater runoff or leachate in numerous studies conducted across four continents. RAP and RCP were frequently studied, both processing these materials once removed from the pavement and then stockpiling them before recycling.

The 18 studies on stormwater runoff explored the impact of different pavement systems and treatments on the quality of stormwater runoff. Sediments near coal tar sealed pavements were shown to have a higher PAH loading. PAHs have very negative impacts on aquatic species. A growing body of evidence has led to the restriction or ban of these coal tar sealers in pavement applications, such as driveways and parking lots. Their aesthetic and fuel resistance values are overshadowed by their potential harm to the environment.

Permeable pavement systems hold great promise for improving stormwater runoff quality and reducing the rate at which stormwater enters receiving bodies of water. This reduces the risk of flooding and improves water quality. However, the ability of these systems to maintain high permeability over time is challenging, since dust and sediments tend to inhibit permeability. Ultimately, clogging of pores negates the benefits of porous pavements. Methods of cleaning these pavements have shown some success in keeping them adequately permeable, but a complete solution is still needed. None of the studies addressed the accumulation of pollutants in the soils under the permeable pavement or the potential for contamination from spills that would be uncontained.

Our assessment of the pavement leachate studies is that leaching both short- and long term are critical in determining the potential to release any materials that could adversely impact water quality. Field studies to validate laboratory studies are recommended to determine realistic levels of leachability as the materials change through their life cycle. These studies help to determine if leaching is diffusion driven or equilibrium driven. The impact of pH and changes in pH over time, depending on the environment and soil that the recycled aggregate is used within, are important to consider. These should all be measured against drinking water and groundwater quality standards; the roadway should not be treated any differently than if these materials were placed in a landfill with limits on leachate. Table 2 summarizes the pavement leaching studies reviewed.

Based on the 42 papers reviewed, the interest in understanding stormwater runoff and leaching of materials from pavements is significant. The studies originated in 10 countries on four different continents and across 8 different US states. Requests for information on pavement

Table 2
Summary of pavement leachate studies.

References	Material	Testing	Lab	Field	Batch	Mono-lith	Column	Comments	Findings/Conclusions
Kriech (1990)	Hot Mix Asphalt (HMA) IN, US	VOCs, SVOCs, PAHs, Metals	✓		✓			AC-20 asphalt cement; aggregate #11 Levi slag, #11 stone, and #24 sand	0.1 mg/L Chromium, no VOCs or SVOCs, trace levels of naphthalene (0.25 μg/L). Below regulatory DW limits.
Kriech (1991)	6 Recycled Asphalt Pavement (RAP) samples IL, US	PCBs, SVOCs, PAHs, and metals	✓		✓			Illinois DOT -concerned about using RAP as clean fill. EPA determined it could be used as a clean fill. One sample high in Ba, Cr, & Pb attributed to surface contamination from crankcase dripping and leaded gasoline.	No PCBs in RAP. Leachate contained no SVOCs, trace levels of naphthalene in 2 of 6 samples and acenaphthene in 1 sample near DL. Other than trace levels of Ba in 4 of the samples, all regulated metals were ND. Sample E, however, contained Cr & Pb.
Kriech (1992a)	Portland Cement Concrete (PCC), Asphalt, and Soil surrounding roadways for use as clean fill IL, US	PAHs, Metals	✓		✓			Performed for Illinois Asphalt Pavement Association. Contiguous sections of Concrete & Asphalt roads – same traffic patterns.	Trace levels of Naphthalene detected in both PCC and asphalt. Barium was detected in all the PCC, but only 2 of the asphalt leachates.
Kriech (1992b)	Cold-Mix Asphalt: Asphalt Emulsion, Cutback Asphalt, Gelled Asphalt IN, US	VOCs, SVOCs, PAHs, Metals	✓		✓			PAH levels detected were similar to HMA & concrete pavements and soils from road shoulders. The aggregate was Indiana Limestone	Barium, naturally found in limestone, leached ~5 ppm, but when coated with asphalt, ND (DL = 2 ppm). No VOC, SVOCs detected other than 2–4 ring PAHs ranging from 0.10 to 8.0 μg/L
Southwestern Lab, 1993	5 types of asphalt, 33 samples, all stockpiled RAP TX, US	Trace metals, VOCs, SVOCs	✓		✓			Synthetic precipitation leaching procedure used by the Texas DOT	Trace levels of metals, VOC, and SVOCs may leach from some asphalt materials, but levels are not present in "environmentally significant amounts"
Townsend and Brantley (1998)	6 different RAP sources FL, US	VOCs, PAHs, Heavy Metals, pH, ORP, DO, Conductivity, TDS, Alkalinity, COD, and NPOC	✓		✓		✓	3 types: TCLP, synthetic precipitation and a deionized water leaching procedures. Batch-scale and leaching columns	Pb in oldest RAP samples at highest conc. (from leaded gasoline and crankcase oil). Batch tests were more dilute than the column test. Overall, RAP would pose minimal leachate risk when used as fill
Brandt and De Groot (2001)	9 asphalt cements, some oxidized, one HMA mix Netherlands	PAHs	✓		✓	✓		Water distribution coefficients calculated for PAHs. Static and dynamic leaching compared. If you know concentration of PAH in the asphalt, you can calculate leachable concentrations from aqueous solubilities	Static leach showed increasing concentrations in first days reaching steady state between 3 and 6 days. Equilibrium concentrations of PAHs stay well below surface water limits
Kriech et al. (2002)	6 paving asphalt cements, 4 roofing asphalt cements IN, US	29 Polycyclic Aromatic Compounds	✓		✓			Paving asphalts selected from the Strategic Highway Research Program Asphalt binder PAC concentrations also reported	Leachates had trace levels of naphthalene and phenanthrene (2 of 29 PACs investigated) in 3 of 10 samples, but < DW levels.
Kriech et al. (2005)	6 paving asphalt cements (same materials used for Kriech et al., 2002) IN, US	Total and leachable metals by neutron activation energy, X-Ray Fluorescence, and ICP-MS	✓		✓			All techniques helpful for results on asphalt cements; ICP-MS best for leachate analysis. Aluminum foil used skewed Al results.	The neat asphalt contains quite a few metals at variable levels based on crude source. All leachable metals (Al, Cr, Ti, Zn) were well below DW standards.
Legret et al. (2005)	RAP vs new conventional asphalt pavement France	PAHs by HPLC, Metals, total hydrocarbons, conductivity, pH, total organic carbon (TOC), chloride & sulfate	✓	✓	✓		✓	Differences between batch leaching tests and column experiments were not very significant. Grain size of the material and the water flow rate influential.	Pollutant leaching is generally weak & below DW standards. RAP sometimes had higher conc. of TH and PAHs but no significant differences. Initial column leaching stages higher but decrease rapidly reaching BDL

(continued on next page)

Table 2 (*continued*)

References	Material	Testing	Lab	Field	Batch	Mono-lith	Column	Comments	Findings/Conclusions
									levels. Core samples from field confirmed results.
Birgisdottir et al. (2007)	Hot mix asphalt drilled from two existing roads –2002 Denmark	PAHs, total and leachable by GC/MS	✓		✓	✓	✓	64-day tank leaching test	Leaching of PAHs was diffusion controlled for 7 PAHs. Bases on calculations, only a small % of PAHs in the asphalt is leached out over 25-years.
Kayhanian et al. (2010)	10 asphalt and concrete pavement specimens, aged & unaged, course & dense graded, modified & unmodified CA, US	Conductivity, Harness, pH, TDS, TSS, COD, DOC, TOC, O&G, TPH, Metals, Nutrients, PAHs, Methylene blue active substances	✓			✓		Special system designed - water flow over pavement specimen and water samples. Nearly all detectable metal concentration was obtained during early experimental stage	Nearly all detected Cr and V concentrations were associated with concrete as compared to asphalt. Most organics and other metals detected in leachates for all pavements were near or below DL.
Engelsen et al. (2012)	Field site, foam glass, RCA, natural aggregates, and RCA + RAP Norway	pH, Al, As, Ca, Cd, Cr, Cu, Mg, Mo, Na, Ni, Pb, S, V and Zn, anions Cl−, Br−, SO4 2− and F−, DOC and DIC. XRD on RCA		✓				Extensive field collected leachate study. Release of major elements as function of time and pH. Simplified method for risk assessment. Mg increased over time due to drop in field pH, while Al and Ca decreased with time.	4-years of monitoring release found that field concentrations of Cd, Ni, Pb and Zn were low. 2 of winter seasons, Cr and Mo levels increased. De-icing salt suspect. Temp influenced amount of infiltration water. Exposure conditions also effected carbonation
Shedivy et al. (2012)	RAP (5 States) + one new asphalt WI, US	PAHs by HPLC, pH, Electrical Conductivity, Oxidation/Reduction Potential, and Metals	✓		✓			Column leaching planned but not yet performed HPLC – Fluorescence was used for PAH analysis	Most PAH concentrations of the RAP leachates were near or < DL and below groundwater intervention values. Metals tested were below MCL concentration in DW, except for Mn & As (Mn 1042.09 μg/L and As 95.66 μg/L from new RAP). Cr and Cd were <DL both in leachate from TCLP fluid and DI water.
Del Rey et al. (2015)	Recycled aggregates from Construction and Demolition Waste (CDW) Spain	Chromium and oxidation states and sulfate	✓				✓	Leached sulfate and Cr were mainly released by bricks and tiles Five unused ceramic materials, two old, crushed concretes and one new mortar.	Chromium and sulfate are focus of study of CDW, which were mainly leached from the ceramic materials (bricks and tiles). Total Cr, Cr (III), Cr (VI) were also tested in the leachates. Generally, Cr (III) was released from bricks and tiles, but recycled aggregates mainly released Cr (VI), which is highly leachable and toxic. Authors encouraged legislation that assess the levels of Cr (VI) in the leachate
Qin and Yang (2015)	Recycled concrete aggregate China	Acid intake and pH drop	✓			✓		Theoretical model the acid intake of in-situ RCA layers Authors point out limitation of the column test, which does not represent the in-situ layer.	Although RCA use is encouraged, when used in road layers, intermittent leaching occurs and neutralizes the alkali of the RCA. Leaching intervals fosters carbonation of the RCA's lingering mortar. Dense pavement on top can block CO_2 to promote carbonation in the RCA, which would slow down the drop in pH of the RCA layer, delaying release of toxic metals influenced by pH.
Paulus et al. (2016)	A hydraulically bound material (concrete) and an	DOC, sulfate, pH, conductivity, and inorganic analyses	✓			✓		Dynamic surface leaching test	Here a 64-day diffusion test was performed on asphalt concretes (AC) and

(*continued on next page*)

Table 2 (*continued*)

References	Material	Testing	Lab	Field	Batch	Mono-lith	Column	Comments	Findings/Conclusions
	asphalt concrete. France								hydraulically bound monoliths. Limited release of toxic constituents in the AC is shown. For the monoliths, ~20,000 mg/ m_2 of sulfate was leached (1 order of magnitude > than chloride diffusion & 2 orders of magnitude > than fluoride.
Roque et al. (2016)	Recycled CDW, crushed (cr) concrete (C), cr mixed C, cr reclaimed (rcld) asphalt pavement (pvt), milled rcld asphalt pvt, natural cr limestone Portugal	Heavy metals, Cl-, SO_4, pH	✓		✓		✓	Batch and lysimeter tests	CDW in civil engineering works required evaluation of leachability. Batch and lysimeter tests were conducted with Cl and SO4 lower in the batch test than lysimeter test and dissolved organic carbon flipped. Batch test results were compared with Portuguese limit values, with the studied CDW samples releasing substances far below these limits.
Cabrera et al. (2019)	Recycled aggregate concrete, and CDW Spain	pH, heavy metals, and other elements, carbonation	✓		✓	✓	✓	Review paper Review includes environmental risks of RAC, the various reactions in CDW (i.e., pH variations on release), the various universal leaching methods, and legal regulations including EPA, WHO, and EU leachate limits. Specific applications should be tested and not just in the laboratory.	With the boom in use of recycled materials, many wastes like fly ash, bottom ash, glass waste, steel slag, tires, and plastics can be used as new raw materials in the manufacture of concrete. Concrete degrades primarily due to decalcinization, attack by sulphates, alkali-carbonate and alkali-silica reactions, attack by sea water or water with chlorides or acid attack; degraded concretes tend to produce more leachate contaminants. Assessment of potential environmental risk, concepts and mechanisms which control release, and leaching characteristics of unbound recycled materials were also discussed.
Xue et al. (2019)	60/80 pen grade asphalt, and SBS modified China	Dissolved Organic Compounds (DOC), fulvic & humic acids, FTIR, XPS, pH	✓		✓			30, 60 and 90 days, pH of leachants significant Thermal (TFOT and PAV aged asphalt binders) aging showed higher depletion rates for long-term leaching periods while UV aging showed higher leachability of DOC during short-term leaching process.	Leachability of DOC from aged asphalt related to aging process (thermal oxidation and UV) and leachants. DOC was time and pH dependent in both short and long-term leaching studies and was significantly influenced by the chemical composition. Aging effects the chemical composition of the asphalt binder and the subsequent leachate. For short-term aged samples, leaching of DOC appeared to be pH-dependent while leaching time was more influential for long-term aging samples. FTIR showed leachates mainly consisted of hydrocarbon and oxygen containing compounds. Fulvic acids and hydrophilic organic carbon fractions were high while a

(*continued on next page*)

Table 2 (*continued*)

References	Material	Testing	Lab	Field	Batch	Mono-lith	Column	Comments	Findings/Conclusions
									small % of humic acids was detected.
Niles et al. (2020)	PG 76-22 Asphalt, polymer modified FL, US	FT-ICR MS Analysis of neat binder and leachate for composition & NPOC	✓		✓			Atypical leaching process and photooxidation HRMS revealed two structural motifs in asphaltenes: an aromatic core with alkyl side chains (island) or several covalently linked aromatic cores (archipelagos). Asphaltenes with high concentration of archipelago motifs were shown to "crack" to produce small water-soluble polyaromatic hydrocarbons (PAHs) through photofragmentation, whereas samples enriched in single-core island motifs were not.	In the study, the 168-h irradiated samples lost 6.56% of the asphalt as water soluble compounds while the water insoluble asphalt fraction increased by 4.1%. Analysis of the leachable compounds using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) high resolution mass spectrometry confirmed the presence of large, oxygenated hydrocarbons. This study concluded that asphalt binders can react with ultraviolet light (UV) in water to generate oxygenated species. The researchers found oxygenated species of Polycyclic Aromatic Compounds (PAC) present in the water.
Yang et al. (2020)	RAP, HMA, and soil NJ, US	Metals		✓	✓		✓	pH important Time-series concentrations of select elements in 6 sets of column experiments showed that Ca, K, Mg, and S leached out fast, i.e., hours to <1 day, in both fresh-HMA and north-RAP samples, and in both RAPs and soil columns showed slower leaching during the 4 days of experiment due to drop in EC of column solutions.	Leachate from a RAP & a soil column were tested for potential release of trace elements. Mn and Ni found in RAP were largely attenuated in the soil. Conclusion: RAP can be used as unbound material except for in acidic (pH < 5) environments. Suspended particulates not included and may add to the environmental load. Unfiltered samples frozen for future study; also plan to include time release and rate studies of trace metals in strong acidic environments.
Engelsen (2020)	Recycled aggregates Norway	pH, Metals,	✓	✓	✓		✓	Globally, C&D waste is one of largest solid waste streams Inorganics in RCA were focus, mainly concrete, bricks, and natural aggregates. External field conditions will influence leachate results due to differences in pH, buffer capacity, water contact, and saturation.	In addition to in-depth chemistry & reaction kinetics of PC, plasticizers, air entrainers, superplasticizers, retarders, accelerators, spray concrete accelerators, & external sources during primary service life were also discussed. RCA with low leachable content is critical to facilitate high material recycling. Simplified dilution models by using the net infiltration were recommended as well as consideration of new formulations of today and in future - accurately determining direct environmental impacts.
Spreadbury et al. (2021)	RAP FL, US	Metals & PAHs	✓	✓	✓		✓	Review with Risk modeling Comparing RAP data is challenging due to variety of approaches. Risk models use different assumptions and calculations, estimates should be followed with field	Factors influencing RAP leachates include pavement materials, external sources, and testing procedures. Review suggests that contamination of underlying or nearby water

(*continued on next page*)

Table 2 (*continued*)

References	Material	Testing	Lab	Field	Batch	Mono-lith	Column	Comments	Findings/Conclusions
								monitoring to ensure human and environmental health	supplies is unlikely from stockpiles of RAP, although on occasion, elevated leached concentrations of certain metals and some PAHs. These elevated RAP leachate data were assessed using US EPA IWEN fate and transport model to estimate dilution and attenuation of select metals and PAHs under typical environmental conditions, reuse, or stockpiling

CDW=Construction and Demolition Waste, HMA=Hot Mix Asphalt EC = Electrical Conductivity.

leaching are frequent, and come from Environmental Regulatory agencies, DOT, Non-Governmental Organizations, as well as private citizens. People want to know if it is safe to pave boat ramps, line fish hatcheries and drinking water ponds with paving materials. Is RAP or RCA safe to use for specific applications and store in stockpiles near water or over drinking water wells? Do pavements diminish water quality near lakes and rivers? These papers help to answer many of these questions. An overall trend shows that both concrete and asphalt pavements, absent of use deposition, appear to have minimal leachate concerns. They tend to not release heavy metals or toxic pollutants when built and constructed using standard road construction materials. New areas of study on the impact of UV (sunlight) will need further research including field validation (Xue et al., 2019; Niles et al., 2020).

Because roads eventually wear out from traffic, aging, and weathering, they eventually reach the end of their life. When these are removed through milling machines, as in the case of asphalt pavements, or demolished in the case of concrete, they should be appropriately managed. Since the 1970's, with the advent of the milling machine, asphalt pavements have been evaluated for recycling into new pavements. Greater than 98% of all pavements are reused or recycled in the US today (Williams et al., 2017). During the process, RAP is stockpiled, crushed, and screened to size, then reincorporated into new paving materials. RAP and reclaimed concrete from pavements were evaluated for alternative reuses in several studies including use of these materials in unbound granular bases underneath new pavements. Results showed that these generally have minimal impact on stormwater runoff and leachate. Old concrete pavements go through a similar process of crushing and separation and removal of reinforcing steel before being made into RCA. In Europe more so than in the US, when buildings are demolished, they are processed to sort concrete, metal, brick, wood, and glass for reuse or recycling. Managing these materials and finding appropriate uses were a focus of some of the papers reviewed. Are they safe and what is an appropriate reuse or recycling use for these materials? Until they are reused or recycled are, they safe for storage in stockpiles? Results show that it depends on what and how they will be used. Typically, if they can go back into their original use there are fewer issues of concern. However, when they are used in new ways such as unbound granular base materials, they need additional study. Understanding their potential to leach in the environment in which they will be placed helps to determine the safety of their new use.

