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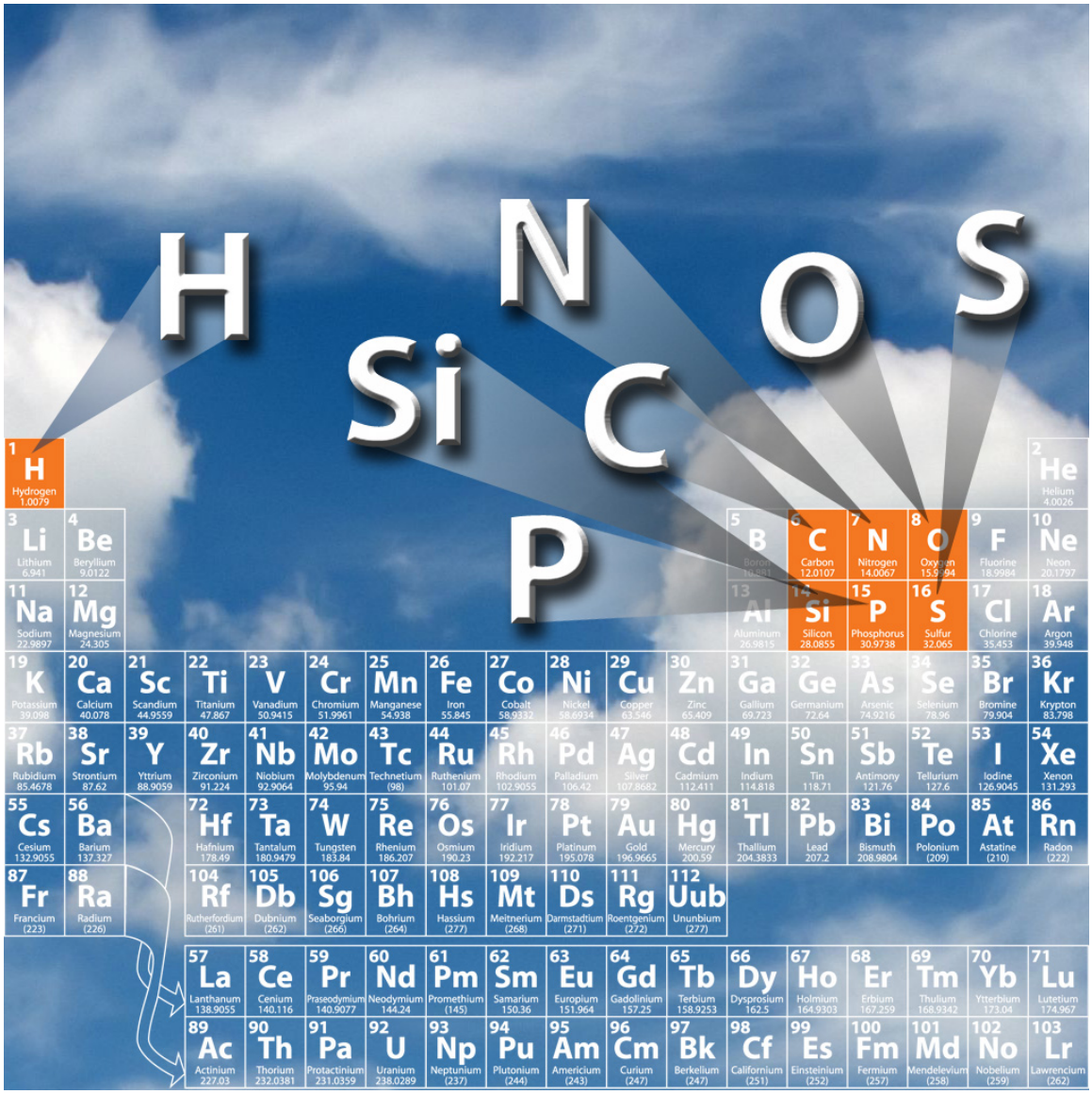
Report on the Elemental Analyses of Samples from the Targeted National Sewage Sludge Survey



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Washington, DC 20460

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Acknowledgments and Disclaimer

The original Targeted National Sewage Sludge Survey (TNSSS) (USEPA, 2009a and 2009b)was made possible by the assistance and cooperation of numerous staff working at each of the sewage treatment facilities involved. The staffs of the facilities contacted during the course of TNSSS were, without exception, knowledgeable, friendly, helpful, and deservedly proud of their efforts to protect the environment and serve their local constituencies.

