



City of Tacoma
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RE: NPDES Municipal Stormwater Permit, Thea Foss Waterway Stormwater Work Plan
Addendum, Quality Assurance Project Plan Update – PCB Method Change and QAPP
Addendum

Dear Ms. Vincent and Ms. Koch:

The City received an email dated May 4, 2020 with Ecology's comments related to the current (2014) Quality Assurance Project Plan (QAPP) for the Thea Foss Waterway Stormwater monitoring program. During development of the new QAPP for monitoring under the 2019 Permit, the City became aware of a typographical error relating to the method used by the laboratory to analyze for PCB aroclors. Table 3-2, Sediment Methods and Detection Limits Goals listed EPA Method 8082 instead of the previously approved EPA method of 8270. Per Ecology's request, the City is submitting updated excerpts from the current QAPP to resolve these discrepancies and a detailed discussion of the PCB method change and method comparison (Appendix A).

Enclosed for your consideration is an Addendum to the City's 2014 QAPP that includes excerpted pages from the document to show the specific updates and additions.

1. Title Page with updated Signatures
2. Updated Distribution List
3. Updated Table of Contents
4. Table 3-2: Sediment Methods & Detection Limits Goals
5. Table 9-2: Sediment Container, Preservation, and Holding Times
6. Appendix A: PCB Method Change Discussion

Please contact Laura Nokes at 253.502.2274 if you have any questions regarding this Addendum. Once the PCB method change is approved, the City will re-submit the new QAPP for the 2019 Permit in its entirety with these revisions incorporated for final approval.

Sincerely,

John Burk, P.E.

John Burk, P.E.
Environmental Services Division Manager

(Response to Ecology Comments)

Enclosure

cc: Brandi Lubliner, Department of Ecology, Quality Assurance Coordinator
Angela Gallardo, City of Tacoma, Environmental Services
Merita Trohimovich, City of Tacoma, Environmental Services

File: Ecology - NPDES

Thea Foss and Wheeler-Osgood Waterways Stormwater Monitoring Quality Assurance Project Plan



September 2014

Prepared for

Washington State Department of Ecology and
U.S. Environmental Protection Agency

Prepared by

City of Tacoma



1.0 TITLE PAGE WITH APPROVALS**Quality Assurance Project Plan**

Thea Foss and Wheeler-Osgood Waterways Stormwater Monitoring for the Thea Foss Consent Decree and Phase I Municipal Stormwater NPDES Permit

Review and Approval

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<i>Dana Blake DeLeon</i>	05/29/20
QA Coordinator (Dana De Leon, P.E.)	Approved On:
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Laboratory Manager (Stuart Magoon)	Approved On:
<i>Angela Vincent</i>	6/12/2020
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<i>Brandi Lubliner</i>	6/9/20
Ecology WQP Quality Assurance Coordinator (Brandi Lubliner)	Approved On:

I certify under penalty of law, that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gathered and evaluated the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for willful violations.

John Burk, P.E. Date: 06/03/20

John Burk, P.E.
Environmental Services, Science and Engineering Division Manager

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Appendix A	PCB Method Change Discussion
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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
BMP	Best Management Practice
BNSF	Burlington Northern Santa Fe
CD	Consent Decree
CFS	Cubic Feet per Second
City	City of Tacoma
COC	Chain of Custody
COCs	Contaminants of Concern
CRM	Certified Reference Material
CTP	Central Treatment Plant
CUW	Center for Urban Waters
DEHP	Di-2-ethylhexyl phthalate (Bis(2-ethylhexyl) phthalate)
DLG	Detection Limit Goals
DQI	Data Quality Indicator
DQA	Data Quality Assessment
DQO	Data Quality Objective
Ecology	Washington State Department of Ecology
EMC	Event Mean Concentrations
EPA	Environmental Protection Agency
ESSE	Environmental Services Department, Science and Engineering Division
FWDA	Foss Waterway Development Authority
IQR	Interquartile Range
LCS	Laboratory Control Sample
LD	Laboratory Duplicate
LIMS	Laboratory Information Management System
MDL	Method Detection Limit
MLLW	Mean Lower Low Water
MQO	Measurement Quality Objective
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
OF	Outfall
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated biphenyls
Permit	NPDES Phase I Municipal Stormwater Permit
QA/QC	Quality Assurance/Quality Control
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan

RL	Reporting Limit
RPD	Relative Percent Difference
RSMP	Regional Stormwater Monitoring Program
SIDIR	Source Identification Information Repository
SOP	Standard Operating Procedure
SR	State Route
SSPM	Stormwater Suspended Particulate Matter
SWMP	Stormwater Management Program
TPH	Total Petroleum Hydrocarbons
TSS	Total Suspended Solids
USGS	United States Geological Survey
UWT	University of Washington Tacoma
WY	Water Year