Nontraditional materials from other industries can find their way into widespread use in the construction industry. Millions of tons of fly ash from coal fired power plants have been used for decades safely to replace 25–40% of Portland cement in concrete pavements. These pozzolanic materials have similar performance characteristics to Portland cement concrete over the lifetime of the pavements. Extensive laboratory and field studies have been conducted to fully understand these materials and qualify them through specifications as replacement for Portland cement. There are many benefits for their use in reducing greenhouse gas emissions from cement manufacturing and improved long-term performance in concrete. As other alternative waste materials are considered for pavement, they will need to be properly assessed for their long-term impact on water quality and recyclability.

5. Conclusions

Results of this review can assist state, county, city managers, engineers, and scientists in understanding and managing the impacts of pavement stormwater runoff and leachate by providing easy identification of studies most relevant to specific circumstances based on materials, testing parameters, and methodologies. In general, stormwater runoff and leachate from asphalt pavements and concrete that are normally constructed show low concentrations of pollutants. When adding waste or new additives to asphalt, robust leaching studies should be conducted to ensure encapsulation. Environmental pollutants that fall on or deposit on the pavement during its life can release low levels of PAHs and other pollutants in storage during rainfall events, especially during "first flush" rainfall events.

Concrete pavements that are reclaimed have similar profiles because they also collect similar contaminants over their life. Since concrete pavements have been found to release low levels of chromium from the cement depending on source and pH, it is important to monitor this element. In all cases, reclaimed pavement materials should be managed considering their surroundings to prevent these first flush pollutants from entering the waterways. Best practices include building these stockpiles on impervious bases with slope control to drain first flush through an absorptive media. However, in environmentally sensitive areas where groundwater is impacted easily, there should be proper evaluations when using these materials in place of conventional natural aggregates.

Porous pavements made from asphalt and concrete conclude that simple filtration of the water through the pavement and underlying drainage layers greatly reduces pollutants entering waterways. One challenge is how to keep these pavements from plugging over time. Also, highly water-soluble compounds such as deicing salts tend to pass through these pavements unabated.

Multiple studies found that coal tar pitch sealed pavements have negative impacts on stormwater and leachate. Particulate flakes from these pavement surfaces over time can get carried in stormwater runoff to ponds, lakes and rivers and negatively impact aquatic fish and invertebrates. Evidence suggests that these materials should be restricted from use on pavements.

Laboratory studies have looked at the impact of sunlight and water on formation of photooxidation products in leachate of neat asphalt binders. Further studies in this area are necessary to understand the impacts on the environment under real-world conditions.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Anthony J. Kriech reports financial support was provided by Asphalt Institute.

Heritage Research Group was hired by the Asphalt Institute to perform a comprehensive literature review to determine if compounds that leach from asphalt pavements pose an environmental risk or hazard under typical conditions.

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ADDENDUM 33-4

MCINTYRE, ET AL., 2016

Environmental Science & Technology

Article

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Confirmation of Stormwater Bioretention Treatment Effectiveness Using Molecular Indicators of Cardiovascular Toxicity in Developing Fish

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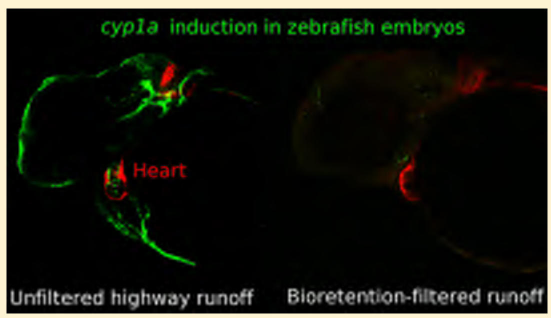
Supporting Information

ABSTRACT: Urban stormwater runoff is a globally significant threat to the ecological integrity of aquatic habitats. Green stormwater infrastructure methods such as bioretention are increasingly used to improve water quality by filtering chemical contaminants that may be harmful to fish and other species. Ubiquitous examples of toxics in runoff from highways and other impervious surfaces include polycyclic aromatic hydrocarbons (PAHs). Certain PAHs are known to cause functional and structural defects in developing fish hearts. Therefore, abnormal heart development in fish can be a sensitive measure of clean water technology effectiveness. Here we use the zebrafish experimental model to assess the effects of untreated runoff on the expression of genes that are classically responsive to contaminant exposures, as well as heart-related genes that may underpin the familiar cardiotoxicity phenotype. Further, we assess the effectiveness of soil bioretention for treating runoff, as measured by prevention of both visible cardiac toxicity and corresponding gene regulation. We find that contaminants in the dissolved phase of runoff (e.g., PAHs) are cardiotoxic and that soil bioretention protects against these harmful effects. Molecular markers were more sensitive than visible toxicity indicators, and several cardiac-related genes show promise as novel tools for evaluating the effectiveness of evolving stormwater mitigation strategies.



INTRODUCTION

Stormwater runoff is a significant source of pollution in urban watersheds. Stormwater transports complex mixtures of chemical contaminants to aquatic habitats,[1] and undiluted runoff can be acutely lethal to fish and aquatic invertebrates within a few hours.[2] More broadly, degraded water quality is an important contributor to the worldwide urban stream syndrome,[3] characterized by losses of aquatic biodiversity and ecological resiliency.[4] In addition to direct species mortality, toxic chemicals can negatively influence ecological processes at the individual, population, and community scales.[5] However, due in part to the chemical complexity of urban runoff, precise cause-and-effect relationships between toxic contaminants and biological decline are still poorly understood.

Despite this uncertainty, efforts to reduce nonpoint source pollution in the urban environment are expanding. These approaches generally fall into two categories. The first includes contaminant source control, such as the ongoing national effort in the United States to limit copper and other metals from motor vehicle brake pads. These phase-outs were initially enacted in Washington and California, in part over concerns related to copper toxicity to Pacific salmon.[6−8] The second approach is implementation of low impact development strategies, also known as green stormwater infrastructure (GSI). Many of these strategies involve bioretention — infiltrating runoff through soil — including porous pavements, green roofs, bioswales, and rain gardens.[9]

Studies on GSI effectiveness have primarily focused on hydrology and contaminant reductions. Recently, effectiveness has been extended to include biological indicators - specifically the health of aquatic species. This is consistent with a core aim

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of urban stormwater management, which is to restore and maintain the environmental health of aquatic communities, as measured by biodiversity, the persistence of pollution-sensitive native taxa, and the health of sentinel species. Recent studies on zebrafish,[10] stream crustaceans and insects,[2] juvenile salmon,[2] and adult salmon[11] have shown that bioretention using simple, inexpensive soil mixtures can substantially reduce the lethal toxicity of untreated stormwater. Species survival is a validation that GSI treatment is working, even when the causal chemical agents have not been identified.[11]

The toxic properties of some contaminants in stormwater are reasonably well-known, and they may not be acutely lethal to aquatic species, particularly as runoff becomes diluted in the environment. Prominent examples are polycyclic aromatic hydrocarbons (PAHs), derived in part from fossil fuels. Motor vehicles are a major source of PAHs in urban watersheds, in the form of oil and grease, tire wear, and combustion engine exhaust. They are ubiquitous in runoff from highways, roads, streets, and parking lots.[12,13] Unlike dissolved metals, which may bind to dissolved organic matter and thereby become less bioavailable,[14] dissolved-phase PAHs are demonstrably available and toxic to aquatic species. This is evident from a range of cardiovascular abnormalities in zebrafish embryos and larvae exposed to highway runoff.[10] Certain PAHs such as phenanthrene and pyrene are known to disrupt normal heart formation and function in fish early life stages.[15,16] The cardiotoxicity syndrome in fish occurs over a gradient of severity, from mild bradycardia to severe arrhythmias, circulatory stasis, and heart failure. Much of our understanding of PAH toxicity to the fish heart results from research on oil spill impacts (e.g., the 1989 Exxon Valdez spill).[17−21] Zebrafish exposed to urban runoff[10] develop a heart failure syndrome that is phenotypically similar to that caused by crude oil.[22]

In the context of PAH toxicity, zebrafish are a promising model for assessing GSI effectiveness, particularly where 1) the biological impacts of untreated urban runoff are more subtle, or 2) the goal is to improve water quality to the extent there are no adverse effects on the most sensitive target organ in fish (e.g., the developing heart).[21] The zebrafish model is also a major biomedical platform for studying the genetic basis for vertebrate heart development.[23] Unlike mice or rats, zebrafish embryos and larvae absorb oxygen across the skin. They can therefore survive circulatory defects to developmental stages that would be lethal in a mammalian model.[24] Intensive research on zebrafish heart development has yielded an abundance of molecular tools unavailable for many other aquatic species.

We have previously shown that untreated stormwater is visibly toxic to zebrafish embryos.[10] In the present study we use these familiar forms of cardiotoxicity as phenotypic anchors[25] to assess the relative sensitivity of molecular indicators for both contaminant exposure and cardiac-related injury. Molecular screens have the potential to be more sensitive, mechanistic, cost-effective, and transferrable to nonmodel fish species.[26] We focused on genes that are classically responsive to contaminant exposures, including cytochrome P450-1A (*cyp1a*; PAHs and other aromatic compounds) and metallothionein-2 (*mt2*; metals). We also examined genes that control zebrafish myofibrillar formation, function, and contractility, including atrial and ventricular myosin heavy chains (*myh6* and *myh7*), cardiac myosin light chains (*myl6* and *myl7*), and atrial and B-type natriuretic peptides (*nppa* and *nppb*). These markers are typically elevated in zebrafish heart failure mutants.[27,28] We applied these tandem visual and molecular analyses to embryos exposed to urban runoff before and after bioinfiltration treatment.

■ METHODS

Highway Runoff Collection. Runoff from an urban highway in Seattle, WA (USA) was collected during three rain events as described in previous studies (May 2012,[10] September 2012,[10] November 2012[11]). Briefly, unfiltered runoff was collected in glass carboys (May and September) or a stainless steel tote (November). Following the earlier experimental designs, the collected May and November runoff samples were directly aliquoted for water chemistry analyses or zebrafish embryo exposures. The September runoff was diluted 40% with collected rainwater to achieve sufficient volume for juvenile salmon exposures and was subsampled after distribution into glass aquaria for that study.[10] Rainwater from this source was not toxic to aquatic animals (not shown). Measured concentrations of conventional water quality parameters, PAHs, and metals for each exposure water are presented in Tables S1 and S2. Analytical chemistry methods are presented elsewhere.[10,11] Pollutant concentrations were highest for the May storm (e.g., 9.1 μg/L total (Σ)PAH), intermediate for the September storm (1.6 μg/L total ΣPAH), and presumably lowest for the November storm (ΣPAH not measured) based on antecedent dry period (Table S1) and relative toxicity to zebrafish (below).

Stormwater Treatment with Bioretention. Runoff from the September event was previously filtered through experimental bioretention columns at the Washington State University stormwater facility in Puyallup, WA (WSU-P).[10] This sample was filtered because it was representative of runoff previously collected from this urban highway, with sufficient volume to test on multiple species.[2,10] Briefly, polyvinyl chloride (PVC) columns (36 × 106 cm) containing 30 cm of gravel overlain by 61 cm of bioretention soil medium (BSM) were used to treat 264 L of highway runoff. Six of the 12 columns were planted with the sedge *Carex flacca*. Influent and effluent waters were held in glass carboys on ice prior to subsampling for water chemistry and zebrafish exposures.

Separation of Dissolved-Phase and Particulate-Associated Contaminant Fractions. The May runoff event was chosen for physical filtration because it had the highest concentration of particulate matter (Table S1), thereby maximizing the likelihood of discerning effects attributable to different fractions. Unfiltered stormwater was sequentially vacuum-filtered using Whatman filter papers with decreasing porosity (100 μm, 40 μm, 0.7 μm) to exclude particles. An equivalent volume of control water (Table S1) was run backward through the filters to resuspend particulates. Zebrafish embryos were exposed for 48 h (see below) to control water, unfiltered runoff, filtrate, or resuspended particulates.

Bioretention Soil Media As a Potential Source of Toxicity. To control for the possibility that the bioretention columns might be a source of toxicity in the treated effluent, the bioretention materials were leached with control water over 5 weeks. Small PVC columns (10.2 cm diameter) were packed with 50 cm (total depth) of either BSM or 34 cm BSM overlying 16 cm gravel. The materials used in the small columns were the same as in the large experimental columns. After filtering 3 L of control water (see below) through each

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column at 25 mL/min, 150 mL aliquots were collected for use in zebrafish exposures.

Zebrafish Exposures. Adult wild-type (AB) zebrafish were maintained and spawned at NOAA's Northwest Fisheries Science Center in control water following standard institutional protocols for animal care and husbandry.[29] Eggs were collected each morning and incubated in control water until 2.5 h postfertilization (hpf). Normally developing embryos were then transferred to glass Petri dishes (15 × 60 mm) and exposed to 10 mL of either control water or highway runoff for 48 h at 28.5 °C. Control water was a 1 g/L solution of Instant Ocean Salt (Spectrum Brands, Blacksburg, VA). Frozen aliquots of runoff were thawed in the morning, prior to each exposure. All waters were brought to room temperature prior to embryo transfer and renewed at 24 h. To maintain environmental realism, the chemistry of runoff samples was not amended prior to or during exposures.

For morphometric analyses, zebrafish were exposed in triplicate (15 embryos/dish). At 48 h, embryos were manually dechorionated, anaesthetized in tricaine methanesulfonate (MS-222), mounted in 3% methylcellulose, and digitally photographed as described previously.[10] For corresponding molecular analyses, embryos were exposed in three or four replicates (25 embryos/dish). At 48 h, embryos were manually dechorionated. Each replicate was placed in a 1.5 mL dolphin tube, frozen in liquid nitrogen, and stored at −80 °C until RNA extraction.

Morphometric and Functional Cardiovascular Analyses. Still and video images were analyzed for heart shape, circulatory function, and vascular integrity. Metrics included pericardial area, common cardinal vein (CCV) area, heart rate, and incidence of cardiovascular abnormalities including atrial regurgitation, yolk sac edema, blood pooling in the CCV, arrhythmia, cranial hemorrhaging, and looping defects. Incomplete looping, a tube-shaped heart, or a collapsed string-heart characterized looping defects. Measurements were made using ImageJ software (www.nih.gov/ij/).

Antibody Staining. Zebrafish embryos were prepared for whole-mount immunofluorescence as previously described.[15,30] Embryos were collected at 48 hpf and fixed overnight at 4 °C in 4% phosphate-buffered paraformaldehyde. Prior to immunofluorescence staining, pigment was bleached from fixed embryos with 20% hydrogen peroxide solution overnight at 4 °C. Primary antibodies included mouse antifish CYP1A monoclonal C10-7 (Biosense Laboratories AS, Bergen, Norway) diluted 1:3000 in blocking solution[31] and antimyosin heavy chain monoclonal MF20 (Developmental Studies Hybridoma Bank, University of Iowa) diluted 1:1000 in blocking solution.[32] Secondary antibodies (Invitrogen-Molecular Probes, Eugene, OR) included AlexaFluor 488 goat antimouse IgG_3 (mAb C10-7) and AlexaFluor 546 goat antimouse IgG_{2b} (MF20) both diluted 1:2000 in blocking solution. Immuno-labeled embryos were stored in 50% glycerol in phosphate-buffered saline at 4 °C until mounted in 3% methylcellulose and imaged using a Zeiss LSM-5 Pascal confocal system with Ar and HeNe lasers (Carl Zeiss Microscopy, Jena, Germany).

Candidate Molecular Indicators of Cardiotoxicity. Six cardiac-specific genes were identified as candidate cardiotoxicity indicators from the literature on zebrafish cardiogenesis and loss-of-function mutations.[23] All have essential roles in cardiogenesis and have been used extensively as indicators of normal heart development following chemical exposure or genetic manipulation.[33] Atrial myosin heavy chain (*myh6*) and ventricular myosin heavy chain (*myh7*) encode atrial- and ventricular-specific myosin heavy chain subunits;[27] cardiac myosin light chains 1 and 2 (*myl6* and *myl7*) encode essential and regulatory cardiac myosin light chains, respectively;[23] and atrial and B-type natriuretic peptides (*nppa* and *nppb*) encode small peptides that regulate homeostatic contractility and respond to cardiac stress.[34] Two genes were used as indicators of exposure to specific groups of contaminants; cytochrome P450-1a (*cyp1a*) encodes a key component of the AhR-mediated PAH metabolism pathway,[35] and metallothionein-2 (*mt2*) is a heavy metal binding protein involved in homeostasis and detoxification of heavy metal ions.[36] These are expressed throughout the body during embryogenesis.[33] A reference gene, WD and tetratricopeptide repeats-1 (*wdtc1*), has uncharacterized localization during early zebrafish development but exhibits no treatment effect ($p > 0.1$).[37]

RNA Extraction, cDNA Synthesis, and Quantitative PCR. Total RNA was extracted from pools of snap-frozen larvae by mechanical homogenization (TissueLyser, Invitrogen Inc.) in TRIzol Reagent (Invitrogen Inc.) and subsequently purified and DNase-treated with DirectZol spin-columns (Zymo Inc.). First strand cDNA was synthesized from 2 μg using High Capacity RNA-to-cDNA Reverse Transcription Kit (random hexamers; Life Technologies Inc.). Quantitative PCR (qPCR) reactions (20 μL) were run in duplicate using Fast SYBR Green chemistry (Applied Biosystems Inc.), 250 nM primer, and 4 ng template on a Viia7 Real-Time qPCR Detection System (Applied Biosystems Inc.) under fast-cycling conditions (95 °C for 2 min, and then 40 cycles at 95 °C for 1 s and 60 °C for 20 s). Information on primers is in Table S3. Dissociation curves were generated as the terminal step of all qPCR reactions to verify single product amplification. All primer pairs demonstrated acceptable efficiency (90−105%).[38] Relative expression data for each gene was normalized to the expression of the unaffected technical reference gene *wdtc1*.[37]

Statistical Analyses. Morphometrics were assessed for each storm event by multivariate general linear model (GLM). For the May filtration fractions, the proportion of zebrafish with looping defects was tested by univariate GLM. Gene expression data were assessed by univariate GLM conducted on $\log_2$-transformed fold-change values.[37] Dunnett posthoc tests compared three or more treatments to controls. All statistics were computed using SPSS v.22 (IBM) with $\alpha = 0.05$.

■ RESULTS

Cardiac Phenotypes. Zebrafish embryos exposed to untreated highway runoff from May and September showed cardiovascular abnormalities including blood pooling in the common cardinal vein (CCV), reduced pericardial:CCV area, and reduced heart rate (bradycardia) (Table 1). Each of these metrics was more severely affected by runoff from the May storm, consistent with higher concentrations of cardiotoxic PAHs. The ∑PAH concentrations in the May and September runoff were 9 μg/L and 1.6 μg/L, respectively (Table S1), and the fraction containing tricyclics with known cardiotoxic potential[15,39,40] comprised 57% and 60% of total PAHs, respectively (Table S2). Although PAH concentrations were not measured for the November event, they were presumably low given the absence of visible developmental defects in exposed embryos (Figure 1).