This document summarizes the elemental analysis of archive samples from the TNSSS and has been reviewed and approved for publication online by the Office of Science and Technology. This report was prepared with the support of CSC, under the direction and review of the Office of Science and Technology. The report describes the sampling and analysis activities performed by CSC and its subcontractors under EPA Contract EP-C-05-045 in a follow-up to EPA's TNSSS and presents summary level data from the elemental analyses of sewage sludge samples.

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Executive Summary

This report describes the sampling and analysis activities performed in a follow-up to the Environmental Protection Agency's (EPA) Targeted National Sewage Sludge Survey (TNSSS) (USEPA, 2009a and USEPA, 2009b) and presents summary level data from the elemental analyses of sewage sludge samples. The Health and Ecological Criteria Division (HECD) and the Engineering and Analysis Division (EAD) within EPA's Office of Water, Office of Science and Technology, jointly conducted the original survey. The elemental analyses were conducted as a follow-up activity not associated with the original survey, but employing archived sewage sludge samples from the TNSSS for the analyses of specific elements.

The objective of the analyses was to obtain data on the concentrations of specific elements and other measures of sewage sludge quality. One goal of the elemental analyses effort was to help further determine the makeup of sewage sludge (e.g., what macro constituents occur in sewage sludge). EPA was interested in determining what percentage of the total mass of the biosolids in the TNSSS specifically, and other biosolids in general, consists of the elements carbon, hydrogen, nitrogen, oxygen, sulfur, and silicon, as well as other major constituents. These results may be used to help further identify constituents of sewage sludge.

The original survey sampling effort successfully collected sewage sludge from 74 randomly selected publicly owned treatment works (POTWs), or Water Resource Recovery Facilities (WRRFs), in 36 states. Sample collection began in late August 2006 and continued through late March 2007. Following collection of TNSSS samples that were analyzed for metals, anions, organics, brominated flame retardants, pharmaceuticals, steroids, and hormones, EPA archived additional samples at a sample repository in Baltimore, Maryland, where they were stored frozen for possible future use.

In July 2009, 66 archive samples were submitted from the repository to a laboratory for elemental analyses. These 66 samples were selected based on the availability of materials in the archive and included samples from 62 facilities, as well as from four facilities that produce more than one type of final sewage sludge product.

The results of the study are provided below. The results are provided as a summary of the results for the 66 TNSSS archive samples analyzed, listing the minimum, maximum, mean, and median results for each parameter. All sample results are reported in percent dry weight.

Summary Results

	All Results in Weight Percent, on a Dry-Weight Basis			
Parameter	**Minimum**	**Maximum**	**Mean**	**Median**
Carbon	12.90	46.31	31.17	31.39
Hydrogen	0.18	6.69	3.94	4.09
Nitrogen	1.15	7.94	3.84	3.97
Oxygen	5.17	29.27	19.64	20.43
Sulfur	0.13	4.05	1.32	1.18
TOC	10.39	45.27	29.93	30.77
TIC (calculated)*	0.00	7.45	1.37	1.02
Silica, Total	3.10	43.50	13.84	10.97
Silicon†	1.45	20.33	6.47	5.13

*In instances where the TOC result was greater than or equal to the result for total carbon, the laboratory reported TIC as "TOC ≥ TC." TIC was converted to 0.00 for the purposes of the survey.

†The results for silica (SiO_2) were converted to silicon (Si) by multiplying the silica result by 0.4675, which is the percentage by weight of Si in SiO_2.

Section 1
Background and Organization

1.1 Background

EPA conducted previous sewage sludge surveys. For example, EPA conducted a National Sewage Sludge Survey (NSSS) in 1988–1989 (USEPA, 1992 Volume I and II) to obtain unbiased national estimates of the concentrations of more than 400 pollutants in sewage sludge collected from 174 wastewater treatment plants that practiced at least secondary wastewater treatment.

EPA conducted a second National Sewage Sludge Survey in 2001(USEPA, 2001) to obtain updated national estimates of dioxins and dioxin-like compounds in sewage sludge managed by land application.

EPA conducted a third survey, the Targeted National Sewage Sludge Survey (TNSSS) in 2009 (USEPA, 2009a and 2009b), to obtain updated concentration data for a group of pollutants that it identified for further evaluation and to support analyses of new and emerging contaminants, including pharmaceuticals, personal-care products, steroids, and hormones. As part of that effort, EPA archived additional samples from each of the facilities in the survey for possible future analyses.