Table 3-2
Sediment Methods and Detection Limit Goals

Analyte	Analysis Method	Detection Limit Goal	Foss and/or NPDES Parameter
Conventionals			
Total Organic Carbon	9060 Mod	0.1%	Foss/NPDES
Grain Size	ASTM D422	NA	Foss/NPDES
Total Solids	SM 2540G	1%	Foss/NPDES
Total Volatile Solids	SM 2540G	0.1%	NPDES
Metals			
Total Recoverable Cadmium	EPA 6020A or 6010	0.1 mg/kg	NPDES
Total Recoverable Copper	EPA 6020A or 6010	0.1 mg/kg	NPDES
Total Recoverable Lead	EPA 6020A or 6010	0.1 mg/kg	Foss/NPDES
Total Recoverable Mercury	EPA 7471B	0.005 mg/kg	Foss/NPDES
Total Recoverable Zinc	EPA 6020A or 6010	0.5 mg/kg	Foss/NPDES
PAHs¹			
2-Methylnaphthalene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Acenaphthene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Acenaphthylene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Anthracene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Benzo(a)anthracene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Benzo(a)pyrene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Benzo(g,h,i)perylene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Benzo(b,k)fluoranthenes ²	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Chrysene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Dibenz(a,h)anthracene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Fluoranthene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Fluorene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Indeno(1,2,3-cd)pyrene	EPA 8270E SIM	70 µg/kg dry	Foss ¹
Naphthalene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Phenanthrene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Pyrene	EPA 8270E SIM	70 µg/kg dry	Foss/NPDES
Phthalates			
Di(2-ethylhexyl)phthalate	EPA 8270E SIM	70 µg/kg dry	Foss
Butylbenzylphthalate	EPA 8270E SIM	70 µg/kg dry	Foss
Diethylphthalate	EPA 8270E SIM	70 µg/kg dry	Foss
Dimethylphthalate	EPA 8270E SIM	70 µg/kg dry	Foss
Di-n-butylphthalate	EPA 8270E SIM	70 µg/kg dry	Foss
Di-n-octyl phthalate	EPA 8270E SIM	70 µg/kg dry	Foss
Insecticides			
Bifenthrin	EPA 8270E SIM	1 µg/kg dry	NPDES
PCBs³			
Aroclor-1016	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Aroclor-1221	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Aroclor-1232	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Aroclor-1242	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Aroclor-1248	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Aroclor-1254	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Aroclor-1260	EPA 8270E SIM	80 µg/kg dry	Foss/NPDES
Nutrients			
Total Phosphorus	EPA 365.4	0.01 mg/kg	NPDES
Total Petroleum Hydrocarbons			
NWTPH-Diesel	NWTPH-Dx	25 mg/kg dry	Foss/NPDES
NWTPH-Heavy Oil	NWTPH-Dx	50 mg/kg dry	Foss/NPDES

SIM refers to Selective Ion Monitoring

¹ Appendix 9 lists 2,6-Dimethylnaphthalene, which is not part of the City laboratory's PAH method. Instead of reporting 2,6-Dimethylnaphthalene, the City will report the acenaphthene, acenaphthylene, anthracene, dibenz(a,h)anthracene, fluorene, and indeno(1,2,3-cd)pyrene to Ecology to fulfill the Permit requirement.

² Benzo(b)fluoranthene and benzo(k)fluoranthene coelute and are reported as a combined parameter, benzo(b,k)fluoranthenes

³ EPA method 8270 was used for PCB analysis for the duration of this QAPP's monitoring permit. Appendix A documents the historic change from EPA method 8082 to EPA method 8270E and the methodology that went into this decision. EPA method 8270D was updated to EPA 8270 in August 2019 as required by the EPA method update rule.