There was a strong dose−response relationship between PAH concentrations in runoff and the occurrence of cardiac

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Table 1. Cardiac Metrics in Zebrafish Exposed to Runoff Events of Varying Toxicity.[g]

runoff event	% runoff	CCVA[a]	% PCA[b]/ CCVA	heart rate (bpm)	% cardiac abnormal[c]
May	0	20.4 (0.3)	81 ()[d]	178 (10)	7 (4)
May	100	40.1 (1.0)[e]	42 ()[e]	110 (11)[e]	100 (0)[e]
Sep	0	20.8 (0.2)	86 ()	186 (2)	10 (4)
Sep	100	30.2 (2.3)[e]	78 ()[e]	163 (9)[e]	54 (4)[e]
Nov	0	24.7 (1.6)	81 (2)	n.m.[f]	6 (0)
Nov	100	23.6 (2.0)	85 (1)	n.m.[f]	9 (4)

[a]Common cardinal vein area, in pixels. [b]Pericardial area. [c]Percent of individuals per treatment. [d]Empty brackets indicate standard error <0.1. [e]Metrics significantly different from control (0% runoff). [f]n.m. = not measured. [g]Values are mean of triplicates (standard error).

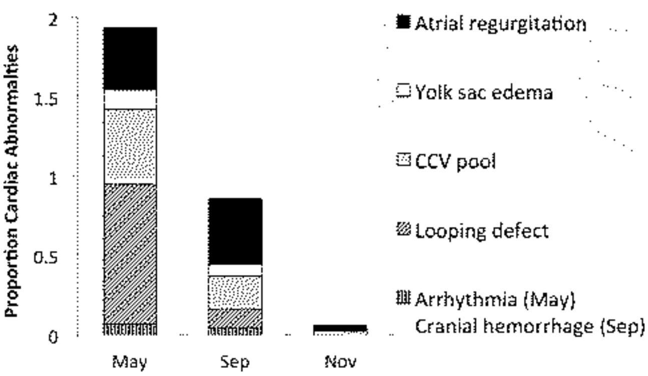

Figure 1. Proportion of individuals with cardiac abnormalities for zebrafish embryos exposed to one of three runoff samples relative to controls. Categories are not mutually exclusive. CCV = common cardinal vein.

abnormalities for the May and September storm events (Figure 1). For the May runoff, looping defects were most prevalent (88% of individuals), followed by atrial regurgitation (39%) and CCV pooling (47%) (Figure 1). For the September runoff, the most prevalent phenotype was atrial regurgitation (41%) followed by CCV pooling (21%) (Figure 1). Stormwater exposure did not significantly increase embryo mortality. Survival for the May controls and runoff-exposed embryos was 96% (SD = 0.04) and 88% (SD = 0.21), respectively, and 100% for controls and exposed treatments in September and November, respectively.

Transcriptional Responses. *Cyp1a* was significantly induced in all three runoff samples (Figure 2). As expected from the relative severity of the cardiac injury phenotype (above), the level of expression was highest for the May runoff, intermediate for the September runoff, and lowest in response to the November runoff. The cardiac-specific markers *nppb*, *myl6*, and *myl7* showed induction corresponding with the presence and severity of the cardiac injury phenotype: May > September > November storm events (Figure 2). Expression of *mt2* and *nppa* was responsive for two or three of the runoff events but did not scale with cardiac phenotypes (Table S4). Expression of *myh6* was induced by the September runoff only. Transcript abundance of *myh7* was unperturbed by exposure to untreated runoff. The most sensitive cardiac gene, *nppb*, showed dose-responsiveness across runoff dilution series for the May and September storm events (Figure S1).

Particulate vs Dissolved-Phase Toxicity. The relatively more toxic May runoff was filtered (0.7 μm) to distinguish between toxicity associated with the particulate versus the

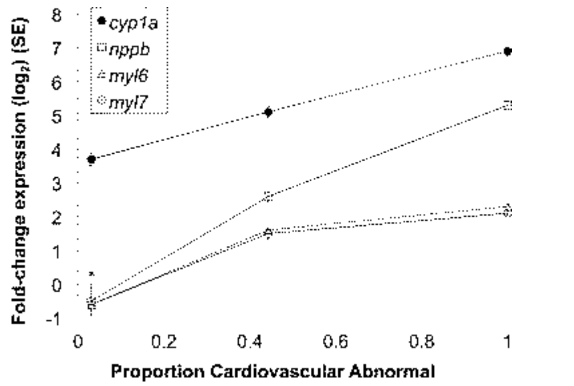

Figure 2. Transcriptional response of four genes correlated with cardiovascular toxicity in zebrafish embryos exposed to three storm events producing three different levels of cardiovascular abnormalities. Fold-changes ($\log_2$) in transcription of each gene are relative to controls for each storm. The asterisk indicates the three cardiac-specific genes that were not significantly different from control expression in the weakest storm (Nov).

dissolved fraction. The filtrate, but not the resuspended particulate fraction, produced the same suite of visible cardiac abnormalities as the unfiltered sample (Figure 3 inset). This extended to the transcriptional level, with significant upregulation of cardiac-specific genes by the unfiltered sample and the filtrate but not the resuspended particulate fraction (Figure 3). Notably, *cyp1a* expression was induced by all three samples (whole, filtrate, particulate), albeit at reduced levels for the particulate fraction. The only cardiac markers that were unresponsive to the filtrate were *nppa* and *myl6*. Although induction of the cardiac genes was reduced in the filtrate relative to the unfiltered sample, the expression of *cyp1a* and *mt2* was essentially unchanged.

Toxicity Reduction in Response to Bioretention Filtration. Following treatment of September runoff with bioretention, the expression of genes indicative of contaminant exposure (*cyp1a* and *mt2*) was reduced relative to unfiltered runoff, with *mt2* expression reduced to control levels (Dunnett posthoc; $p_{\text{Plants}} = 0.63$; $p_{\text{NoPlants}} = 0.81$; Figure 4). Similarly, the post-treatment expression of genes associated with cardiac injury (*nppb*, *myl6*, *myl7*, *myh6*) was reduced to control levels ($p = 0.15-0.33$). Only *cyp1a* and *nppa* (treatment with plants) remained significantly induced in zebrafish exposed to treated stormwater ($p = 0.01-0.02$).

There was no evident immunolabeling of CYP1A in the tissues of unexposed zebrafish in control water (Figure 5A). By contrast, the metabolically protective CYP1A protein was present in the epidermis as well as the cranial, trunk, and endocardial vasculature of zebrafish exposed to unfiltered runoff (Figure 5B, Figure S2). Following bioretention treatment, the immunofluorescent CYP1A signal was reduced in the cranial and trunk vasculature (Figure S2) and lost from the epidermis and the endocardium (Figure 5C,D). The presence or absence of plants in the bioretention columns had no influence on the localization of CYP1A.

Leaching Test. When control water was passed through the bioretention materials, the effluent did not significantly induce the expression of *cyp1a* - one of the genes significantly upregulated in response to highway runoff following bioretention treatment (Table S5). The other molecular indicator induced in post-treatment runoff, *nppa*, showed a small but significant response to bioretention material leachate, but this

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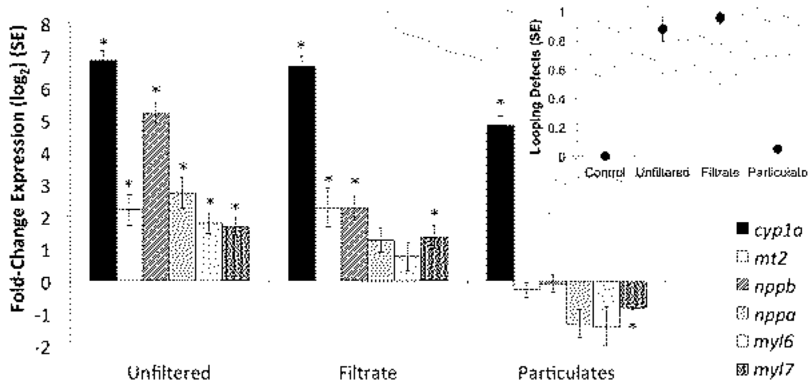

Figure 3. Expression of genes and proportion of individuals with cardiac looping defects (inset) in fractions of May runoff or control water (inset). Fractions were unfiltered whole runoff, filtrate (<0.7 μm) of whole runoff, and resuspended particulates. Gene expression is relative to controls. Error bars are ±1 SE. Asterisks indicate values significantly different from controls.

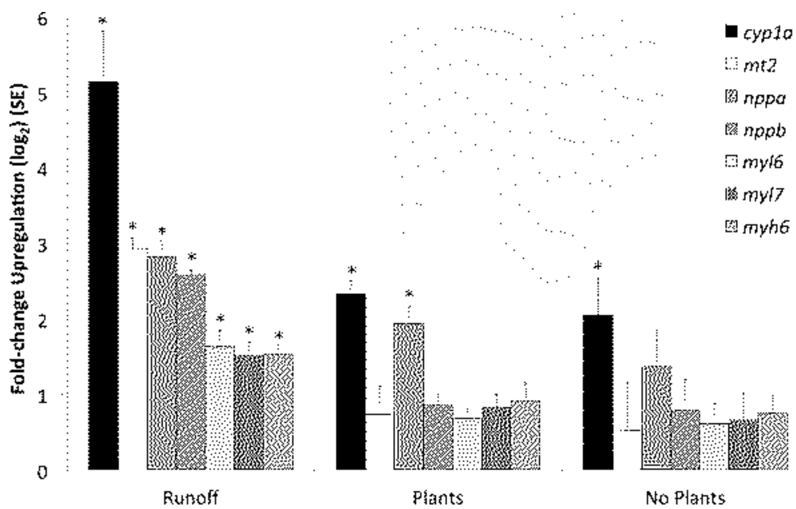

Figure 4. Effect of bioretention treatment on gene expression in zebrafish embryos exposed to unfiltered runoff, runoff filtered with bioretention with plants, or runoff filtered with bioretention without plants. Error bars are ±1 SE. Asterisks indicate significant induction relative to controls.

was lost when the leachate also passed over the gravel drainage layer.

■ DISCUSSION

Fish early life stages are very sensitive to the toxic effects of untreated urban runoff, as evidenced by cardiac-related abnormalities as well as microphthalmia, delayed hatching, and abnormal swim bladder inflation.[10,41] Conversely, embryo-larval fish have the potential to be equally sensitive indicators of clean water technology effectiveness. This is particularly true of zebrafish, given the depth of our understanding of heart development in this species and the availability of molecular markers for both contaminant exposure (e.g., *cyp1a*) and toxicant-induced cardiovascular stress (e.g., *nppb*[28]). Here we confirm this by extending visible cardiac injury to the molecular scale, thereby phenotypically anchoring the transcriptional responses of *nppb*, *myl6*, and *myl7* to cardiac dysfunction. We also show that these indicators of stormwater toxicity are measurably reduced or eliminated when runoff from an urban roadway is treated using a relatively simple and inexpensive bioretention method. Our findings are consistent with cardiotoxic PAHs causing many of the observed developmental defects. However, urban highway runoff is chemically complex, and there may also be a role for as-yet unidentified toxicants.

Bioindicators of contaminant exposure have long been incorporated into environmental monitoring studies.[42] In recent years certain transcriptional biomarkers have shown promise in terms of improved sensitivity and diagnostic accuracy.[43] As anticipated from the presence of PAHs and metals in the stormwater samples in this study, the markers *cyp1a* and *mt2* were highly responsive to untreated highway runoff. Induction of *cyp1a* is a canonical indicator of exposure to PAHs and halogenated aromatic hydrocarbons.[42] In addition to PAHs, urban stormwater likely contains a rich assortment of other, less well characterized, AhR receptor agonists such as azaarenes.[44,45] Our *cyp1a* results are a confirmation that PAHs and/or other aromatic hydrocarbons were bioavailable in the May and September storm events at cardiotoxic concentrations. Consistent with this, the *cyp1a* induction pattern followed the severity of the cardiac injury phenotype, across stormwater samples before and after bioretention treatment.

The induction of *mt2* in response to all three runoff samples may indicate an exposure to metals. However, similar exposures to urban runoff were not sufficient to cause structural toxicity in the form of cell death among mechanoreceptive neurons in the zebrafish lateral line.[10] This was likely due to relatively high DOC levels complexing metals (e.g., copper).[46] The induction of *mt2* may correspond to more subtle functional deficits in peripheral sensory neurons, but this requires further study.

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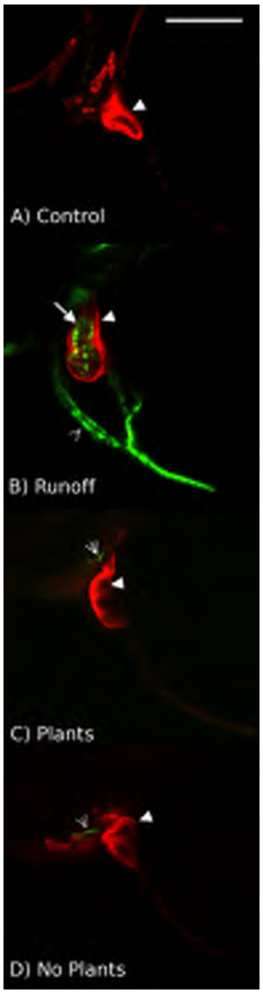

Figure 5. Immunofluorescence in 48 hpf zebrafish exposed throughout development to control water (A), Sep highway runoff (B), and Sep runoff filtered through soil bioretention with plants (C) or without plants (D). Red staining (MF20) marks myosin heavy chain of the heart and skeletal muscles. Green staining (C10−70) marks CYP1A protein expression. Filled arrow heads point to myocardium (heart), the stalked arrow shows endocardial CYP induction (B), and the open arrow heads show CYP induction in the epidermis (B) and aortic arch (C, D). Scale bar is 50 μm.

Although responsive to metals exposure, *mt2* can also be induced by agonists of the glucocorticoid receptor (GR).[42] The coinduction of AhR and GR has recently been shown to synergistically induce *mt2*.[47]

The most consistent cardiac abnormalities observed here in response to untreated stormwater were atrial regurgitation and associated pooling of blood in the common cardinal vein. The zebrafish heart is undergoing morphogenesis at 24 hpf, transitioning from a tube into a looped and expanded heart at 48 hpf.[23] At 48 hpf, blood flows anteriorly from the sinus venosus into the right-sided atrium, the left-sided ventricle, and is pumped out via the bulbus arteriosus. Retrograde blood flow is prevented during myocardial contraction by the compression of the endocardial cushions, precursors of the atrioventricular valve at the point of constriction between the two chambers.[48] The increase in atrial regurgitation among stormwater-exposed zebrafish at 48 hpf is likely due to a combination of looping and contractility defects, as observed following crude oil exposure in zebrafish.[30,49] Reduced myocardial contractility is a consequence of PAHs inhibiting excitation-contraction coupling in individual cardiomyocytes, thereby reducing the internal calcium cycling necessary for rhythmic heart muscle cell shortening.[50] For fish that survive transient stormwater exposures during cardiac morphogenesis, these types of adverse effects on heart form and function will likely lead to permanent changes in heart shape and physiological performance at later life stages, as previously shown for zebrafish embryos exposed to PAHs derived from crude oil.[51]

Relative to other sources of PAH mixtures in the aquatic environment (e.g., oil spills), the mixture dynamics associated with PAHs in highway runoff are not well understood. Developmental cardiotoxicity was evident following exposures to measured $\sum$PAH concentrations of 9 and 1.6 μg/L for the May and September storms, respectively, but these levels are lower than those in crude oil that cause proportionally similar rates of edema in zebrafish. This suggests there may be interactions among PAH compounds within the stormwater mixture to enhance toxicity relative to crude oil on a $\sum$PAH basis. Determining the underlying mechanisms will be challenging. Highway runoff is more complex than chemical mixtures in crude oil. Runoff contains lower molecular weight PAHs that are cardiotoxic but weak *cyp1a* inducers (phenanthrene, dibenzothiophene), pyrogenic higher molecular weight PAHs that are cardiotoxic and strong *cyp1a* inducers (benzo[a]pyrene, benzo[k]fluoranthene), and noncardiotoxic yet strong *cyp1a* inducers (chrysene). Moreover, metabolic interactions among these different PAHs may be both dependent and independent of AhR activation. Notably, however, the absence of myocardial CYP1A labeling observed here is consistent with AhR-independent cardiotoxicity driven by lower molecular weight PAHs (e.g, phenanthrenes).[30] Nevertheless, the zebrafish experimental platform has proven advantageous for studying synergistic PAH cardiotoxicity,[52] as a precursor to validating novel mechanisms in wild fish.

The response magnitude of several cardiac genes corresponded to the severity of visible cardiac abnormalities in the following order: *nppb* > *myl6* > *myl7*. Robust *nppb* induction was expected because B-type natriuretic peptide is an established molecular indicator of poor cardiac function in mammals[53] and fish.[28,54] The increasing *nppb* signal in zebrafish embryos exposed to stormwater with relatively higher levels of measured PAH concentrations is consistent with tricyclic PAHs reducing cardiac contractility via pharmacological channel blockade.[50] The *myl6* and *myl7* transcripts encode the cardiac-specific essential and regulatory myosin light chains required for proper sarcomere formation and contractility, and secondarily, chamber looping,[55] and their increased expression likely represents a compensatory response.

Bioretention Effectiveness. Treating the September highway runoff with bioretention protected against most visible forms of toxicity to early life stage zebrafish,[10] including cardiac dysfunction. Our findings here suggest that the loss of cardiotoxicity is primarily attributable to the removal of PAHs (or other AhR agonists), as indicated by a reduction in CYP1A induction at both mRNA and protein levels in fish exposed to post-treatment stormwater. While bioretention materials are expected to retain contaminant-associated particulates, our results comparing the filtrate and particulate fractions of highway runoff indicate that bioretention also removes bioavailable cardiotoxic PAHs from the dissolved phase. This finding agrees with earlier analytical chemistry, showing >90%

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reduction in total PAH concentrations following bioretention treatment.[10,11]

The molecular marker for PAH metabolism (*cyp1a*) was more sensitive than visible indicators of cardiotoxicity after bioretention treatment. The induction of cardiac-specific genes in zebrafish embryos in bioretention-treated runoff was reduced to that of controls, consistent with the reversal of the overt cardiac injury phenotype. However, the expression levels of *cyp1a* did not return to that of controls. While not necessarily evidence for an adverse health outcome in developing fish, this suggests that low levels of PAHs passed through the columns. Consistent with this, juvenile coho salmon exposed to the September bioretention-treated stormwater in a previous study had slight but significant increases in PAH metabolites in their bile compared to controls,[2] despite an absence of measurable PAH concentrations in water (i.e., below analytical detection limits).[10]

Control water passed through the bioretention media did not induce *cyp1a* in zebrafish embryos but did cause a slight induction of *nppa*. The control leachate was considerably more alkaline relative to the influent embryo medium. Changes in osmolarity are known to influence *nppa* expression,[56] and this may lessen the usefulness of this gene as a specific biomarker for cardiac injury under environmental conditions where osmolarity fluctuates.