1.2 Elemental Analyses

Some of the archived material from the TNSSS was used to obtain data on the concentrations and support analyses of the elements carbon, hydrogen, oxygen, nitrogen, sulfur, and silicon, as well as other measures of sewage sludge quality (e.g., phosphrous, total organic carbon, and total, fixed, and volatile solids) that may be used to help further identify constituents of sewage sludge.

1.3 Content of this Report

Many details regarding study design and sampling can be found in the original TNSSS reports (USEPA, 2009a and USEPA, 2009b). This report focuses on the results from the elemental analyses of the TNSSS samples and presents summary level data relevant to the elemental analyses in the following topics:

- Study Objective and Design
- Sample Collection
- Sample Analyses
- Data Review Procedures
- Study Results
- References

Section 2
Study Objective and Design

2.1 Study Objective

The objective of the analyses was to obtain data on the concentrations of specific elements and other measures of sewage sludge quality as a follow-up to the Environmental Protection Agency's (EPA) Targeted National Sewage Sludge Survey (TNSSS) (USEPA 2009a and 2009b). The objective of the broader original TNSSS was to obtain national estimates of percentiles of concentrations for select pollutants in sewage sludge. EPA used a stratified random sampling design to select publicly owned treatment works (POTWs), or Water Resource Recovery Facilities (WRRFs), to be sampled. The target population and the selection process are briefly outlined below. Additional details regarding the survey design and the facility selection process are described in the TNSSS Sampling and Analysis Technical Report (USEPA, 2009a, as well as TNSSS Statistical Analysis Report (USEPA, 2009b).

2.2 Target Population

EPA defined the target population for the TNSSS as WRRFs that met the following criteria:

- Existed in 2002 or 2004
- Have flow rates greater than or equal to 1 million gallons per day (MGD)
- Employ at least secondary treatment
- Produce a final treated biosolid product
- Are not known to employ a pond or lagoon as the final stage of treatment
- Located in the contiguous United States.

Beginning with a national estimate of 16,255 WRRFs, EPA narrowed the list to 3,337 WRRFs that met the definition of the target population mentioned above that represented about 94% of the flow in the country. EPA originally selected a national sample of 80 WRRFs from that list of 3,337 facilities in the target population, using a stratified design. The final selection of facilities reduced the total number of facilities to 74 WRRFs in 36 states for the reasons described below.

2.3 Stratification

EPA selected WRRFs using a random sampling design stratified for flow. EPA divided the 3,337 facilities into three categories, or strata, based on their design flow:

- 1 to 10 MGD, representing approximately 75% of the WRRFs nationwide
- 10 to 100 MGD, representing approximately 15% of the WRRFs nationwide
- greater than 100 MGD, representing approximately 10% of the WRRFs nationwide

After EPA determined the total number of facilities to be included in the study, EPA selected a proportionate number of WRRFs from each stratum at random.

2.4 Final Selection

Figure 1 presents a map of the contiguous United States showing the approximate locations of the 80 WRRFs original randomly selected for this survey. The purpose of this figure is to illustrate the national scope of the survey. It does not indicate locations of specific wastewater discharges.

Figure 1. Geographic Distribution of 80 WRRFs Originally Selected for Sampling

EPA sent each facility a formal written invitation, which was followed by a telephone call. These initial telephone contacts identified a small number of facilities that provided only partial treatment or were not of interest for this survey. Ultimately, EPA determined that samples would be collected at the 74 facilities listed in Table 2. As noted earlier, additional details on the facility selection process can be found in USEPA (2009a and 2009b).

The 66 archived samples submitted for elemental analysis for this effort represent 62 of the 74 facilities in Table 2 (four of those 62 facilities produce more than one final product). The choice of the specific samples to be analyzed was based largely on the number and / or condition of containers remaining in the EPA sample archive. Not all of the original sample volume that had been sent to the laboratories for analyses of analytes for the original TNSSS effort, and that had been shipped back to be archived, was in good shape; some samples were broken in transit, lost in laboratory accidents, or where not used due to data quality concerns. Therefore, some samples were not suitable for elemental analysis. Samples from 12 facilities for which elemental analyses were not performed are shown at the end of Table 2.