Table 9-2
Sediment Container, Preservation, and Holding Time

Parameter	Container ¹	Preservation	Maximum holding time	Reference ²
Total solids	P, FP, G	Cool, ≤6 °C	7 days.	40 CFR 136
Grain size	P, FP, G	Cool to 4°C	6 months	PSEP 1997
Total organic carbon	P, FP, G	Cool to 4°C	14 days, 12 mos if frozen to -18°C	PSEP 1997
Total recoverable metals (zinc, lead, copper, cadmium)	P, FP, G	Cool to 4°C	6 months	EPA200.8
Total recoverable mercury	P, FP, G	Cool to 4°C	28 days	EPA7471
PAH	G, FP-lined cap	Cool to 4°C	14 days, 12 mos if frozen to -18°C	PSEP 1997
Phthalates	G, FP-lined cap	Cool to 4°C	14 days, 12 mos if frozen to -18°C	EPA8270D
Phenolics	G, FP-lined cap	Cool to 4°C	14 days, 12 mos if frozen to -18°C	PSEP 1997
PCBs	G, FP-lined cap	Cool to 4°C	14 days, 12 mos if frozen to -18°C	PSEP 1997
Pesticides	FP, G	Cool to 4°C	14 days, 12 mos if frozen to -18°C	EPA8270D
Pyrethroids (bifenthrin)	G, FP-lined cap	Cool to 4°C	14 days, 12 mos if frozen to -18°C	EPA8270D

¹“P” is polyethylene; “FP” is fluoropolymer (polytetrafluoroethylene (PTFE; Teflon[®]supreg;), or other fluoropolymer, unless stated otherwise in this Table II; “G” is glass; “PA” is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); “LDPE” is low density polyethylene.

²40CFR136 Accessed August 13, 2008; Puget Sound Estuary Protocols 1997, EPA Method 8270D – revision 4 (2007). EPA Method 8270D was updated to EPA Method 8270E as required by the 2018 EPA Method Update Rule.

Appendix A.

Change of Analysis methods of Chlorinated Pesticides and Polychlorinated Biphenyls from EPA 8081/8082 (Gas Chromatograph/Electron Capture Detector) to 8270 (Gas Chromatograph/Mass Spectrometer).

The City of Tacoma (City) notifies Ecology of minor updates to the City's NPDES monitoring programs Quality Assurance Project Plan (QAPP) through annual data validation reports. Significant changes to the QAPP are negotiated with EPA and Ecology through communications and QAPP amendments prior to implementation. Recently it was noted the analysis method for PCBs listed in the 2014 QAPP (Tacoma 2014) did not match what has been used in this project. The change was made prior to the 2014 QAPP for both chlorinated pesticides (EPA 8081 – Superfund required) and PCBs (NPDES and Superfund). The following describes the change in analysis methods, with emphasis placed on PCB analyses.

The City changed legacy pesticide and PCB laboratory methods from EPA8081/8082 to 8270C in 2007. Method 8270 was subsequently updated in accordance with EPA Method Update Rules to 8270D in 2008 and 8270E in 2018. The City obtained and annually maintained Ecology accreditation for 8270 since 2007. The City is currently State accredited for PCB analysis by method 8270E_6 (as well as 625.1, accreditation #G681-19c).

A.1 Background

The City stormwater sampling program fulfills both the City's Superfund and NPDES obligations. The program started in 2001 under Superfund requirements, and incorporated new NPDES requirements in 2007. At the start of the NPDES program, Superfund monitoring guidance (restricted to 40CFR136) conflicted with Ecology guidance for certain surface water analyses (i.e., SW846 surface water methods were not contained within 40CFR at the time). In WY2009 based on the new NPDES permit requirements, the City was required to analyze several parameters twice, in some cases using the same science but different QAQC procedures, in order to meet the varying regulatory requirements. In the WY2009 Data Validation Report (Tacoma 2010), the City presented a regulatory harmonization scheme for surface water and Suspended Sediment Particulate Matter (SSPM) for use in WY2010. Relevant language includes, 'The intent of harmonization is to bring all methods up to date with current accreditations, permits and authorities. While several methods are equivalent for each test, the chosen method was prioritized by:

- Special approval by EPA regional administrator (hardness, method 200.8)
- Accreditation by Ecology's Laboratory Accreditation Unit (LAU), a requirement for all data submitted to Ecology for regulatory decision-making (Superfund or otherwise, Ecology 2006 and Ecology 2004)
- Being listed as an acceptable method in Appendix 9 of the Phase I Municipal Stormwater Permit
- Being listed within the current federal guideline establishing test procedures for the analysis of pollutants (40 CFR Part 136) current as of March 7, 2011.' (Tacoma 2010).

The harmonization scheme stated the intent to move the PCB method from 8082 to 8270D in the following water year, and presented tables detailing guidance for use under Superfund, Clean Water Act and Ecology permitting; and implications for meeting quality control

performance and required reporting limits. Harmonization also included utilization of the lowest detection limits of either the Superfund or NPDES monitoring programs.