Finally, while the cardiotoxicity phenotype caused by untreated runoff is very similar to that associated with crude oil exposure in zebrafish,[49] and there is relative enrichment of tricyclic PAHs (e.g., phenanthrene) in both, stormwater and crude oils are chemically complex. There are likely components of each that modulate gene expression in ways that contribute to subtle phenotypic differences at the visual scale—for example, more frequent atrial regurgitation in the hearts of zebrafish exposed to urban runoff. The developmental toxicity of many chemicals present in stormwater, including alkenes (e.g., alkylated oxyphenols), oxygenated PAHs (e.g., fluorenone), nitrated PAHs (e.g., nitropyrene), and azaarenes (e.g., quinolines), has not been characterized. A future zebrafish screen using model compounds in the aforementioned groups could reveal novel contributors to the untreated stormwater toxicity syndrome, much as the tricyclic PAHs were previously shown to underlie consistent features of the crude oil syndrome in embryo-larval fish.[15]

In summary, untreated highway runoff caused cardiac looping defects and atrial regurgitation in zebrafish embryos. The severity of these visible defects corresponded with the expression of the detoxification enzyme *cyp1a*, as well as genes associated with defective cardiac contractility. These effects appear to be driven primarily by contaminants (e.g., PAHs) in the dissolved phase. As a model green stormwater infrastructure technology, infiltration through bioretention significantly reduced *cyp1a* induction and protected zebrafish embryos from overt cardiotoxicity. While there was no corresponding injury phenotype, zebrafish exposed to bioretention-treated runoff still showed elevated levels of expression of some genes, most notably *cyp1a*. This indicates that zebrafish embryos are transcriptionally responsive to contaminants in treated stormwater at concentrations that may be near or below detection limits for conventional analytical chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04786.

> Tables summarizing analytical chemistry (Tables S1, S2), describing primers (Table S3), describing changes in transcript abundance of all candidate genes relative to control expression for zebrafish exposed for 48 h to runoff from each storm event (Table S4), and describing the isolated effect of clean water leachate on transcriptional responses (Table S5), figure showing the effect of dilutions of the May and September runoff on cardiac-related morphometric and transcriptional response of *nppb* (Figure S1), and an expanded figure showing CYP1A tissue expression for zebrafish exposed 48 h to Sep runoff unfiltered or filtered with bioretention with and without plants (Figure S2) (PDF).

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Notes

The authors declare no competing financial interest.

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Agency

Assessment of Water Quality of Runoff from Sealed Asphalt Surfaces

SCIENCE

Office of Research and Development
National Risk Management Research Laboratory - Water Supply and Water Resources Division

Assessment of Water Quality of Runoff from Sealed Asphalt Surfaces

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Abstract

This report discusses the results of runoff tests from recently sealed asphalt surfaces conducted at the U.S. Environmental Protection Agency's (EPA) Urban Watershed Research Facility (UWRF) in Edison, New Jersey. Both bench-scale panels and full-scale test plots were evaluated. Full-scale tests were performed on an asphalt portion of the UWRF parking lot; no parking was allowed on any of the surfaces to minimize cross-contamination from other sources. A variety of water quality analyses of the runoff were conducted. The whole water sample was analyzed rather than analyzing the particle and dissolved phases separately. The primary measurement was polycyclic aromatic hydrocarbons (PAHs). Sealants applied to asphalt surfaces leached measurable quantities of PAHs. Results indicated that the time from the initial sealant application is a major factor in observed PAH concentration in runoff. The highest PAH concentrations measured were in initial runoff samples where sampling was performed twenty-four hours after application of sealants to the asphalt surface. Toxicity screening assays produced inconclusive data due to matrix effects of prepared samples.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of a congressional request. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally C. Gutierrez, Director
National Risk Management Research Laboratory

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Acronyms and Abbreviations

APWA	= American Public Works Association
AR	= Annual Runoff
BOD	= Biochemical Oxygen Demand
CF	= Correction Factor
COD	= Chemical Oxygen Demand
C_{PAH}	= Polycyclic Aromatic Hydrocarbon Concentration
CWA	= Clean Water Act
DO	= Dissolved Oxygen
EPA	= United States Environmental Protection Agency
K_{OW}	= Octanol Water Partitioning Coefficient
NPDES	= National Pollutant Discharge Elimination System
NPS	= Nonpoint Source
NRMRL	= National Risk Management Research Laboratory
NURP	= Nationwide Urban Runoff Program
ORD	= Office of Research and Development
ORISE	= Oak Ridge Institute of Science and Education
PAH	= Polycyclic Aromatic Hydrocarbon
PEC	= Probable Effect Concentration
SC	= Stormwater Center (of University of New Hampshire)
SM	= Standard Methods
SOP	= Standard Operating Procedure
TMDL	= Total Maximum Daily Load
TOC	= Total Organic Carbon
TPAH	= Total Polycyclic Aromatic Hydrocarbons
TSS	= Total Suspended Solids
U.S.	= United States
USGS	= U.S. Geological Survey
UWRF	= Urban Watershed Research Facility
VSS	= Volatile Suspended Solids
WQS	= Water Quality Standards
WWF	= Wet-Weather Flows

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Executive Summary

Background

Determining the impact of wet-weather discharges on receiving water quality remains an elusive goal given the various potential pollutants in the urban environment and the common practice for many storm drainage systems to discharge to the nearest receiving water with little or no treatment. In general, stormwater runoff from roads and parking lots has been shown to have high levels of pollutants and has been documented to be toxic to both freshwater and marine organisms. This document could be used to assist in the determination of the potential impact to receiving water quality from stormwater runoff in urban areas due to asphalt sealant use.

Sealants as Potential Sources of Water Quality Impairments

Asphalt pavement sealants are applied to parking lots and driveways to enhance appearance and protect surfaces and are widely used in commercial and residential products. Due to the tendency of these coatings to wear over time, manufacturers recommend reapplication of sealants to surfaces every two to three years. There are two types of sealcoats generally used in the U.S. today: asphalt emulsion and coal tar emulsion. Coal tar has been shown to have a detrimental effect on the overall health of a variety of aquatic organisms. Recent literature has suggested that coal tar-based asphalt sealants have impacted survival and development of amphibians, embryo and larval mortality in fish, and growth and biodiversity of macroinvertebrates and benthic phytoplankton. The primary components of coal tar that are presumably responsible for these toxic effects are polycyclic aromatic hydrocarbons (PAHs).

Why EPA?

This research project was conducted by the Water Supply and Water Resources Division of the Office of Research and Development's National Risk Management Research Laboratory. PARS Environmental Inc., an on-site contractor at EPA's Urban Watershed Research Facility (UWRF) in Edison, New Jersey, performed sampling, analysis and logistical support. The UWRF had an existing unsealed asphalt parking lot specifically designed to assist scientists and engineers in the collection of runoff. The parking lot was modified specifically for this project so that separate sections of runoff from test plots could be collected concurrently.

Analysis

The primary analyses conducted in this study were for the PAH content of the collected samples. A range of other water quality constituents were also measured. Toxicity analysis through the use of a Microtox® screening unit was also performed, though the results of these analyses were inconclusive due to matrix effects of the prepared samples. These toxicity results are therefore not reported.

Experimental Design

The project was initiated with the development of bench-scale testing. The project culminated with a full-scale, six-month study of three asphalt test plots with different or no surface treatments: coal tar emulsion sealant, asphalt emulsion sealant, and an unsealed control. Both the bench- and full-scale studies were tested over a time period of 1 to 30 days after application of sealants. The full-scale study had additional testing of test surfaces at six months.

Results

The products examined in this study are a subset of the products available on the market and do not represent all products. Asphalt emulsion- and coal tar emulsion-based sealcoat products are the most widely used in the U.S. Coal tar products have PAH levels about 1,000 times higher than the asphalt sealcoat (Mahler et al., 2005). Precise national use is not known; however, USGS data suggest that asphalt-based sealcoat is more commonly used in the western U.S. and coal tar-based sealcoat use is more common in the other regions of the U.S. (Van Metre et al., 2005). There may be differences in water quality parameters observed in the runoff from surfaces of other sealants; therefore, the results herein cannot be translated across sealant product lines.

Results of the full-scale study indicate that PAHs are present in the runoff of surfaces coated with sealants. The PAH concentrations in the runoff were observed to decrease with time. When focusing on samples immediately after recommended curing time (24 hrs), there are correspondingly higher concentrations of PAHs. The asphalt emulsion and unsealed control surfaces did not contain concentrations of PAHs of the same order of magnitude as found in the runoff from the coal tar sealant plot.

Conclusions and Recommendations

PAHs were observed in the runoff from all three testing surfaces. The findings were consistent between the full-scale and the bench scale studies.

- The coal tar-sealed surfaces released 100 to 1000 times more PAHs to the runoff than the other surfaces. This release of PAHs from the surface to the runoff diminished with time. There was a measurable shift in the individual PAH components in the runoff, with fewer lower molecular weight PAHs observed in the runoff over time.

- The initial wetting after sealing may be the most crucial flush of PAHs into the environment.

- Additional testing is warranted on a representative variety of asphalt emulsion products. Even though low levels of PAH were observed in relation to the coal tar sealant runoff, increased total organic carbon (TOC) and chemical oxygen demand (COD) loadings were observed for the initial runoff samples collected, indicating an increased organic chemical load being released.

- Measurement of COD and TOC water quality parameters cannot be used as surrogates to identify potential release of PAHs from sealed surfaces.

- It is recommended that toxicity assays be performed with a variety of representative organisms (invertebrates, amphibians, fish, etc.) using standard procedures. This would require significant technical and financial resources. This more intensive toxicity testing is needed in order to more fully understand the effects of exposure to runoff from sealed asphalt surfaces. The literature lacks an in-depth study of sealant runoff examining both coal tar sealants or asphalt emulsion alternatives and the potential for acute toxicity, or lack thereof, to aquatic organisms in the water.

Chapter 1 Introduction

Background

The Clean Water Act (CWA) is the Nation's primary mechanism for protecting and improving water quality with the broad purpose of the CWA "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters," (33 U.S.C § 1251 (a)). Several sections of the CWA apply to urban runoff, both as point and nonpoint sources of pollution.

Point sources, including municipal and industrial stormwater discharges, are controlled by the National Pollution Discharge Elimination Program (NPDES) permits (33 U.S.C § 1342 (p)). Because of the difficulty in identifying specific origins of pollution associated with nonpoint sources (NPS), mitigation of associated pollution is approached with management strategies. The CWA allows for both environmental quality and technology-based (treatment processes and best management practices) approaches for controlling water pollution. States are required to develop and adopt water quality standards (WQS) that specify the designated uses of each water body, and determine specific criteria deemed necessary to protect or achieve those designated uses. The CWA requires states to develop and implement WQS in accordance with EPA regulations and guidance.

Implementation of water quality programs at the federal, state, and local levels, along with accompanying research, that address both point and nonpoint sources continue to evolve with the cumulative knowledge of the impacts of urban development. Stormwater runoff from impervious surfaces in urban areas has emerged as a potential threat to water quality. Pollution problems stemming from these wet-weather flows (WWFs) are a challenge throughout the Nation. National estimates have projected costs for WWF pollution abatement in the tens of billions of dollars (APWA, 1992).

A variety of physical, chemical, and biological processes influence the type and the degree of impacts that urban WWFs can have on receiving-water capacity and aquatic ecosystems by directly or indirectly affecting the concentration of pollutants and organisms present (House et al., 1993). These processes include transport (by advection or diffusion), sedimentation, erosion, sorption, pH impacts, gas exchange, oxygen demanding pollutants, die-off and growth of organisms, bio-accumulation of contaminants in the food-chain, and species selection (Lijklema et al., 1993). Pratt et al. (1981) identified two plausible means, immediate and long-term, in which urban runoff can impact receiving waters and the aquatic ecosystems. Discharging untreated urban runoff containing solids, toxins, nutrients, and organic oxygen-demanding pollutants can have an immediate, i.e., “shock-loading effect,” on receiving waters. The second long-term effect is the accumulation of contaminated sediments or the contamination of existing sediments. During a storm event, the depletion of oxygen in receiving water due to organic loading may occur; however, it is more likely to be a problem several days later due to increased sediment oxygen demand (Pitt 1979).

Runoff from roads and parking lots has been shown to contain high levels of pollutants and to be toxic to both freshwater and marine organisms (Maltby et al., 1995; Pitt et al., 1995; Herricks et al., 1997; and Greenstein et al., 2004). Runoff has been known to be toxic for some time. Specifically, Spiegel et al. (1984) sampled receiving water and rainwater, combined sewage, and urban runoff. Nineteen out of 85 samples induced a detectable mutagenic response as measured by the Ames test (Ames, 1971). The greatest response was due to urban runoff as nine (47%) of these 19 samples were urban stormwater runoff, with 57% of these samples indicating a strong dose-related response. However, there is limited research on the potential toxicity of the individual components of pollution in urban stormwater runoff.

One component of urban stormwater runoff that may contribute to toxic loading is runoff from surfaces coated with asphalt sealants, which are often applied to asphalt parking lots and driveways for aesthetic purposes. Runoff from sealed surfaces may contain polycyclic aromatic hydrocarbons (PAHs). PAHs are a large class of typically hydrophobic compounds with varying degrees of water solubility (Aldstadt et al., 2002). PAHs are known carcinogens and are known to be toxic to aquatic life (EPA 1984; Long and Morgan 2000; and Ankley et al., 2003). It has also been known for some time that PAHs are a component of urban runoff (EPA 1983, and Pitt et al., 1995).

The overall objective of this project was to qualify and quantify pollutants in the runoff from an asphalt surface sealed with either coal tar or asphalt emulsions. This study concentrated on the immediate effect on water quality of the runoff from sealed asphalt surfaces and did not address the long-term issue of PAHs accumulating in sediment. Bench- and full-scale tests were performed at EPA's Urban Watershed Research Facility (UWRF) located on the grounds of the Edison Environmental Center in Edison, NJ. The UWRF has a parking lot, constructed in 1999, with drainage channels to assist researchers in collecting runoff samples.

This study used collected rainwater for all tests. Unlike other studies cited in literature that have allowed traffic on the surfaces, the parking lot surfaces were not parked or driven on for the duration of this study. This lot was parked on prior to the study, but was cleaned prior to study initiation. This avoided confounding variables such as surface abrasion, tire wear, and automotive exhaust.

Literature Review: Asphalt Sealant Studies

Asphalt sealants are commonly used in the United States due to the prevalence of asphalt driveways and parking lots. Because of its tendency to abrade with time and use, asphalt sealants are used repeatedly over the same surface. It is often recommended that the sealants be reapplied to driveways and parking lots every two to three years (Dubey 1999). Scoggins et al. (2009) reported that an estimated 320 million liters of coal tar sealant are sold each year. Crenson (2007) used a conservative application rate of 1 liter per meter squared (L/m^2). This leads to 160,000 kilograms (kg) of PAHs delivered to the environment each year if a sealant abrasion rate of 0.51 g/m^2/year is used (Scoggins et al., 2009). Coal tar emulsion sealants can contain up to 35% refined coal tar, which is made up of 50% PAHs by mass (NIST 2006). Asphalt emulsion sealants do not contain coal tar and usually contain less than 35% petroleum asphalt by weight; however, it is suspected that PAHs are present in these types of sealants as well, because asphalt contains PAHs (Mahler et al., 2004 and Wess et al., 2004). PAH concentrations in asphalt emulsion sealant have been measured at approximately 1,000 times less than those in coal tar sealant (Mahler et al., 2005).

Recent literature has suggested that coal tar-based sealants have contributed to alterations in the survival, growth, and development of amphibians (Bryer et al., 2006 and Bommarito et al., 2010). In one study, dried coal tar sealant flakes were added to water containing frog embryos (Bryer et al., 2006). The coal tar sealant flakes were added in low (approximately 3 ppm TPAH, where TPAH was total PAH, a sum of 16 parent PAHs), medium (approximately 30 ppm TPAH), and high concentrations (approximately 300 ppm TPAH), as well as a control with no sealant flakes. No frog embryos survived the high treatment, but the other treatments showed that embryos exposed to the sealant took longer to hatch and were developmentally delayed when compared to those in the control treatments. The study's authors could not directly link the toxicity seen to PAH concentrations, but inferred the link due to the large percentage that PAHs contributed to the makeup of sealants (20-35%).

It has also been shown that coal tar contributes to embryo and larval mortality in fish (Kocan et al., 1996) and that coal tar inhibits the growth and biodiversity of macroinvertebrates and benthic phytoplankton (Oberholster et al., 2005). Crunkilton et al. (1997) reported PAH concentrations in runoff and observed that even low concentrations harmed organisms by weakening their immune systems and changing their metabolisms.

Greenstein et al. (2004) also examined runoff from parking lots after simulated rainfall and quantified PAHs, but did not note whether the parking lots were sealed. Lots were separated into low versus high use and maintained versus unmaintained for the purpose of examining the effect of antecedent dry period on the toxicity of runoff from the parking lots. Toxicity was evaluated using a purple sea urchin fertilization test. Every sample showed positive toxicity results. Unpublished data from these authors' laboratory showed that PAH concentrations must be greater than 100 micrograms per liter (μg/L) to show toxicity to the sea urchin sperm, but concentrations in the sampled runoff, from what is assumed to be unsealed asphalt parking lots, were below 30 μg/L. All toxicity seen in those samples was attributed to high concentrations of zinc.

Case Studies

Case Study – U.S. Geological Survey: Austin, TX

A recent U.S. Geological Survey (USGS) study showed that runoff from sealed parking lots could account for a majority of PAH loadings to urban watersheds (Mahler et al., 2004 and 2005). A variety of surfaces were examined for PAHs in simulated runoff: coal tar-sealed asphalt lots; asphalt emulsion-sealed asphalt lots; unsealed asphalt lots; and unsealed concrete lots. There were four test plots that had no traffic and 13 in-use parking areas. The test plots were sealed prior to the study, while the active lots were studied in their "as is" condition, with the sealant application dates known. Each parking area was sprayed with distilled water to simulate a light rain. The active lots were sampled once each, while the test plots were sampled three times each. The parking areas were also scraped to collect solid particles for direct examination of the lot surfaces (no wetting). PAHs in sealant products were analyzed by the City of Austin by painting the sealant product on glass, allowing it to dry for three days, and measuring the PAH concentration of the dried sealant after it had been scraped from the glass.

The highest PAH concentrations were seen in the products themselves, followed by the scrapings, and then the distilled water wash-off. In the wash-off samples, independent of sealant type, the PAH concentrations in the sediment (particle-phase) were several orders of magnitude larger than those in the water column (dissolved-phase). This research defined the term "probable effect concentration" (PEC). The PEC, the concentration above which adverse effects on benthic biota are expected to occur, was 22,800 μg/kg (ΣPAH_{part}) for the particle phase (MacDonald et al., 2000). The PAH concentrations from the test plot samples all exceeded the PEC. Coal tar sealant runoff exceeded the PEC by a factor of about 150, whereas those from unsealed pavement exceeded the PEC by a factor of about two. Dissolved phase coal tar runoff averaged 9 μg/L. The in-use parking lots generally showed greater PAH concentrations than the test plots with no traffic, generally 20 to 150 times greater, with the coal tar-sealed lots showing higher concentrations than the asphalt sealed and unsealed. The unsealed asphalt lots and unsealed concrete lots showed ΣPAH_{part} concentrations on the order of 70,000 μg/kg, which were also above the PEC.