Table 2. 74 WRRFs Originally Sampled, by State and City

Facility Name	City	State
Sugar Creek WWTP	Alexander City	AL
Aldridge Creek WWTP	Huntsville	AL
Valley Sanitary District STP	Indio	CA
San Francisco	San Francisco	CA
El Estero WWTP	Santa Barbara	CA
Santa Rosa	Santa Rosa	CA
Stockton Water Quality Plant	Stockton	CA
Los Angeles County Sanitation District	Whittier	CA
Boulder WWTP	Boulder	CO
South Windsor	South Windsor	CT
Three Oaks WWTF	Estero	FL
Orange County Northwest WRF	Orlando	FL
Tampa	Tampa	FL
Albany	Albany	GA
Americus-Mill Creek	Americus	GA
Boone STP	Boone	IA
Calumet Water Reclamation Plant	Chicago	IL
Plainfield WWTP	Plainfield	IL
Lake County DPW, New Century STP	Vernon Hills	IL
Blucher Poole WWTP	Bloomington	IN
William Ross Edwin WWTP	Richmond	IN
Parsons	Parsons	KS
Topeka	Topeka	KS
Mayfield WWTP	Mayfield	KY
Eunice	Eunice	LA
Jefferson Parish East Bank WWTP	Marrero	LA
Nantucket	Nantucket	MA
Mechanic Falls Treatment Plant	Mechanic Falls	ME
Benton Harbor-St. Joseph WWTP	St. Joseph	MI
Wixom WTP	Wixom	MI
Elizabeth City WWTP	Elizabeth City	NC
Beatrice	Beatrice	NE
Wildwood Lower WTF	Cape May Court House	NJ

Middlesex County Utility Authority WRC	Sayreville	NJ
Verona TWP DPW	Verona	NJ
Buffalo	Buffalo	NY
Geneva A-C Marsh Creek STP	Geneva	NY
North Tonawanda STP	North Tonawanda	NY
Clermont County Commissioners	Batavia	OH
Metropolitan Sewer District Little Miami WWTP	Cincinnati	OH
Delaware County Alum Creek WWTP	Delaware	OH
Mingo Junction STP	Mingo Junction	OH
City of Klamath Falls WWTF	Klamath Falls	OR
Western Westmoreland Municipal Authority	Irwin	PA
Allegheny County sanitary Authority	Pittsburgh	PA
Greater Pottsville Area Sewer Authority	Pottsville	PA
Punxsutawyney	Punxsutawney	PA
South Kingstown WWTF	Narragansett	RI
Plum Island WWTP	Charleston	SC
Lawson Fork WTP	Spartanburg	SC
Elizabethton	Elizabethton	TN
Amarillo	Amarillo	TX
Dallas Southside WWTP	Dallas	TX
Trinity River Authority of Texas	Ellis County	TX
Fredericksburg	Fredericksburg	TX
Odo J. Riedel Regional WWTP	Schertz	TX
Wagner Creek WWTP	Texarkana	TX
Spanish Fork City Corporation	Spanish Fork	UT
Buena Vista	Buena Vista	VA
Beaver Dam	Beaver Dam	WI
Elkins WWTP	Elkins	WV
Huntington	Huntington	WV
Facilities for which elemental analyses were not performed due to lack of archived material		
Phoenix WWTP	Phoenix	AZ
Dupage County-Knollwood STP	Wheaton	IL
Salisbury	Salisbury	MD
Festus Crystal City STP	Crystal City	MO
Hillsborough WWTP	Hillsborough	NC
Canajoharie WWTP	Canajohaire	NY
NYC DEP - Jamaica WPCP	New York City	NY
Bedford	Bedford	OH
Northeast Ohio Regional S D Southerly WWTP	Cleveland	OH
Duncan Public Utilities Authority	Duncan	OK
Tyler Southside WTP	Tyler	TX
Everett City SVC Center MVD	Everett	WA

Section 3
TNSSS Sample Collection

3.1 Sample Collection

For the original TNSSS, EPA collected samples of the final sewage sludge product(s) produced at each of the 74 WRRFs. The TNSSS Sampling and Analysis Technical Report (USEPA, 2009a) describes the sample collection procedures in detail, which was revised periodically as needed during conduct of the survey. A summary of some of the sample collection procedures are provided below for the current effort to analyze for the target elements.

EPA began sampling in August 2006 and completed sampling in March 2007. As described in the original TNSSS report, grab samples were taken using sampling equipment appropriate to the type of sewage sludge products produced (liquid or solid). Liquid samples were collected as free-flowing materials from storage tanks, transfer lines, taps, and hoses. After purging any lines used to collect samples, the liquid samples were placed directly into the final sample containers. If liquid sewage sludge was held in storage tanks, facility staff turned on mixing equipment in such tanks prior to sampling so that the collected liquids would be representative of the bulk product.