The tables and discussion describing the switch between EPA 8082 and 8270 appeared in WY2010-WY2012 Data Validation Reports. Subsequent data validation reports (2013, 2014) and the 2014 QAPP contained an incorrect analytical methods table listing method EPA 8082 and a sample containers table listing 8270. Thereafter the incorrect table stating EPA method 8082 was mistakenly used in data validation reports.

PCB QC performance greatly improved following the change in methods. Detection limit targets were being met and performance evaluation was the focus of data validation reports. Tracking of what was thought to be a consistent method was not emphasized since QC performance greatly improved.

A.2 Decision for Change

Methods 8081/8082 and 8270 use a gas chromatograph (GC) to separate compounds for analysis. The detector is the primary variable. Traditionally, the electron capture detector (ECD) used in method 8081/8082 was more sensitive and specific (in terms of identification) than the mass spectrometer (MS) used in method 8270. As the City's MS capabilities improved, especially through use of selective ion monitoring (SIM), support for a switch to GC/MS increased. Several factors contributed to the desire for change:

A.2.1 Detection Limits and Quality Control Performance The most important justification for changes include accuracy of identification in difficult matrices (which is difficult to quantify in this addendum), detection limit and quality control performance. Detection limits and QC performance are presented below.

Sensitivity. Performance evaluates the variability of reported method detection limits, on a per sample basis, due to background noise, analytical/matrix issues, sample size and procedural changes. A performance method detection limit (pMDL) greater than the reporting limit goal, for non-detect data, represents a loss of information and a measurement quality objective (MQO) exceedance. If a compound is detected and the pMDL is greater than the detection limit goal, then no information is lost. The pMDL is considered a rejection data point if the pMDL (for a nondetect result) is greater than five times the reporting limit goal, recognizing a significant loss of information. The detection limit MQO for the 2014 Quality Assurance Project Plan is 80 µg/kg. Table 1 presents method detection limit performance results for 2005-2006 by GC/ECD (method 8081/8082) and 2010-2019 by GC/MS (method 8270). Target detection limits were achieved in 99% of tests conducted under the 2014 QAPP.

Laboratory Analysis Recovery. Recovery of 'known' concentrations of analytes is useful when estimating sample bias (see Tables 2 and 3). Bias is reported as a percent of the true value. For instance, an analyte which has a low recovery (ideal is 100%, low is 30%) across the majority of control samples (surrogate, laboratory control sample, matrix spike, certified reference material) will be classified as 'biased low'. This means the reported sample result is likely an underestimate of the actual environmental concentration. Underestimation is more common for analyte recoveries than overestimation. Bias control samples take several forms:

- A surrogate is a pure substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.
- The laboratory control sample (LCS) is an uncontaminated sample matrix spiked with known amounts of analytes from a source independent from the calibration standards.
- The Matrix Spike (MS) is a sample which is spiked with a known amount of an analyte. The difference in MS and LCS recoveries is a function of the sample matrix (chemistry). This is also called the matrix effect.
- A Certified Reference Material (CRM) is a type of LCS that has been tested and characterized by several certified laboratories (20 or more).

Table 1. Detection Level Performance (µg/kg)

Aroclor	GC/ECD							GC/MS						
	1016	1221	1232	1242	1248	1254	1260	1016	1221	1232	1242	1248	1254	1260
N	33	32	32	32	33	33	31	155	155	155	155	155	157	155
Min	10	10	10	10	10	12	10	1	1	1	0.8	0.8	0.8	0.8
5%	10	10	10	10	10	12	10	1	1	1	0.8	0.8	0.8	0.8
10%	11	11	11	11	11	12	11	2	2	2	1	1	1	1
25%	12	12	12	12	12	18	12	2	2	2	2	2	2	2
Med	30	30	30	30	30	33	30	8	8	8	6	6	6	6
75%	48	48	48	48	48	48	48	11	11	11	10	19	19	19
90%	55	121	102	87	82	80	110	17	17	17	17	20	20	20
95%	158	158	158	158	158	118	152	22	22	22	22	56	52	56
Max	310	310	310	310	310	160	160	38	22	22	22	86	86	86

Dates align with readily available data (2005-2006 and 2010-2019)

GC/ECD Gas Chromatograph/Electron Capture Detector performance data 2005-2006

GC/MS Gas Chromatograph/Mass Spectrometer performance data 2010-2019

Measurement Quality Objective is 80 µg/kg

A.2.2 Surrogates. A primary issue with the 8081/8082 analysis involved surrogate recoveries (Table 2). Performance indicated the analysis was highly variable, providing both positive and negative bias depending on the analytical run. While performance improved from 2005 to 2006 (conducted by separate commercial laboratories), surrogate performance was less than desirable and GC/MS appeared the better option. Resultant data has less variability and bias. NPDES sites have been sampled since 2001 and continue through this and the future (WY2021) QAPPs.