Case Study – University of New Hampshire Stormwater Center Study: Durham, NH

Researchers at the Stormwater Center (SC) at the University of New Hampshire undertook a large-scale study (Watts et al., 2010) similar to the study done by the USGS. The purpose of the study was to examine PAH export from three test parking lots; one sealed with a coal tar-based sealant, one sealed with asphalt-based product, and one unsealed control lot. However, according to the study, it was discovered that both of the sealant lots were coated with coal tar sealant and one lot was left unsealed. All parking lots were traditional asphalt surfaces and the lots were in use for the duration of the study. The coal tar-based sealcoat was applied to the two coated parking areas prior to the beginning of the study and sampling commenced thereafter. Precipitation events generated stormwater runoff for this study. Dependent on rainfall events, samples were taken prior to sealing and then routinely after the sealant application. The study also examined PAH concentrations downstream of the sites to see how far the "reach" of the runoff extended.

Both water column samples and surface sediment samples were taken, and the ambient air was also sampled for PAHs as part of another study. All three study lots were monitored over a two-year period.

The study calculated the mass total ΣPAHs using the measured flow volume and concentrations of the stormwater runoff from the test lots. The two sealed lots had a mass of 9.8-10.8 kg total Σ16PAHs per hectare exported in stormwater runoff and 0.34 kg total Σ16 PAHs per hectare from the unsealed control. The surface sediment sample PAH concentrations were very low prior to the sealcoat application, spiked soon after application, and had decreased from those peak values after twelve months. The coal tar-based sealants showed PAH concentrations that were significantly higher than those of the control (unsealed) parking lot in all sample phases (dissolved, particle, surface sediments).

Case Study – U.S. Geological Survey: Madison, WI

This study examined PAH concentrations in runoff from six urban source areas, including sealed and unsealed asphalt parking lots (Selbig, 2009). The study analyzed runoff from one sealed parking lot and two unsealed, while also investigating streets, roofs, and a mixed-use strip mall. The runoff from the strip mall consisted of combined runoff from the roof, parking lot, sidewalks, and grassy areas. The strip mall parking lot was sealed, but the authors stated that the type of sealant was unknown. The three parking lots examined were each at least five years old and the sealed lot had been coated with a coal tar-based product. The other two lots were maintained only with asphalt-based crack filler. Stormwater runoff from precipitation events was the source water for this study. Sampling events varied for each location, ranging between nine and twenty-seven events from 2005 to 2008. Whole water samples were taken and processed without filtering.

Results showed that runoff from the sealed parking lot had the highest total PAH concentrations; with a mean concentration of 54 μg/L. For most individual PAH compounds, the concentrations observed from the sealed parking lot were significantly greater than those seen in the unsealed lots. The runoff from the roof had the lowest total PAH concentrations, with a mean concentration of 3.4 μg/L; many of the individual compounds detected were at or near the detection limit (detection limits ranged from 0.04 – 0.5 μg/L depending on the individual PAH under consideration).

Case Study – City of Austin: Austin, TX

Scoggins et al. (2007) studied the occurrence of PAHs in receiving waters downstream from coal tar-sealed parking lots and their effects on stream benthic macroinvertebrate communities. The study matched pairs of upstream (control) and downstream (treatment) sites that were immediately above or below coal tar-sealed parking lots. Organisms were collected in both riffles and pools and nine stream community metrics were used to compare the upstream and downstream sites. Within-habitat variability was not addressed in this study and replicate samples at one site were composited. Sediment PAH concentrations were also measured upstream and downstream of the parking lots.

Total PAH concentrations were markedly higher at the downstream sites compared to the upstream ones in five of the seven sites. Four biological measures indicated that the benthic macroinvertebrate community in pools was degraded at the downstream sites relative to the upstream sites, while three biological measures indicated degradation in riffles. Taxon richness was the most robust metric used in the study. The decrease in taxon richness indicated species loss downstream compared to upstream, which can lead to decreased ecosystem function.

The authors stated that the elevated PAH concentrations could be a primary cause of the degraded streams studied, but other WWF effects, e.g., other pollutants and increased flow from impervious cover, may also be impacting the macro-invertebrate population of the downstream sites. The authors also concluded that current PEC values for PAHs in sediment may not be sufficient to predict toxic effects of bioavailability.

Chapter 2 Methods

Bench-Scale Sealant Study

A bench-scale study was performed prior to the full-scale investigation to provide preliminary results regarding polycyclic aromatic hydrocarbon (PAH) concentrations. Hot-mix asphalt was poured into three open wood frames that were 60 centimeters (cm) x 60 cm wide and 10 cm deep (Figure 1) in March 2007. The runoff area of the asphalt panels was 43 cm x 48 cm due to internal framing to prevent leakage on the edges and to assist in collection of runoff. The asphalt panels were stored in a greenhouse at EPA's research facility in Edison, NJ, in order to protect the panels from precipitation, but to allow exposure to varying temperatures. Figure 2 shows the asphalt panels in the greenhouse prior to application of sealants. All of the asphalt panels were swept, vacuumed, and washed before application of the sealants to two of the asphalt panels.

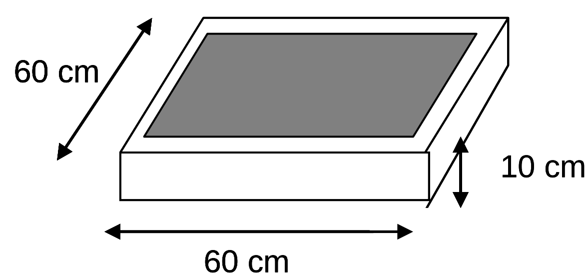

Figure 1. Schematic of asphalt panel and frame.

Figure 2. Three asphalt panels during preparation of study.

Rainwater was collected in a conical 7570 Liter (L) (2000 gallon) tank at the UWRF and transferred to the greenhouse where it was homogenized. Sealants were brushed onto the panels. One asphalt panel was sealed with coal tar sealant, one panel was coated with asphalt emulsion sealant, and one panel surface was left unsealed and treated as a control. Two coats of sealant were applied per manufacturer instructions. During the runoff experiments, the sealed panels were supported at a 14 degree (°) angle while the control panel was raised to 20° to ensure runoff as some water was observed to infiltrate through the unsealed panel. Each panel was pre-wetted to encourage even sheetflow over the entire width of the panel during the experiment. A 43 millimeter (1.7 inch) rain event was simulated for each asphalt frame, equal to a volume of 10 L (2.4 gallons). This rainwater application mimics the volume of a storm event that falls between a one-year and two-year event for New Jersey (NJDEP, 2004). Collected rainwater was pumped with a peristaltic pump from a carboy to a spray bar apparatus that delivered the water to the panels. The rainwater was applied for twenty minutes, and all runoff was collected from the bottom of the sloped sample surface in a catch trough that drained through a rubber hose to a carboy (Figure 3). The first experiment with applied rainwater was performed after the manufacturer-recommended 24-hour sealant curing time. This sampling process was repeated the next day, and seven and thirty days after sealing.

Figure 3. Sealed asphalt panel with rainwater delivery apparatus, angled to promote runoff.

The asphalt panels were porous, as hand tamping the asphalt in the wooden frames did not produce sufficient compaction; however, this was not a problem for the panels that had sealant applied to them. Runoff losses for the coal tar and asphalt emulsion panels were less than 30 percent (%) and some of this loss was due to a poor seal between the panel and the wooden box, not infiltration. However, the control was losing a majority of rainwater applied, i.e., 60%, despite a higher elevation angle to promote runoff. Some of the rainwater leaked out the sides of the asphalt panels, as well. In response to this, a square panel was cut out of the asphalt from the driveway of the research facility. This cutout was poured the same day as the asphalt panels during pavement installation at the UWRF and was subject to compaction by a steam roller. This cutout asphalt panel did not infiltrate runoff, and was used as an additional unsealed control panel for the later bench-scale tests, i.e., seven and thirty days after sealing.

Full-Scale Sealant Study

Applied runoff of collected rainwater was sampled from three asphalt test plots with different or no surface treatments. One test plot was coated with coal tar sealant, another plot was coated with asphalt emulsion sealant, and the third plot remained unsealed and served as the control. Sampling was also performed in a composite tank that combined the runoff from the three treatments. The sealants used in the full-scale study were the same products as the ones used in the bench-scale study. Comparisons of runoff PAH concentrations are presented as well as other standard water quality parameters. The first sampling event was performed one day after application of sealcoats to pavement, followed by events two, seven, 30, and 162 days after application.

Rainwater Collection

The full-scale study used the asphalt half of a parking lot at EPA's research facility. The lot, constructed in 1999 as a runoff testing platform for two surfaces, asphalt and concrete, is shown in Figure 4, from an aerial view facing generally north. Each surface slopes to a central drain, with asphalt runoff flowing south and concrete runoff flowing north. Once in the central drain, runoff flows into a collection chamber to the left (note: blue tarp to left of shed).

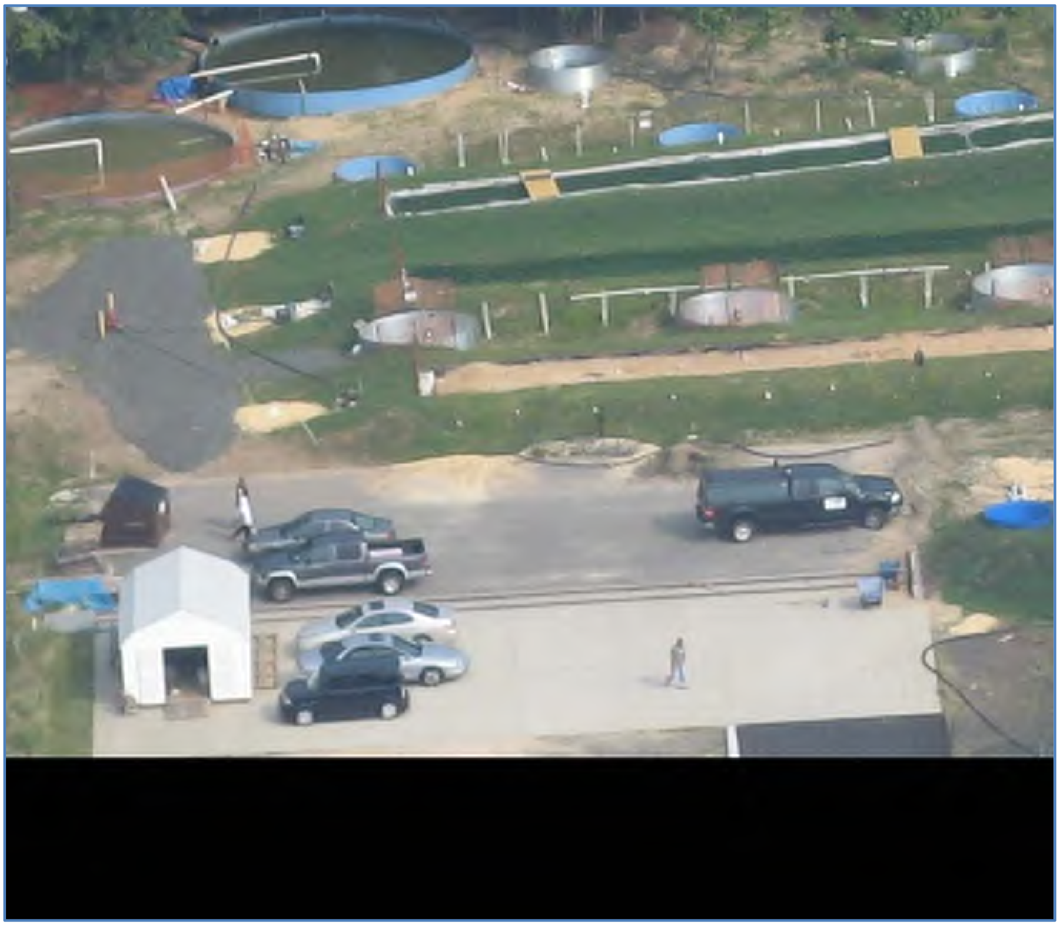

Figure 4. Aerial view of EPA's Urban Watershed Research Facility parking lot.

Rainwater for the full-scale study was captured by placing plastic sheeting on the parking lot and using the central drain to collect the rainwater (Figures 5, 6, and 7). The total area used to collect rainwater from the parking lot was approximately 260 meters squared (m^2) (2800 ft^2). The rainwater was stored and homogenized in lined steel tanks. After sufficient rainwater was collected to apply during experiments, the plastic was taken off the lot and preparations for the experimental study were undertaken. During the study, no cars were allowed to park on the asphalt half of the parking lot; staff parking on the concrete side only.

Figure 5. Parking lot covered in plastic sheeting for rainwater collection.

Figure 6. Parking lot central drains covered in plastic for rainwater collection.

Figure 7. Parking lot drain outlet into sampling box for rainwater collection.

Test Plot Configuration

A schematic of the experimental design of the parking lot is presented in Figure 8. Each test plot was separated from the next with dividers. The dividers for the test plots were constructed of UV-resistant high-density polyethylene (HDPE) plastic that were laid flat and attached to the asphalt with screws and silicone to provide a water-tight seal. At the bottom of each test plot, the HDPE strips were placed vertically and angled to direct the runoff flow to a ramp where the runoff could either enter the common drain or be collected for sampling (Figure 9). Four test plots were built in the anticipation that an extra test plot might be required for further testing (Figure 10). Each test plot was 3.8 m x 7.6 m, giving a surface area of 29 m^2. The test plots were swept, vacuumed, and power washed before application of the sealants.

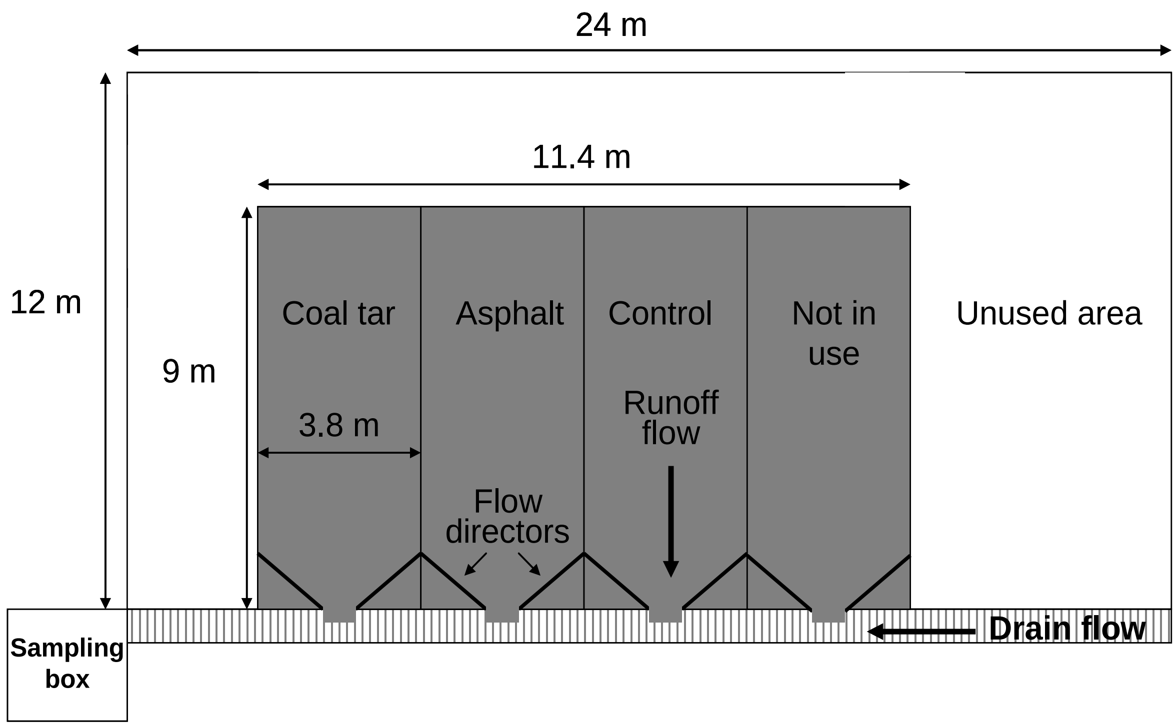

Figure 8. Schematic of the full-scale sealant study.

Figure 9. Asphalt test plot showing the flow directors and the ramp into the drain.

Figure 10. The four test plots at EPA's Urban Watershed Research Facility prior to sealing.

Study Details

Sealants were applied when the air temperature was 13° Celsius (C) (55° Fahrenheit). Manufacturers specify a minimum air temperature of 10°C (50° Fahrenheit) for application. The sealant was applied with a combination of brushes and squeegees; a new set of tools was used for each sealant. One test plot was sealed with coal tar sealant, another plot was sealed with asphalt emulsion sealant, and another test plot was left unsealed as a control.

One coat of sealant was applied to each of the two test plots that were being tested (coal tar and asphalt emulsion). Manufacturer instructions recommend the application of two coats for best results, but there was not sufficient sealant of either type to fulfill this requirement. One 5-gallon bucket of each sealant type should have been more than sufficient to cover the surface area of one test plot, assuming the asphalt was previously sealed. However, the UWRF parking lot was never sealed and would have required additional sealant to achieve two coats.

It is suspected that the age and wear condition of the UWRF parking lot asphalt led to the reduced coverage of the sealants, with the asphalt being rough and becoming slightly porous with time. This led to the sealant soaking into the asphalt rather than just coating the surface. For both types of sealants, the manufacturer's instructions on the containers recommended a minimum 24-hr cure after application before returning to general usage of surface.

After the 24-hr cure time, each test plot was pre-wetted prior to the simulated rain event to encourage an even sheet flow. The pre-wetting did not result in runoff, but some of this water was captured with the initial runoff that was sampled. The previously collected rainwater was applied using a hose and an attached spray nozzle. An in-line paddle wheel flowmeter measured the volume applied.

Approximately 436 L (115 gallons) was delivered over one hour for each asphalt test plot. This volume was equivalent to 15 mm (0.6 inches) rain event, which is approximately half the New Jersey water quality design storm (NJDEP, 2004) and ensured equal application to each test plot. Samples were collected at the discharge point from each test plot (white ramp as pictured in Figure 9) after running off the asphalt but before reaching the common drain.

Samples of the mixed flow were collected at a catch basin where all the runoff was collected. The runoff was then pumped into the composite tank and combined to simulate mixing of runoff from a variety of surfaces. This was done in order to compare runoff from sealed asphalt surfaces to runoff that has been mixed and transported downstream.

Samples were collected immediately after runoff appeared at the collection point (time zero), at 30 minutes, and at 60 minutes. For the first sampling event, one day after sealing, the time-sliced samples were collected separately; but for all other events (two, seven, 30 and 162 days after sealant application), the time-sliced samples were composited. The first sampling event was broken down into several time slices with the intent to discern if the runoff from the first flush had measurable differences.