Solid samples included dewatered sewage sludge collected from a belt press, filter press, drying bed, centrifuge, compost pile, or other source on site. Small grab samples were collected from multiple areas of any large piles, or multiple grabs from any continuous processes (e.g., belt press), so that samples were more likely to be representative of the bulk product. Several kilograms of material were collected and mixed for each final product. The person collecting the sample composited these small grabs in a large precleaned container of appropriate construction, mixed them well, and transferred the mixed material to the final sample containers. Any excess material remaining after all the sample containers had been filled was returned to the sewage sludge process.

The grabs of solid samples ultimately used for the elemental analyses were collected with a large precleaned plastic serving spoon, mixed in a precleaned plastic wastebasket, and placed in high density polyethylene (HDPE) jars. Separate sampling equipment was used for each facility and all equipment was cleaned with a non-phosphate detergent, rinsed three times with tap water, and then reagent water prior to shipment to the facility.

All containers used to sample sewage sludge for the TNSSS were purchased from commercial suppliers who provided certificates of analysis for common contaminants of interest (e.g., metals, semivolatile organics, pesticides, PCBs). The cleaning procedures applied by the vendors were presumed to be sufficient for the other analytes in the survey for which routine testing by the vendor was not performed.

3.2 Representative Samples

Collecting materials during 2006 to 2007 for the TNSSS that were representative of the bulk sewage sludge product was more difficult at some facilities than at others. For example, at one facility that composted its final sewage sludge, samples were collected from one of the long piles of sewage sludge mixed with woods chips. The sampling piles measured approximately 50 feet long and over 6 feet high, with sides sloping up at roughly a 45 degree angle. Samples were collected from the oldest of the rows at facilities, which ranged from one to six months, depending on the season. The sampler exposed the materials by digging into the side of the pile at roughly six points along its length, on both sides of the pile, and a foot or more off the ground to avoid materials in contact with the concrete substrate.

3.3 Packing and Shipping Samples to the Repository

After all the sample containers were filled and labeled, the sampler packed them for shipping, using procedures described in the sampling and analysis procedures (USEPA, 2009a). The sampler encased the glass jars in bubblewrap bags or layers of bubblewrap sheeting. The HDPE jars sometimes were placed in similar bags, or were packed with loose bubblewrap around them to prevent movement of the jars during shipping. Samples were packed into sturdy plastic ice chests. All of the samples from a given site were packed, with ice and bubblewrap, in either one 48-quart ice chest or two 28-quart ice chests, depending on availability.

Ice was purchased near each facility and packaged in 1-gallon self-sealing plastic bags (in some cases, the facility provided ice). Approximately one pound of ice was used for each sample container (e.g., 4 bags containing 2 pounds of ice each were used to cool 8 samples in a 28-quart ice chest).

Ice chests were shipped overnight from a full-service FedEx office to the sample repository operated by Microbac Laboratories in Baltimore, Maryland. Each sample shipment was tracked until receipt was confirmed at the repository.

When samples arrived at Microbac, the repository staff inspected all the ice chests for external damage or leakage (none occurred). The repository staff did not measure the temperature of the cooler contents on receipt, but placed the samples in one of two walk-in freezers dedicated to EPA samples that were maintained at -11°C. Staff at the repository reported significant amounts of ice still present in the coolers, indicating that the samples were at or below appropriate temperature upon arrival.

3.4 Storage and Shipments to Laboratories

The original TNSSS samples were stored frozen from the time of collection during 2006 to 2007 until early in July 2009 when 66 samples were shipped frozen from the EPA sample repository in Balitmore, MD to the elemental analysis laboratory (Columbia Analytical Services) for elemental analyses. The samples were shipped frozen, with large quantities of dry ice added to each cooler. Two shipments of two coolers each were sent to the elemental analysis laboratory. Despite the fact that one of the shipments was delayed a day en route by FedEx due to weather, all of the samples were received still frozen with visible dry ice remaining in each cooler. The cooler temperatures were recorded on receipt, and were -12^{o}C or lower.

Section 4
Sample Analyses

4.1 Parameters of Interest and Analytical Techniques

The 11 parameters of interest for analysis are shown in Table 3, organized in four categories, along with the analytical techniques employed. Where formal methods exist, they are cited in the table; full citations are provided in USEPA (1996a, 1996b, 1997, 2001), ASTM (2005), and Kahn (1988).