Table 2. Surrogate Performance

%Recovery Surrogate	GC/ECD		GC/MS	
	Decachlorobiphenyl	Tetrachloro-m-xylene	Decachlorobiphenyl	Tetrachloro-m-xylene
N	82	82	78	77
Stdev	143.9	25.1	18.3	18.3
Min	0	8	55	49
5%	0	49	60	62
10%	4	60	85	65
25%	80	71	95	68
Med	99	80	104	87
75%	162	93	112	103
90%	384	107	123	107
95%	435	119	136	112
Max	745	173	147	121

Dates align with readily available data (2005-2006 and 2010-2019)

GC/ECD Gas Chromatograph/Electron Capture Detector performance data 2005-2006

GC/MS Gas Chromatograph/Mass Spectrometer performance data 2010-2019

Measurement Quality Objective is 50% to 150%

Censor (qualify data and bias assessment) range <25% and >175%

A.2.3 Laboratory control sample, matrix spike/duplicate and certified reference materials.

The SSPM analysis is performed annually, therefore there are very few companion LCS, MS and CRM results for comparison. LCS recoveries are slightly lower, and MS recoveries slightly higher for GC/MS analysis when compared to GC/ECD. One CRM was run in 2006 and the recovery was 33% for Aroclor 1254. CRM were run yearly from 2010 through 2019 with a median recovery of 99% and a range of 88% to 114%. CRMs are the ideal measure of acceptable bias since they incorporate variability of performance due to sample matrix, spiking, extraction and analysis. The Prediction Interval of the CRM describes a range of recoveries that is achievable by 19 of 20 laboratories, and the interval is 34% to 165% for Aroclor 1254. City of Tacoma performance since switching to the GC/MS is well within this range.

Table 3. Laboratory Control Sample, Matrix Spike and Certified Reference Material performance

%Recovery Aroclor	LCS			MS*			CRM	
	GC/ECD	GC/MS	GC/MS	GC/ECD	GC/MS	GC/MS	GC/ECD	GC/MS
	1242	1260	1260	1242	1260	1254	1254	1254
N	9	9	18	6	6	12	1	8
Stdev	10.7	13.5	18.0	44.6	10.7	33.0		7.8
Min	80	82	38	83	88	91		88
5%	82	86	42	85	89	95		90
10%	83	90	60	86	90	99		91
25%	86	92	72	90	94	102		94
Med	90	97	79	92	104	107	33	99
75%	103	114	91	96	111	116		101
90%	103	114	99	96	111	176		106
95%	108	120	101	174	113	187		110
Max	111	122	109	199	113	193		114

Dates align with readily available data

LCS Laboratory Control Sample

MS Matrix Spike

CRM Certified Reference Material

GC/ECD Gas Chromatograph/Electron Capture Detector performance data 2005-2006

GC/MS Gas Chromatograph/Mass Spectrometer performance data 2010-2019

Measurement Quality Objective is 50% to 150%

Censor (quality data and bias assessment) range <25% and >175%

A.2.4 Other Factors for Change. In addition to improved detection limits and recovery performance, the following supported a change in methods,

- **Identification and difficult matrices.** Urban sediment traps collected in the Thea Foss system tend to have a wide variety of difficult matrices, including oils, plastics/precursors, a high organic load and/or saltwater saturation (some sites). ECD is able to gain low detection levels but quantification is less reliable in difficult matrices. When variability is increased, then the information gained from a lower detection level is reduced. Use of GC/MS Selective Ion Monitoring improved identification, lowered detection limits and improved recovery performance.
- **Efficiency.** Replacing ECD analyses with a more comprehensive GC/MS analysis improves efficiency through:
 - The ECD requires maintenance of a radiation source and associated monitoring/permitting requirements. Safety is improved and the regulatory burden lessened.
 - Staff time and expertise is increased on an instrument system that performs additional NPDES analytes and Superfund contaminants of concern including PAHs, phthalates and pesticides, along with PCB development.
 - Capital funds are preserved, allowing access to more sensitive detectors (triple quadrupole).

A.3 Conclusion

GC/MS has been listed as a confirmation technique for 8082 since 2007, as long as the desired sensitivity was achieved (EPA 2007). Both the ECD and MS detector methods met City detection level needs for pollutant source control, effectiveness evaluation and stormwater characterization. Therefore, the method was changed to the one which was more reliable with the matrices the City encounters and was more efficient, the GC/MS.

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