There was no rain during the first week after the sealant application. Three small (less than 2.5 mm) rain events and one large rain event (13 mm) occurred after the seven-day event and before the 30-day event. There were numerous precipitation events between 30 and 162 days, but these were not quantified. No samples were taken during any of these precipitation events.

Analytical Procedures

PAH Analyses

The runoff samples were analyzed for PAH concentrations by EPA Method 8270C "Semi-volatile organic compounds by gas chromatograph-mass spectrometer (GC-MS)" (EPA 1996). Lists of the 17 PAHs examined during this study are presented in Table 1 and include the 16 PAHs that are classified as EPA Priority Pollutants, as well as 2-methylnaphthalene (EPA 2009). Most of the PAHs examined here are considered semi-volatile, while naphthalene and 2-methylnaphthalene are considered volatile. The table shows the individual PAH analytes, their detection limits, and the lowest standard used in the generation of a calibration curve. The method detection limit for ∑PAH for these 17 compounds was calculated as the sum of the individual detection limits, which was 0.29 microgram (µg)/L.

Water Quality Parameters

In addition to PAH, the samples were also tested for a variety of water quality parameters including: total suspended solids (TSS), volatile suspended solids (VSS), total organic carbon (TOC), chemical oxygen demand (COD), pH, and Microtox® toxicity. Both TOC and COD assess the amount organic matter in a water samples. The COD test is used as a surrogate for biochemical oxygen demand (BOD), as COD is a shorter, easier test to run. COD represents the amount of oxidizable material in the water, which in turn represents the potential for reducing dissolved oxygen (DO) in the receiving water. The full name of the analytical procedures and method references for the testing for these parameters can be found in Table 2. The Microtox® analyses were performed but the results were inconclusive and are not reported.

Table 1. Polycyclic aromatic hydrocarbons, detection limits and lowest standards.

Polycyclic Aromatic Hydrocarbon	Detection Limit (µg/L)	Lowest Standard (µg/L)
Naphthalene	0.02	1.00
2-Methylnaphthalene*	0.01	1.00
Acenaphthylene	0.01	1.00
Acenaphthene	0.02	1.00
Fluorene	0.01	1.00
Phenanthrene	0.03	1.00
Anthracene	0.02	1.00
Fluoranthene	0.02	1.00
Pyrene	0.02	1.00
Benzo[a]anthracene	0.02	1.00
Chrysene	0.02	1.00
Benzo[b]fluroanthene	0.02	1.00
Benzo[k]fluoranthene	0.01	1.00
Benzo[a]pyrene	0.02	1.00
Indeno[1,2,3-cd]pyrene	0.01	1.00
Dibenz[a,h]anthracene	0.01	1.00
Benzo[g,h,i]perylene	0.02	1.00

* 2-Methylnaphthalene is not an EPA priority pollutant.

Table 2. Analytical procedures.

Parameter	**Method**	**SOP**	**Discrete Bottle Identifier**
Total Organic Carbon (TOC)	SM 5310-TOC		None (composite only)
Microtox® toxicity[1]	SM 8010-F		Composite unless otherwise noted
Total Suspended Solids (TSS)	SM 2540-D	30	None (composite only)
Volatile Suspended Solids (VSS)	SM 2540-E	30[2]	None (composite only)
Chemical Oxygen Demand (COD)	SM 5220-COD-D	55	None (composite only)
Polycyclic Aromatic Hydrocarbons (PAHs)	SM 6440-C/EPA Method 8270C		Composite unless otherwise noted

[1] Method number refers to general toxicity guidance only
[2] Residue from TSS analysis will be treated according to SM 2540-E
SOP = Standard Operating Procedure

Chapter 3 Results

Bench-Scale Study Results

Polycyclic Aromatic Hydrocarbon (PAH) Results

A list of the 17 polycyclic aromatic hydrocarbons (PAHs) examined during the bench-scale study is presented in Table 3. This table shows the range of PAH concentrations found in runoff samples from each panel for the bench-scale study, where “n” is the total number of samples taken. Many individual PAHs were found to be above the detection limit, but below the lowest standard so these reported concentrations may not be as reliable as those that fall within the points on the calibration curve. Non-detect results were counted as zeroes in the sum PAH (∑PAH) values.

PAH results of the collected runoff are shown in Figure 11. Results are shown as the ∑PAH of 17 semi-volatile PAHs. Note that the concentrations are shown on a log scale. The whole water sample was analyzed rather than analyzing the particle and dissolved phases separately. Three samples were taken for each sealed asphalt panel for each rainwater application event. The unsealed panel had two samples taken at each event, with the exception of the first event, which had three samples taken; this is why no error bars are shown in Figure 11. The results below are daily averages of the samples and the error bars are the 95 percent (%) confidence intervals for the coal tar and asphalt emulsion runoff. The coal tar runoff samples contained 16 of the 17 analyzed PAHs in the one-day sample, while five of the 17 PAH analytes were detected in the one-day asphalt emulsion runoff sample, and eight of the 17 PAHs were found in the one-day control sample.

The runoff from the coal tar-sealed asphalt panel had the highest PAH concentrations at every sampling event for the bench-scale study. The PAH concentrations in the runoff samples from the coal tar panel were more than two orders of magnitude higher than those of the asphalt emulsion and unsealed panel. PAH concentrations observed in the runoff generally decreased with time. The asphalt emulsion and the unsealed panels both showed low ∑PAH concentrations and were not significantly different from each other (least square mean test, $p = 0.1973$). The runoff from the coal tar panel had significantly higher means than the unsealed or asphalt emulsion panels (least square mean test, $p < 0.0001$ for both comparisons).

The individual PAH compounds that contributed to the total PAH concentrations for the runoff samples were variable among the three test plots. The PAHs in the asphalt emulsion sealant runoff samples consisted of only five of the 17 PAH compounds examined, and all of those are considered low-molecular weight and more soluble and prone to volatilization. The coal tar runoff samples contained 16 of the 17 compounds analyzed, but the constituency was dominated by phenanthrene (44%). The unsealed control runoff contained eight of the 17 analytes, with phenanthrene contributing 30% to the total PAH concentration. Figure 12 shows a breakdown of individual contribution of PAHs to the ∑PAH in the runoff on a percent basis for the sample numbers (n) taken 24 hours after sealant application ($n = 2$ for unsealed, $n = 3$ for asphalt emulsion and coal tar). The runoff in the bench-scale study showed the presence of

PAHs with samples from the coal tar-sealed panel yielding the highest values; maximum ΣPAHs = 164 micrograms /liter (µg/L).

Table 3. Polycyclic aromatic hydrocarbons (PAHs) observed ranges for the bench-scale study runoff.

Polycyclic Aromatic Hydrocarbon	Observed Range (µg/L)		
	Unsealed n = 8	Asphalt emulsion sealant n = 12	Coal tar sealant n = 12
Naphthalene	ND – 0.04	0.02 – 0.04	0.17 – 8.45
2-Methylnaphthalene*	ND – 0.02	ND – 0.02	0.03 – 1.26
Acenaphthylene	ND	ND	ND
Acenaphthene	ND – 0.06	ND – 0.02	0.32 – 22
Fluorene	0.02 – 0.06	ND – 0.03	0.54 – 27.3
Phenanthrene	0.03 – 0.13	0.03 – 0.09	3.29 – 72.4
Anthracene	ND – 0.04	ND	0.35 – 12
Fluoranthene	ND – 0.04	ND – 0.02	0.85 – 13.4
Pyrene	ND – 0.03	ND	0.58 – 6.67
Benzo[a]anthracene	ND – 0.04	ND – 0.03	0.03 – 0.98
Chrysene	ND – 0.05	ND – 0.03	0.07 – 0.57
Benzo[b]fluroanthene	ND – 0.05	ND – 0.03	0.02 – 0.19
Benzo[k]fluoranthene	ND – 0.05	ND – 0.03	0.02 – 0.19
Benzo[a]pyrene	ND – 0.04	ND – 0.02	ND – 0.18
Indeno[1,2,3-cd]pyrene	ND – 0.04	ND – 0.03	ND – 0.13
Dibenz[a,h]anthracene	ND – 0.05	ND – 0.03	ND – 0.14
Benzo[g,h,i]perylene	ND – 0.04	ND – 0.03	ND – 0.12

* 2-Methylnaphthalene is not an EPA priority pollutant
ND = Non-detect
n = Sample size

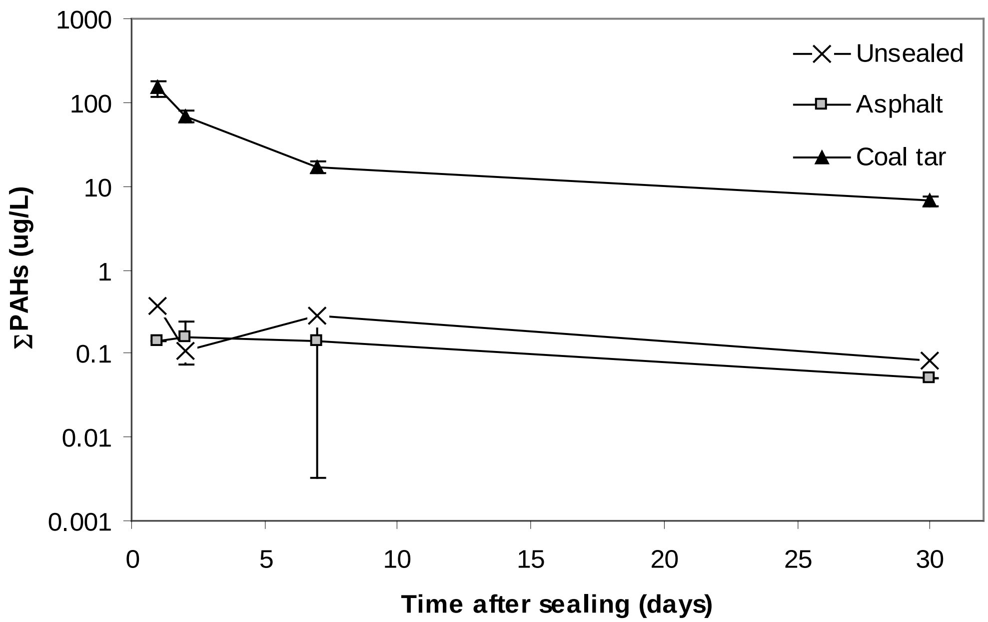

Figure 11. Summation of 17 polycyclic aromatic hydrocarbons (∑PAH) concentrations for four sampling events of bench-scale study.

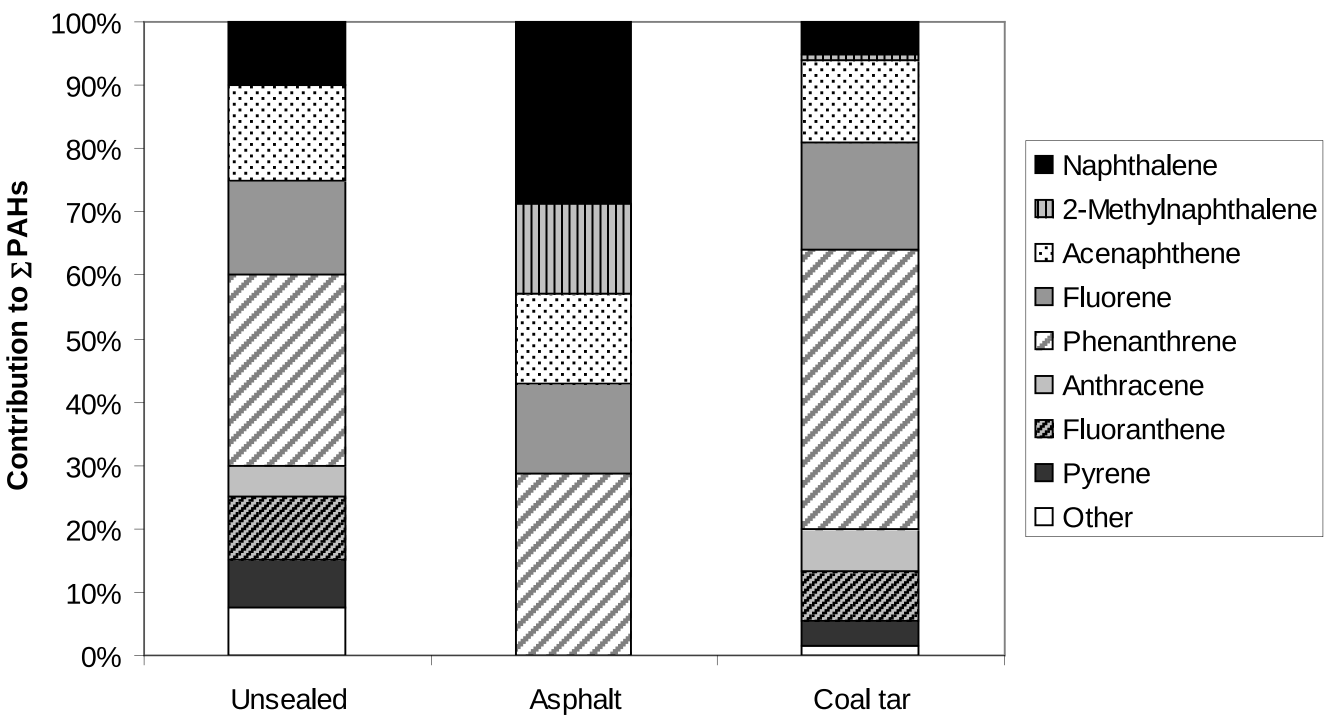

Figure 12. Percent contribution of individual to sum of polycyclic aromatic hydrocarbons (PAHs) of bench-scale study.

Water Quality Results

The water quality parameters of the chemical oxygen demand (COD) and total organic carbon (TOC) were especially interesting for the one-day sampling event (Figure 13). The COD values for all three panels were elevated above concentrations typically measured in stormwater runoff samples. Lager et al. (1977) found a mean COD concentration of 115 mg/L with a range of values of 48-170 mg/L. All exceeded the 90% observed range for urban sites of 140 mg/L, (EPA, 1983). The asphalt emulsion runoff samples exceeded 500 mg/L, which for comparative purposes, is more typical of a COD concentration of medium-strength untreated domestic wastewater (Tchobanoglous and Burton, 1991) than runoff. The asphalt emulsion COD runoff concentrations dropped dramatically the first day after sealant application.

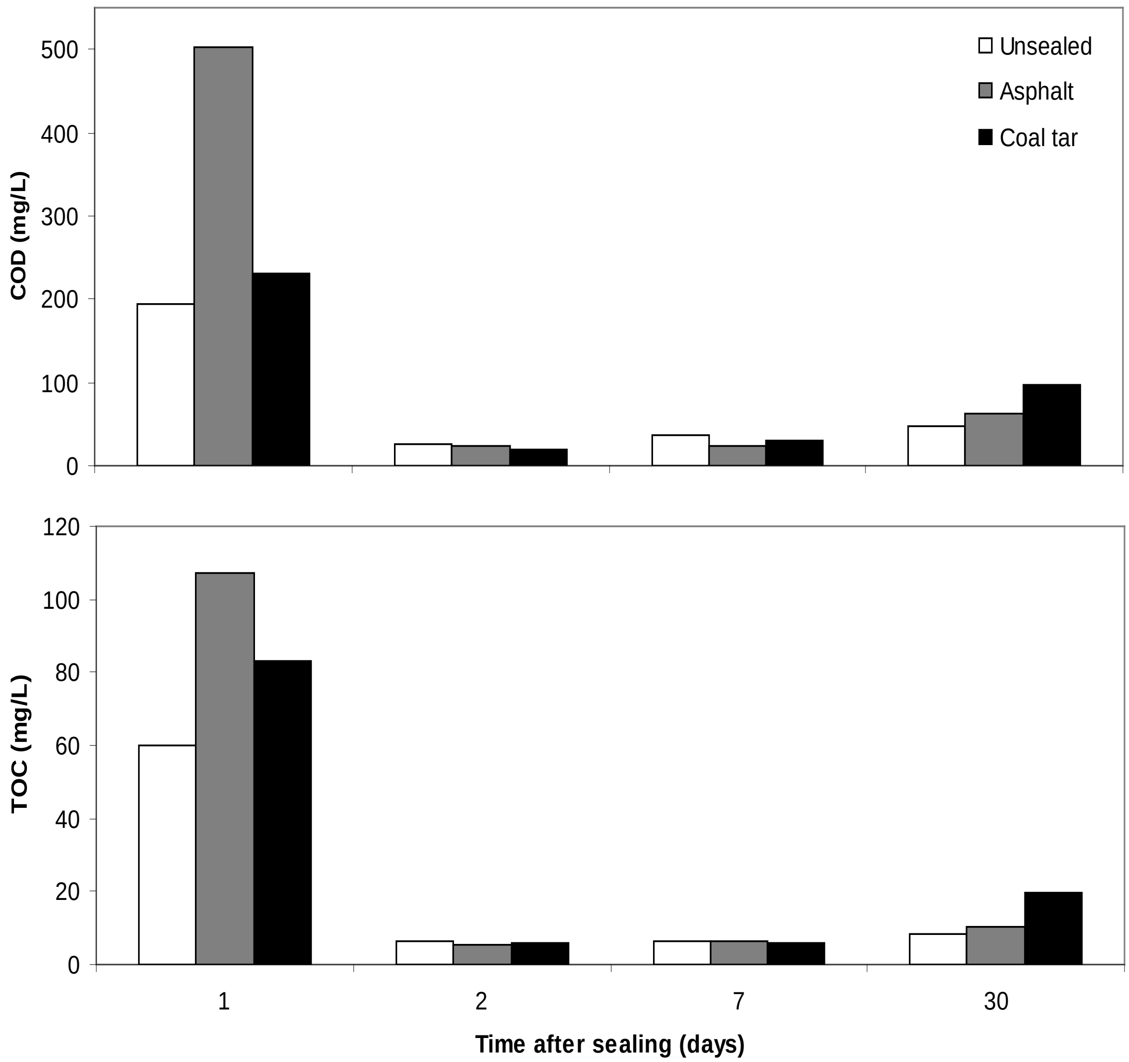

Figure 13. Total organic carbon (TOC) and chemical oxygen demand (COD) concentrations of bench-scale study.

The TOC concentrations follow a similar pattern to the COD values, producing runoff of both the coal tar and asphalt emulsion sealant in a range of untreated wastewater from weak, 80 mg/L to medium, 160 mg/L (Tchobanoglous and Burton, 1991). The direct impact to receiving water of increased COD and TOC loading is difficult to predict as both analyses convert organic matter regardless of "the biological assimilability of the substances" (Sawyer and McCarty, 1978); specifically, PAHs and the other organic components of the sealants may not exert a large oxygen demand due to potential toxicity of PAHs and limited biodegradability of other organic components. Total suspended solids (TSS) concentrations ranged from 1.4 – 9.5 mg/L, which is surprisingly low but can be attributed to the preparation of the surfaces, i.e., cleaning before sealing as per manufacturer instructions.