Table 3. Parameters of Interest

Category	Parameter	Analytical Technique or Method
Elements	Total Carbon	EPA Method 440: An aliquot of the air-dried and ground sample is combusted at 950°C, followed by detection of CO_2, H_2O, and N (after reduction of NO_x)
	Hydrogen	
	Nitrogen	
	Oxygen	Modified EPA Method 440: An aliquot of the air-dried and ground sample is heated in a graphite pyrolysis furnace at 1300°C, converting the oxygen to CO_2, which is measured by infra-red detection. This modified method employs an oxygen analyzer module designed specifically for this purpose by the manufacturer
	Sulfur	ASTM Method D4239: An aliquot of the air-dried and ground sample is combusted at 1350°C, followed by infra-red detection of SO_x
Forms of Carbon	Total organic carbon (TOC)	SW-846 Method 9060, as modified by Lloyd Kahn (EPA Region 2): An aliquot of the air-dried and ground sample is pre-treated with HCl to remove inorganic carbon. The sample is combusted at 1350ºC, followed by infra-red detection of CO_2
	Total inorganic carbon (TIC)	TIC is a calculated value, as total carbon minus TOC
Solids	Percent solids (total solids)	An appropriate size aliquot is air dried at 30-40°C until approximately 95% dry. The air dry loss is determined gravimetrically and the air-dried sample is ground to < 60 mesh. The ground sample is further dried at 105°C and analyzed gravimetrically for residual moisture. The percent solids are determined based on the overall loss of weight during both drying steps
	Volatile solids	EPA Method 1684: An aliquot of the sample is heated to 550°C and the volatile solids are determined gravimetrically, as the material lost at 550°C. Volatile solids are reported as the percentage of the total solids that they represent
	Fixed solids	EPA Method 1684: The fixed solids are determined gravimetrically, as the material that remains after heating the sample to 550°C. Fixed solids are reported as the percentage of the total solids that they represent
Metal	Silicon (as silica, SiO_2)	SW-846 Methods 3052 (digestion) and 6010 (analysis): An aliquot of the air-dried and ground sample is digested with HNO_3 and H_2O_2 in a PTFE vessel, followed by digestion with HF and HCl. Excess HF is neutralized with boric acid. This procedure results in the complete dissolution of the sample. The digestate is analyzed by inductively coupled plasma (ICP) optical emission spectroscopy

4.2 Laboratory

As with the earlier portions of the TNSSS, EPA prepared for this effort a study-specific statement of work (SOW) for the elemental analyses and competitively solicited bids from multiple laboratories. EPA awarded the contract for the elemental analyses to Columbia Analytical Services, Inc., in Tucson, Arizona.

4.3 Analytical Challenges

From an analytical standpoint, sewage sludge is a challenging matrix with which to work. The concentrations of pollutants present in a given sample can vary widely, depending on the nature of the inputs to the treatment plant (e.g., domestic or industrial), and sewage sludge contains other components that are potential interferences in the analyses of the pollutants of interest. These interferences can manifest themselves at all stages of the analytical process, from sample preparation through the final determinative analysis.

Fortunately, the elemental analyses described in this report involved fewer challenges. For example, the elements of interest are present in substantial quantities in sewage sludge and analytical sensitivity was never an issue and "nondetects" were not a concern.

The one substantive problem encountered by the laboratory involved air drying the samples prior to analysis. Some of the samples were liquid that contained large amounts of water (up to 99%). Even though only a few grams of sample were required for the various analyses, wet samples were slow to dry at 30 to 40°C. In addition, some WRRFs treat wastewater with chemical thickeners during production or with lime (calcium carbonate) prior to use or disposal. These treatment agents can cause the sewage sludge to retain moisture and may make it more difficult to air dry the samples.

The laboratory reported that some samples required as much as two weeks to air dry, compared to a more typical two days for other solid matrices such as soils. In response, the laboratory made minor changes to their sample preparation procedures, including using larger plastic drying trays for some samples. The larger tray surface allowed the sample to be spread in a thinner layer for air drying.

The laboratory also reported minor QC problems during the oxygen analyses. They obtained higher than expected results for some calibration verification standards analyzed at the end of a batch of sewage sludge samples. The calibration verification standards are QC samples used to ensure that the instrumentation is under control during the analyses of the field samples. Based on other QC measures, they believe that the problem was a function of some component of the sewage sludge matrix itself that affected the instrument over time. They overcame the problem by reducing the number of samples in each analysis batch, thereby increasing the frequency at which the calibration verifications were analyzed. Using this approach, the laboratory was able to meet the acceptance criteria for the calibration verification standards, thus demonstrating that the instrumentation was in control for each smaller batch of field sample analyses.