Full-Sale Study Results

Polycyclic Aromatic Hydrocarbon (PAH) Results

A list of the 17 PAHs examined during the full-scale study is presented in Table 4. This table shows the range of PAH concentrations found in runoff samples from each plot in the full-scale study, where "n" is the number of samples taken. Many individual PAHs were found to be above the detection limit, but below the lowest standard; therefore, these reported concentrations may not be as reliable as those that fall within the points on the calibration curve. Non-detect results were counted as zeroes in the ∑PAH values.

Table 4. Polycyclic aromatic hydrocarbons (PAHs) observed ranges for the full-scale study runoff.

Polycyclic Aromatic Hydrocarbon	Observed Range (µg/L)		
	Unsealed n = 11	Asphalt emulsion sealant n = 15	Coal tar sealant n = 15
Naphthalene	ND – 0.16	ND – 0.44	0.86 – 19.4
2-Methylnaphthalene*	ND – 0.04	ND – 0.1	0.14 – 2.48
Acenaphthylene	ND – 0.02	ND – 0.03	0.02 – 0.15
Acenaphthene	ND –0.2	ND – 0.84	1.3 – 25.4
Fluorene	0.02 – 0.5	0.03 – 1.14	3.47 – 40.4
Phenanthrene	0.16 – 1.13	0.39 – 1.64	33.1 – 125
Anthracene	ND – 0.08	0.02 – 0.19	3.04 – 16.1
Fluoranthene	0.04 – 1.04	0.07 – 0.47	12 – 28.8
Pyrene	0.02 – 0.81	0.05 – 0.37	4.43 – 15.8
Benzo[a]anthracene	ND – 0.45	ND – 0.14	0.28 – 3.28
Chrysene	ND – 0.71	0.02 – 0.23	0.4 – 2.59
Benzo[b]fluroanthene	ND – 0.58	ND – 0.22	0.11 – 1.59
Benzo[k]fluoranthene	ND – 0.56	ND – 0.18	0.1 – 1.65
Benzo[a]pyrene	ND – 0.51	ND – 0.18	0.08 – 2.08
Indeno[1,2,3-cd]pyrene	ND – 0.4	ND – 0.1	0.04 – 1.18
Dibenz[a,h]anthracene	ND – 0.15	ND – 0.04	0.02 – 0.59
Benzo[g,h,i]perylene	ND – 0.44	ND – 0.11	0.03 – 1.17

* 2-Methylnaphthalene is not an EPA priority pollutant
ND = Non-detect
n = Sample size

Results of the runoff are shown in Figure 14 as the ∑PAH sum of 17 semi-volatile PAHs. Note that the concentrations are shown on a log scale. The whole water sample was analyzed rather than analyzing the particle and dissolved phases separately. The method detection limit for ∑PAH for these 17 compounds is 0.29 µg/L (the sum of the individual detection limits). Individual non-detect results were counted as zeroes in the ΣPAH values. The analysis of the coal tar runoff samples detected all 17 PAHs in every sample. Three runoff samples were taken for each sealed test plot (coal tar and asphalt emulsion) and the composite tank for each rainwater application event; the unsealed plot had two runoff samples taken at each event. The results below are averages of the collected samples and the error bars are the 95% confidence intervals. The composite tank was not sampled at 162 days because the general mixing trends were known by that time.

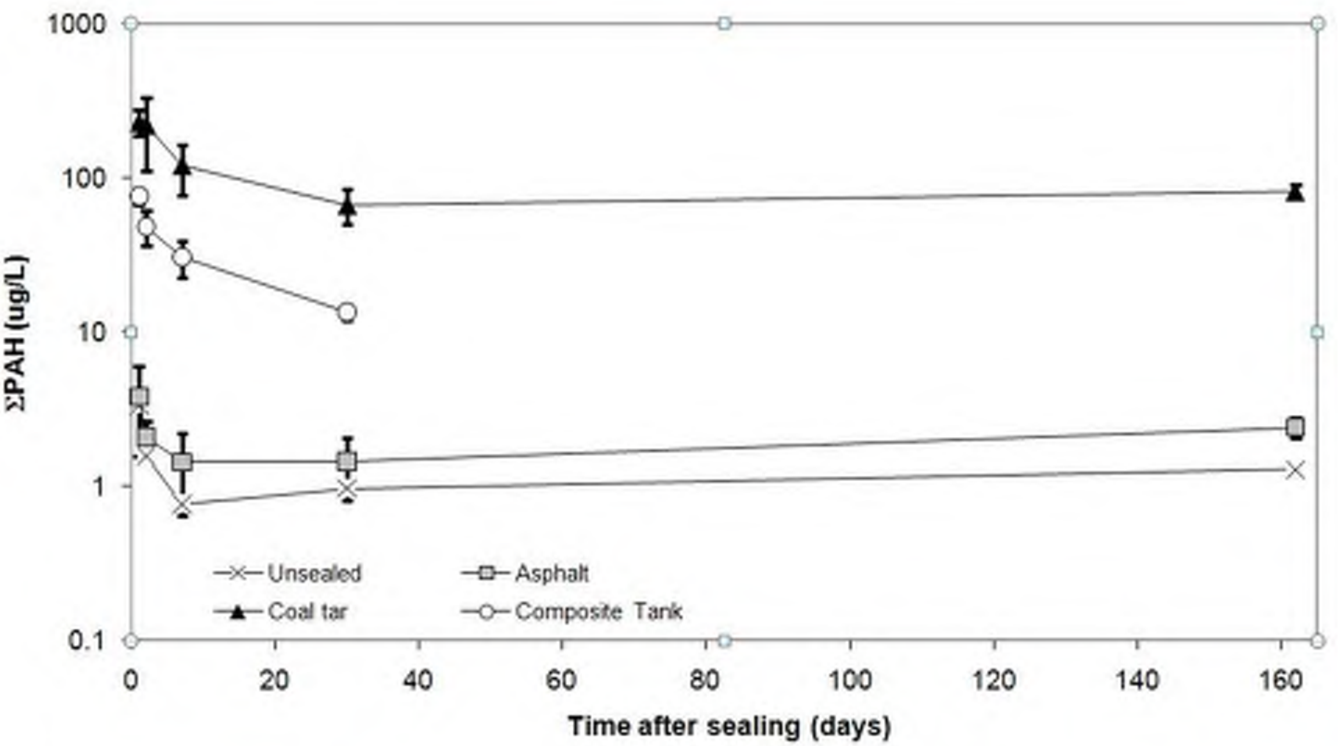

Figure 14. The sum of the polycyclic aromatic hydrocarbon concentrations (∑PAH) in runoff for the five sampling events of full-scale study (∑PAH =17).

The runoff from the coal tar-sealed asphalt plot had the highest PAH concentrations at every sampling event. The PAH concentrations of the runoff from the coal tar plot were more than an order of magnitude higher than runoff concentration from the asphalt emulsion section. Runoff from the asphalt emulsion and the unsealed plots both showed low ∑PAH concentrations, and concentrations were significantly different from each other (Least square mean test, $p = 0.0006$). The asphalt emulsion and coal tar runoff samples were significantly different from each other with regard to PAH concentrations (Least square mean test, $p < 0.0001$) The coal tar runoff samples were also significantly different from those from the unsealed test plot (Least square mean test, $p < 0.0001$). The results from the composite tank were generally about a third of the coal tar runoff values, as expected because the tank samples were a combination of the unsealed (low PAH concentrations), the asphalt emulsion (low PAH concentrations), and the coal tar runoff. PAH concentrations in the runoff generally decreased rapidly over the first three sampling events.

The individual PAH compounds that contributed to the ΣPAHs for each runoff sample were variable for the one-day sampling event (Figure 15). More PAH compounds were found in the asphalt emulsion runoff samples here in the full-scale study than in the bench-scale; however, the presence of 2-methylnaphthalene was conspicuously diminished. In the bench-scale, 2-methylnaphthalene contributed 14% to the total PAHs for the asphalt emulsion runoff samples, while in the full-scale study it contributed less than 2%. The coal tar runoff samples contained each of the 17 compounds analyzed, but the constituency was dominated by phenanthrene (47%). The unsealed control contained all 17 analytes, with only phenanthrene contributing more than 16% to the total PAH concentration; the concentrations were very low compared to those in the runoff from the coal tar-sealed test plot. The composite tank samples were dominated by the coal tar runoff with regard to PAH constituents. Figure 16 compares the individual PAH concentrations in the runoff for the three surfaces. PAHs are presented in order of elution (low molecular weight on the left, to increasing molecular weight on the right).

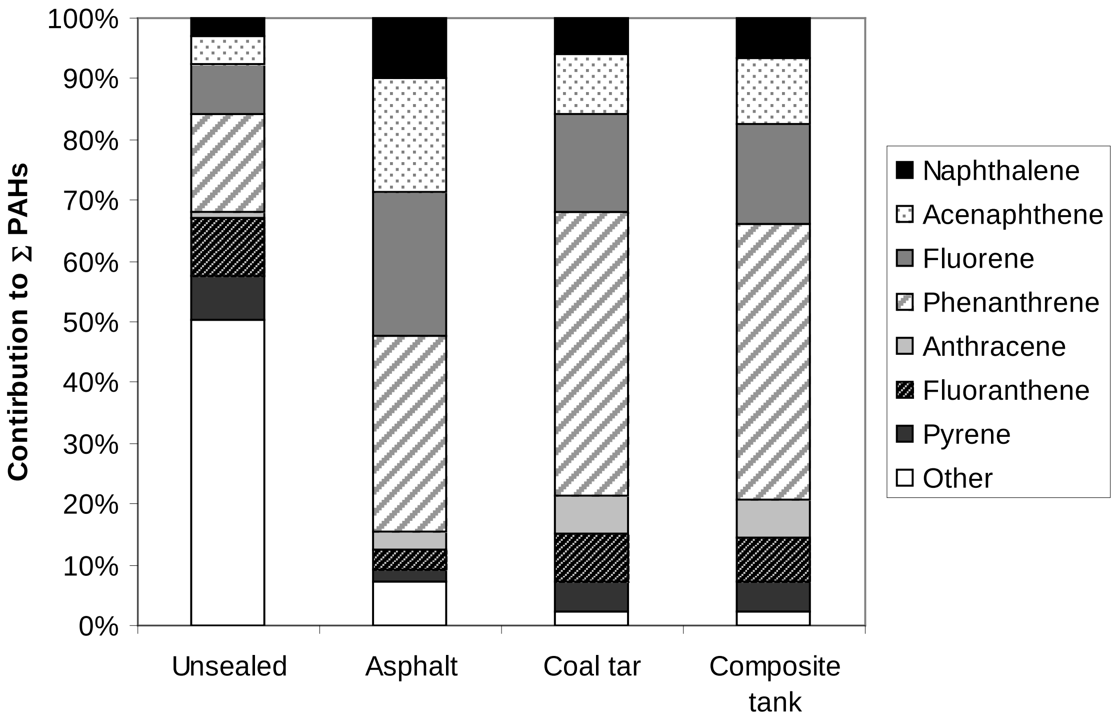

Figure 15. Percent contribution to the sum of polycyclic aromatic hydrocarbons (∑PAH) for individual polycyclic aromatic hydrocarbons in runoff for the one-day sampling event for the full-scale study.

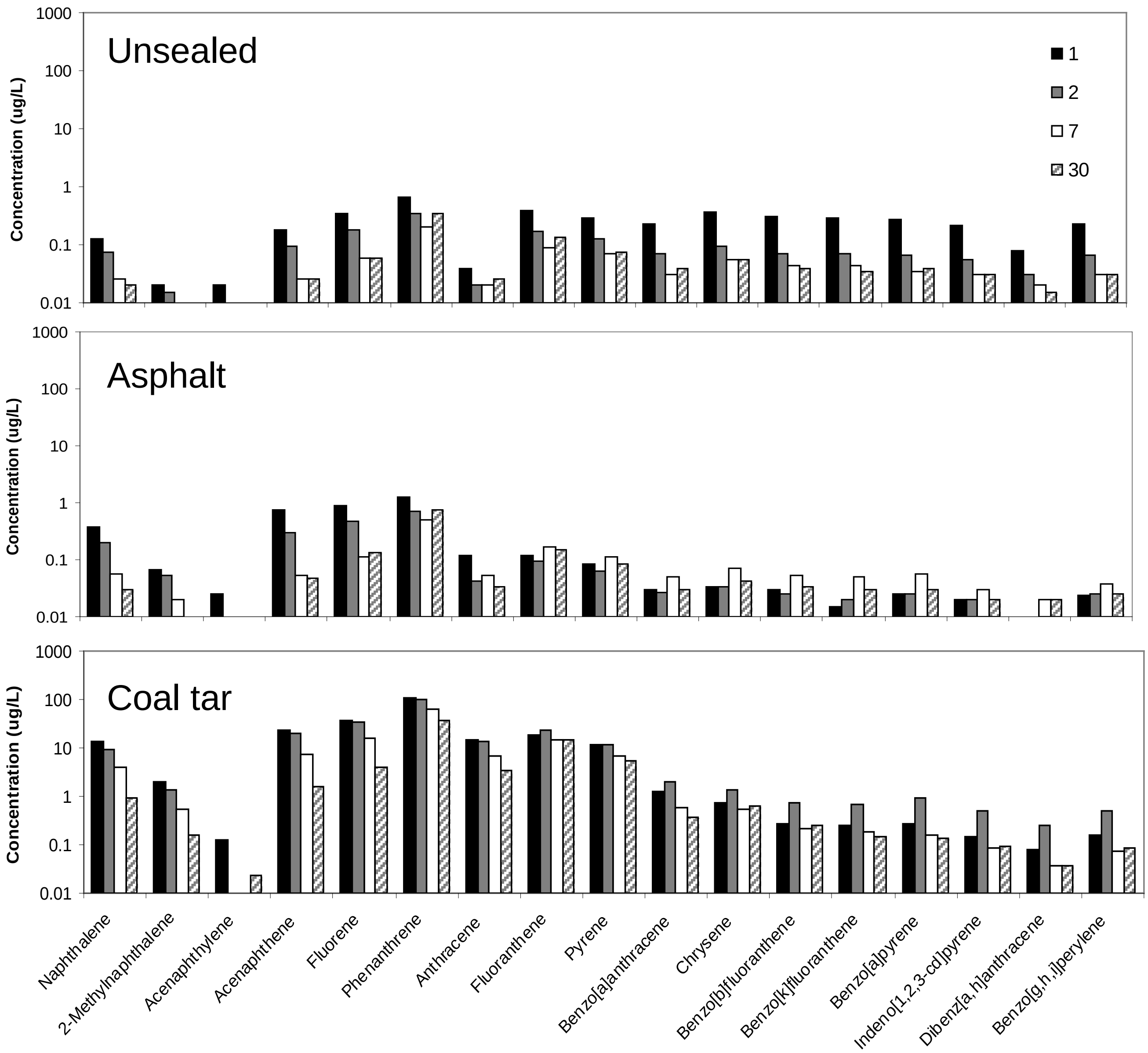

Figure 16. Polycyclic aromatic hydrocarbon concentrations in runoff for each compound for the 1-, 2-, 7-, and thirty-day sampling events for each surface of full-scale study.

The individual PAH makeup of the runoff samples changed with time as shown in Figure 17, which shows the compounds in order from lower to higher molecular weights. The runoff from the sealed surfaces lost the lower molecular weight PAHs as the sealant aged. For runoff samples from the asphalt emulsion-sealed plot and the coal tar-sealed plot, the contributions of naphthalene, 2-methylnaphthalene, and acenaphthene decreased from one to 162 days after sealing. In the runoff samples from the asphalt emulsion-sealed plot, the higher molecular weight compounds comprised a greater percentage of the total PAHs in the last sample, which was five and one-half months after sealing. Watts et al. (2010b) observed a similar pattern and attributed it to weathering.

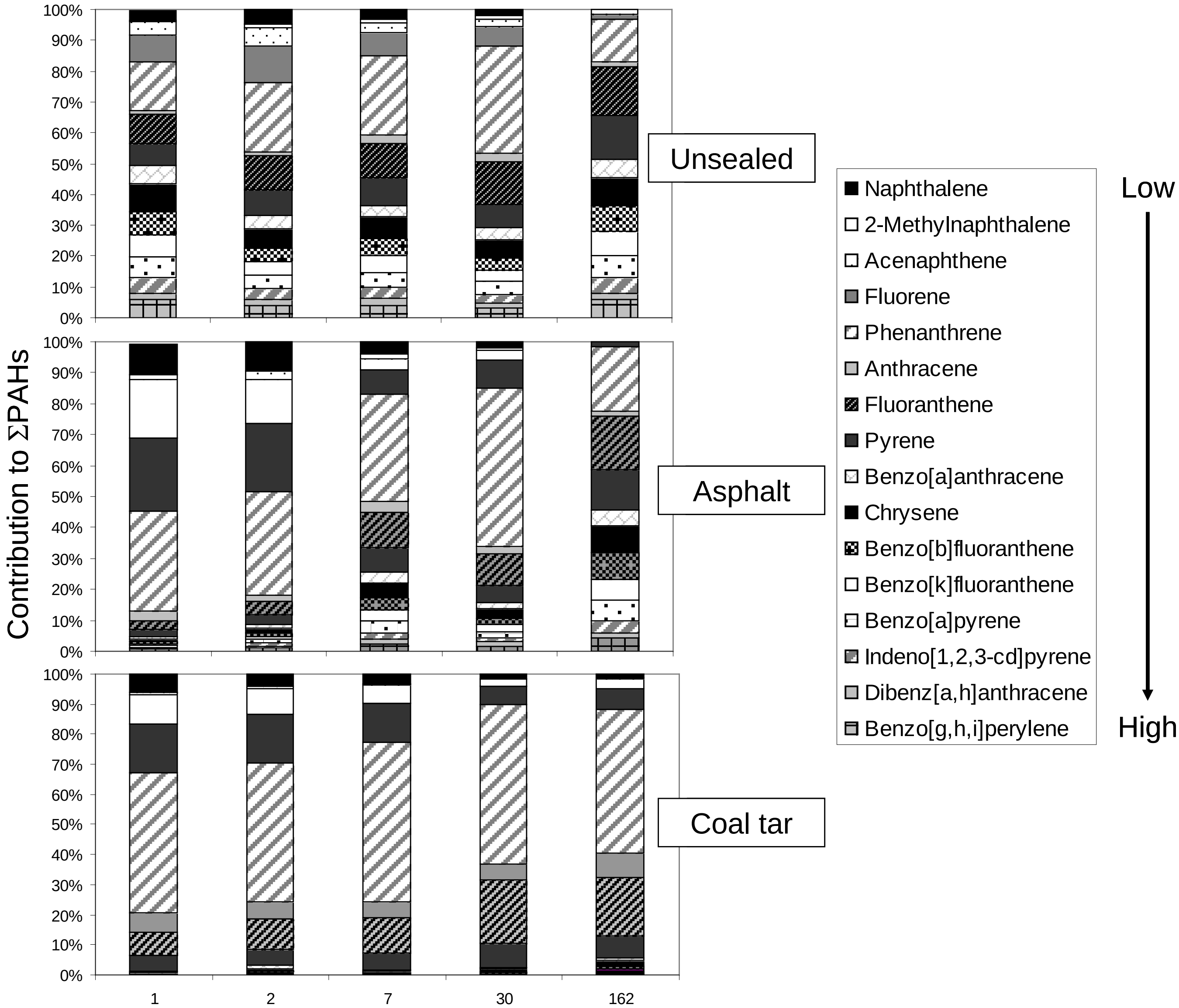

Figure 17. Percent contribution of individual polycyclic aromatic hydrocarbons (PAHs) in runoff to the total PAHs observed (∑PAH) over all sampling events for the full-scale study.

Water Quality Results

The water quality parameters of COD and TOC presented in Figure 18 (note: scales of y-axes are different) showed values that were more typical of urban runoff than the very high concentrations seen in the bench-scale (Figure 13). As noted previously, the composite tank was not sampled at the 162-day sampling event. The TOC results are characteristic of urban stormwater runoff (Winer, 2000). COD and TOC concentrations in the runoff were relatively consistent over the first 30 days, with the exception of the asphalt emulsion, which peaked on the initial sampling time. Not including the initial sample of the asphalt emulsion sealant runoff, both COD and TOC concentrations peaked at the 162-day sampling event, which may be indicative of the degradation of recalcitrant organic compounds over a longer time period; general accumulation of organic matter via atmospheric deposition; or wind-swept local transport. This is supported by the TSS results, which also peaked at the 162-day sampling event.

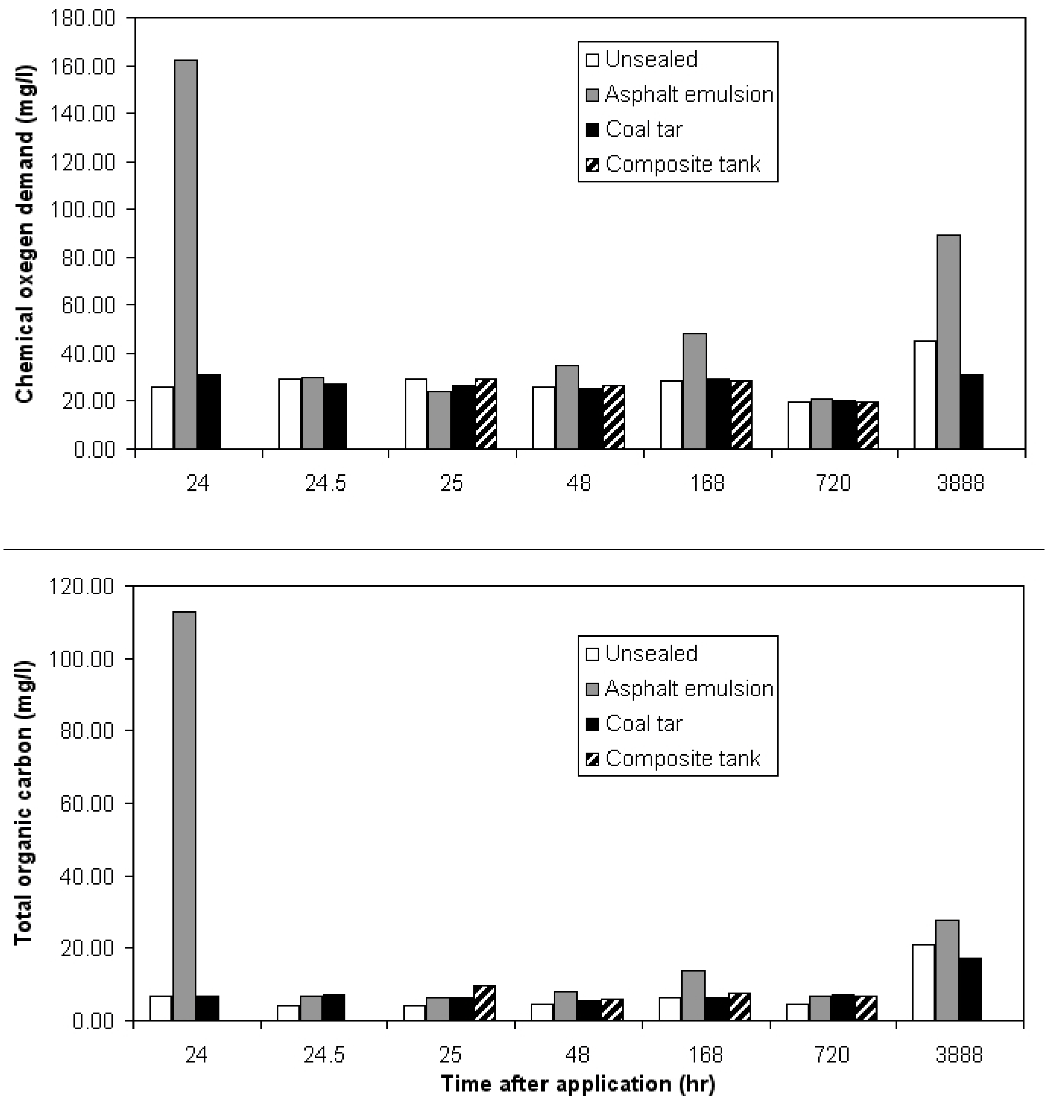

Figure 18. Total organic carbon and chemical oxygen demand concentrations in runoff for full-scale study.

TSS concentrations were generally very low for the first sampling events (1-, 2-, 7-, and 30-day samples) and concentrations ranged from 2.8 – 14.8 mg/L. Peak TSS concentrations in the runoff were seen at the 162-day sampling event for all plot types, with concentrations of 25.7 mg/L for the unsealed, 82.2 mg/L for the asphalt emulsion, and 22.5 mg/L for the coal tar sealant. The high TSS concentrations seen at the long-term sampling event most likely represent the accumulation of atmospheric deposition of particles and other material, the degradation of the sealant, or the degradation of the asphalt surface over 4-5 months.

While TSS values were low, the observed ratio of volatile suspended solids (VSS) to TSS in sampled runoff was high. This is an indication of an organic component loading in the runoff. The composite tank averaged 0.96 on the first day and ranged from 0.69 to 1.0 for the study. Similarly, coal tar runoff was 0.81 the first day and ranged from 0.54 to 0.94 for the study; asphalt emulsion runoff was initially 0.84, ranging from 0.43 to 0.98; and the unsealed runoff was initially 0.89 and ranged from 0.44 to 0.96.

Chapter 4 Discussion

Comparison to Literature Values

Polycyclic Aromatic Hydrocarbon (PAH) Concentrations

The maximum PAH concentrations in this study are comparable to those reported in other studies for sealed asphalt sites. Figure 19 shows concentrations for this and two other studies. The University of New Hampshire (UNH) data are from Watts (2009, 2010a) and the U.S. Geological Survey-Wisconsin (USGS-WI) data are from Selbig (2009).

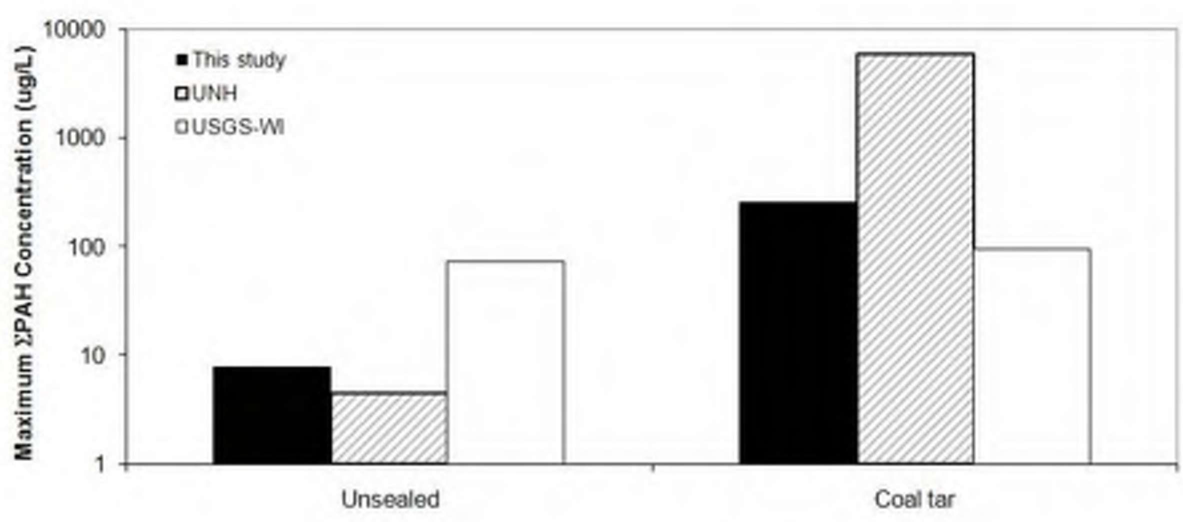

Figure 19. Maximum sum of polycyclic aromatic hydrocarbon (∑PAH) concentrations in runoff for full-scale study and two other studies.

The USGS study examined runoff from one coal tar-sealed parking lot and two unsealed parking lots. The sum of PAHs for the full-scale research associated with this study consisted of 17 compounds, 16 for the UNH study, and 18 for the USGS-WI study. It should be noted that during the UNH and USGS-WI studies, the parking lots were active and parking was allowed, while parking was prohibited for the duration of this study. The EPA study results represent the PAH runoff that could be expected from runoff and weathering without contributions from vehicular use.

A survey of in-use parking lot runoff in Alabama showed that the mean total PAH concentration, based on seven reported PAHs, was 286 μg/L (Pitt et al., 1995). In comparison, the sum of the day one sampling event in this study for these same seven PAHs was much lower: 4.11 μg/L for the unsealed and 48 μg/L for the coal tar-sealed runoff.

The above discussion only relates the observed concentrations from this and other studies. Because of the variations in urban runoff, due to variability in usage conditions and climate (e.g., antecedent moisture conditions and rainfall intensity), the NURP study (EPA, 1983) recommended comparing loadings (not concentrations).

In the runoff samples from the asphalt emulsion-sealed plot, the higher molecular weight compounds comprised a greater percentage of the total PAHs in the last sample. This is most likely due to the low molecular weight PAHs volatilizing off earlier, leaving the heavier PAHs to contribute a higher percentage to the total PAH concentration. Similar observations were made by Mahler et al. (2005), who reported a general (but not uniform) decrease in the concentration of PAHs in both the particulate and dissolved phase in runoff from test plots (no vehicle traffic) and a decrease in the ratio of the low molecular weight to high molecular weight PAHs, which was attributed to volatilization and leaching.

The varied PAH makeup of the unsealed control samples is potentially from some combination of atmospheric deposition; the asphalt surface itself; and/or possibly wind-driven cross-contamination from the nearby coal tar emulsion- and asphalt emulsion-sealed test plots. The concentrations seen in the unsealed runoff and the asphalt emulsion runoff samples are only slightly higher than detection limits, while those of the coal tar runoff samples are two orders of magnitude higher.

Water Quality Parameters and Polycyclic Aromatic Hydrocarbon (PAH) Concentrations

The chemical oxygen demand (COD) concentrations seen in EPA's full-scale study here are generally high compared to the total suspended solids (TSS) concentrations, which is unusual for urban runoff. Table 5 compares COD concentrations, TSS values, and the COD/TSS ratio of several urban sites and EPA's full-scale study. The observations in this study are unusual in comparison to other literature values as COD values are exceeding TSS values. The initial runoff from the asphalt emulsion sealant had the highest observed COD values.

Table 5. Mean total suspended solids, chemical oxygen demand, and ratios for runoff from literature and this study.

Location	Total Suspended Solids (mg/L)	Chemical Oxygen Demand (mg/L)	Chemical Oxygen Demand Total Suspended Solids Ratio
Urban Stormwater[1] (mean)	415	113	0.27
NURP[2] (median)			
Residential	101	73	0.72
Mixed	67	65	0.97
Commercial	69	57	0.83
Open/Nonuban	70	40	0.57
NSQD[3] (median)	58	53	0.91
EPA Full-scale runoff			
Unsealed (mean)	12	29	2.3
Asphalt emulsion (mean)	25	55	2.2
Coal tar (mean)	11	27	2.4

[1] Lager et al. (1997)

[2] EPA (1983) Nationwide Urban Runoff Program (NURP)

[3] Pitt et al. (2004) National Stormwater Quality Database (NSQD)

Crunkilton et al. (1997) noted a strong correlation between TSS and PAHs in runoff samples, but also observed dissolved PAHs in waters that tested toxic, although PAHs were only one of several observed potential toxicants in the runoff. In toxicity testing of PAH-laden stormwater runoff, Ireland et al. (1996) observed a reduction in toxicity when the organic PAH containing fraction was removed from the samples. They also observed in all runoff samples where TSS were removed by filtration, an increase in toxicity indicating the PAHs were either in solution or sorbed to organic carbon. The high COD/TSS ratio for this study indicates that most of the constituents in the runoff are either in the aqueous phase or bound to colloidal material that passes through traditional TSS filters. While particulate release due to vehicular abrasion is demonstrated in other studies (Mahler et al., 2004 and 2005), even without abrasion sealants may release PAHs.

PAH concentrations were regressed against COD concentrations, TOC concentrations, and volatile suspended solids (VSS) concentrations. None of these regressions showed a correlation, despite literature suggesting that VSS is a good surrogate parameter for organic compounds that have an octanol-water partition coefficient (K_{ow}) greater than 10^5 (Novotny and Olem, 1994). Ten of the 17 PAH compounds analyzed in this study have a K_{ow} coefficient greater than 10^5. This lack of relationships among PAHs and other water quality parameters (COD, TOC, and VSS) suggests that these water quality parameters are not surrogates for PAHs.

Instituting Stormwater Controls and Management Options for Sealed Surfaces

In the full-scale testing, runoff collected from the coal tar-sealed surface indicated greater PAH concentrations than the asphalt emulsion and the unsealed runoff. Pitt et al. (1995) observed that treatment processes, particularly sediment removal can reduce toxicity of runoff. Therefore, routing, such as travel time, distance and disconnection (i.e., not directly connecting impervious surfaces to receiving water bodies), and storage and treatment can have a dramatic effect on the content of PAHs in a runoff discharge. Treatment by sedimentation, however, does not actually reduce the toxicity of the PAHs, which will still be present in the aqueous phase or in the sediments. These sediments need to be managed and disposed of properly. The long-term accumulation of PAHs in the sediment potentially leads to chronic toxicity effects. Prevention of PAH contaminated particles from entering the waterway through application of stormwater best management practices (BMPs), such as berms or stormwater ponds, was demonstrated by Bommarito et al. (2010) and Crane et al. (2010), respectively. Any resuspension of sediments in a stormwater control can ultimately reach a receiving water body, therefore transferring the sediment load to the receiving water body.

Routing and treatment of stormwater runoff appear to be effective controls in reducing the toxicity of runoff in general. PAHs are assumed to be bound to particulates, which could imply that sedimentation might treat runoff and remove PAHs. This study indicates that there is increased risk in the period immediately after sealant curing when the PAHs may not be associated with sediments. PAHs in the dissolved-phase or particle free state are not readily removed by conventional treatment methods (Crisafully et al., 2008) used in stormwater (e.g., sedimentation, filtration) or even advanced methods used in wastewater treatment plants (e.g., coagulation, flocculation). In PAH-contaminated wastewater (specifically creosote-contaminated), fixed-film bioreactors removed and degraded the PAHs, while only removal by sorption was observed in wetlands (Tremaine et al., 1994). Biodegrading was easier for the lower molecular weight PAHs and was less effective on larger molecular weight PAHs. The current suite of recommended stormwater BMPs are passive systems that are not subject to the same level of oversight and operational rigor as wastewater treatment plants, the latter of which appears necessary to thoroughly treat PAHs.

There are still many parts of the country where stormwater routing is insufficient in both time and length to reduce toxicity to receiving waters. Directly connected surfaces can deliver large volumes and concentrations of toxic substances in runoff during and after a sufficient rainfall event. In a study by Scoggins et al. (2007), PAHs were measured in the receiving water downstream of parking lots with a corresponding reduction in the biodiversity of benthic communities.

Due to the expense of retrofitting control measures into existing stormwater sewage and discharge systems, many municipalities may opt for banning coal tar-based sealants due to PAH content and related chronic toxicity effects on the environment. An alternative is to implement retrofitted stormwater controls at the point of discharge; however, there is currently no authorizing regulatory framework nationally. Implementation of a retrofitted stormwater treatment and control system would require a municipality to manage and control sediments collected in the control system, including those sediments contaminated by PAHs. Crane et al. (2010) found high enough concentrations of PAHs in stormwater BMPs to require contaminated sediment disposal, an additional expense to municipalities.

Sealant Application Issues

The Pavement Coatings Technology Council has issued a fact sheet regarding the correct application of sealant in order to reduce PAH impacts to receiving waters. The recommendations include: ensuring that no significant rainfall will occur within forty-eight hours after sealant application; applying sealant when temperatures are higher than 15°C and rising; and prohibiting parking for at least twelve hours after sealant application (Pavement Coatings Technology Council, 2010). These recommendations may differ from the manufacturer's instructions given on the containers for sealant products.

A regional analysis dividing the continental U.S. into eight regions found that the mean interval for runoff-producing rainfall events in the summer ranges from a low of 76 hours in the Northeast, to a high of 425 hours in the arid Southwest; annual means range from 73 hours to 277 hours (Driscoll et al., 1986). All eight regions have coefficient of variations exceeding values of 1, which indicates that the standard of deviation of the predicted period between storms never drops below that predicted period. One therefore cannot statistically predict the period between rainfall events to a precision that would eliminate the potential for runoff. Sub-regional and local analysis may increase the precision of inter-event period, but broad metrics like these are typically used in stormwater routing and treatment design.

Future Research Needs

The literature is still lacking an in-depth study of asphalt sealant runoff examining both coal tar sealants or asphalt emulsion alternatives and the potential for acute toxicity, or lack thereof, to aquatic organisms in the water. Unless runoff samples are measured for PAH content and tested for toxicity, there is no direct linkage to the acute toxicity threat to aquatic life in receiving waters due to the prevailing assumption in the literature that PAHs are attached to particulate matter, and that the resulting water quality issue is primarily a problem of contaminated sediment and associated chronic toxic effects. The needed study must evaluate multiple screening studies for health endpoints so as to pass adequate judgment on the toxicity discussion.

Alternatives to asphalt- and coal tar-based sealants are limited. There are acrylic co-polymers available on the market but they are more expensive; although they claim to be less toxic, the actual toxicity of these alternatives is unknown. Some organic concrete sealants include acrylic sealers, epoxy coatings, urethane sealants, polyureas, and polyaspartics but these may not be relevant to sealing asphalt. The ability of these concrete sealants to be effective on unsealed asphalt surfaces is unknown. Future research needs include finding an inexpensive alternative to either asphalt- or coal tar-based products (i.e., new soy-based sealants).

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