The total inorganic carbon (TIC) is determined as the difference between the results from the separate analyses of total carbon and total organic carbon (TOC). In an organic-rich matrix, such as sewage sludge, most or all of the carbon may be present as organic carbon. Given the separate potential uncertainties in the measurements of total carbon and TOC, there were a few instances in which the calculated TIC result was zero or a negative number. In these instances, the laboratory reported the results as "TOC ≥ TC."

Section 5
Data Review Procedures

5.1 General Review Procedures

EPA subjected every laboratory data package submitted under this study to a comprehensive review for data completeness and compliance with project and method specifications and subcontract requirements to ensure that the data met the objectives of the study. Trained staff performed these reviews and identified and corrected data deficiencies as early as possible to maximize the amount of usable data generated during the study.

5.2 QC Elements

As noted in Section 4, the elemental analyses and other analyses in this phase of the survey are simpler than many of the analyses conducted earlier (USEPA, 2009a and 2009b), and presented fewer analytical challenges. Another advantage for these elemental analyses is that well-characterized reference materials are available for the majority of the parameters that can be used as quality control (QC) checks. Table 4 lists the QC elements and acceptance criteria that the laboratory employed for each of the analysis types.

Table 4. QC Elements			
Category	**Parameter Method**	**QC Element**	**Acceptance Limit**
Elements	Total Carbon EPA Method 440	Method blank LCS[1] using S-benzyl thiuronium or phenacetin Sewage sludge reference material CN 1702 Duplicate sample analysis	Blank <0.01 wt.% LCS Recovery 95–105% RM[2] Recovery 90–110% RPD[3] of duplicates <10%
	Hydrogen EPA Method 440		
	Nitrogen EPA Method 440		
	Oxygen EPA Method 440 (modified)	Method blank LCS using benzoic acid or acetanilide Duplicate sample analysis	Blank <0.01 wt.% LCS Recovery 95–105% RPD of duplicates <20%
	Sulfur ASTM D4239	Method blank Coal reference material AR2776 run in replicate Sewage sludge reference material CN 1702 Duplicate sample analysis	Blank <0.01 wt.% RM Recovery 90–110% RPD of duplicates <20%
Forms of Carbon	Total organic carbon (TOC) SW-846 9060	Method blank Coal reference material AR2781 run in replicate Duplicate sample analysis	Blank <0.01 wt.% RM Recovery 90–110% RPD of duplicates <20%
Solids	Total solids EPA Method 1684	Method blank Rice flour reference material AR2028 run in replicate Duplicate sample analysis	Blank <0.01 wt.% RM Recovery 85–115% RPD of duplicates <20%
	Volatile solids EPA Method 1684		
	Fixed solids EPA Method 1684		
Metal	Silicon (as silica, SiO_2) SW-846 6010	Method blank NIST SRM 2710 Montana soil Duplicate sample analysis	Blank <0.01 wt.% RM Recovery 85–115% RPD of duplicates <20%

[1] LCS = Laboratory control sample

[2] RM = Reference material (may be a NIST Standard Reference Material®, or a certified reference material from another source)

[3] RPD = Relative percent difference

Because a reference material for oxygen was not readily available, the laboratory employed two laboratory control samples (LCS)analyses, one prepared from benzoic acid and a second one prepared from acetanilide were utilized. Conversely, because two reference materials were available for the sulfur analyses, no LCS was employed for that analysis. An LCS was not employed for the TOC analyses.

Since total inorganic carbon (TIC) is a calculated value, there are no QC elements exclusive to this parameter. Rather, the quality of the TIC results is dependant on the QC associated with the total carbon and total organic carbon measurements.

5.3 Data Review Findings

The data review efforts did not identify any substantive issues with the quality of the analytical results for the elemental analyses. As noted earlier, the laboratory reran some samples because of issues they identified during their internal reviews. The availability of applicable reference materials for these analyses also aided in ensuring data quality.

We did identify a small number of data reporting errors and inconsistencies, including a few instances of transposed results and spreadsheet cells formatted as text instead of numbers. These issues were found in the electronic data during efforts to compile the data from several electronic data deliverables into a single file of the study results. EPA examined the corresponding hard copy results, contacted the laboratory to confirm the errors, and requested that the laboratory submit corrected data. The few errors and consistencies that we identified were readily resolved by working with the laboratory.

Section 6
Study Results

6.1 Summary Results

Table 5 provides a summary of the results for the 66 TNSSS archive samples analyzed, listing the minimum, maximum, mean, and median results for each parameter. All sample results are reported in percent dry weight.

Table 5. Summary Results

	All Results in Weight Percent, on a Dry-Weight Basis			
Parameter	**Minimum**	**Maximum**	**Mean**	**Median**
Carbon	12.90	46.31	31.17	31.39
Hydrogen	0.18	6.69	3.94	4.09
Nitrogen	1.15	7.94	3.84	3.97
Oxygen	5.17	29.27	19.64	20.43
Sulfur	0.13	4.05	1.32	1.18
TOC	10.39	45.27	29.93	30.77
TIC (calculated)*	0.00	7.45	1.37	1.02
Silica, Total	3.10	43.50	13.84	10.97
Silicon†	1.45	20.33	6.47	5.13

*In instances where the TOC result was greater than or equal to the result for total carbon, the laboratory reported TIC as "TOC ≥ TC." TIC was converted to 0.00 for the purposes of the survey.
†The results for silica (SiO_2) were converted to silicon (Si) by multiplying the silica result by 0.4675, which is the percentage by weight of Si in SiO_2.

Table 6 provides a similar summary of the results for total solids, volatile solids and fixed solids for the 66 samples. The results for the total solids are reported as percent dry weight. The fixed and volatile solids are calculated as a percentage of the total solids content. In addition, because the fixed solids and volatile solids are complementary to one another (e.g., volatile solids represent the material lost when the sample is heated to 550ºC, while fixed solids represents the material that remains), the minimum/maximum value for the fixed solids and the minimum/maximum value for volatile solids do not occur in the same sample.

Table 6. Summary Results for Solids

	All Results in Percent, on a Dry-Weight Basis			
Parameter	**Minimum**	**Maximum**	**Mean**	**Median**
Total Solids (weight percent)	0.49	88.43	22.72	18.23
Volatile Solids (as percentage of total solids)	16.87	83.80	56.56	59.14
Fixed Solids (as percentage of total solids)	16.20	83.13	43.44	40.87

6.2 Analytical Completeness

"Completeness" is a quality assurance measure of the number of samples collected and analyzed compared to the number of useable results. All of the results for this elemental analysis study met the acceptance criteria in the applicable analytical methods and the laboratory provided usable results for every sample submitted for analysis. Thus, analytical completeness is 100% for the overall effort.

6.3 Analytical Sensitivity

EPA did not expect that sensitivity would be a concern for the elemental and other analyses in this portion of the survey; all sewage sludge contains the elements of interest and all sewage sludge contains solids. The laboratory routinely air dries and grinds all samples prior to analysis and the elements of interest are not lost during drying.

The only instances of "nondetects" occurred for the total inorganic carbon (TIC). In ten samples, the results for total organic carbon (TOC) were greater than or equal to the results for total carbon (TC), and the calculated TIC was a negative number.

EPA examined the ten cases where this occurred. In 7 cases the percent difference between the TC result and the TOC result was less than or equal to 2%. Thus, even a 1% uncertainty in each of the two measurements might have caused the TOC to exceed the total carbon result. The remaining three cases involved percent differences between 6 and 15%, all within reasonable uncertainty estimates for the two measured values involved in the calculation. Because negative values for the TIC have no physical meaning, all ten of those TIC results were set to 0.00 for the purposes of the reporting results from this study.

6.4 Accounting for the Total Mass of Sewage Sludge

One goal of the elemental analyses effort was to help further determine the makeup of sewage sludge. EPA was interested in determining what percentage of the total mass of the biosolids in the TNSSS specifically, and in sewage sludge in general, consisted of the elements carbon, hydrogen, nitrogen, oxygen, sulfur, and silicon, as well as other major constituents (e.g., phosphorus, total organic carbon, and total, fixed, and volatile solids). Table 7 provides information on the percent makeup for two elemental combinations of treated sewage sludge.

Table 7. Percent of Sample Mass Comprised of Selected Elements

	C,N,H,O,S, and Si only	C,N,H,O,S, Si, plus Al,Ca,Fe,Mg,P, and Na
Minimum (%)	36.83	52.30
Maximum (%)	86.39	94.55
Mean (%)	66.37	77.37
Median (%)	66.52	80.42

On average across all 66 samples, we can account for approximately 66.4% and 77.4% of the mass of the sewage sludge, respectively, using these two groups of analytes from Table 7. Using all 12 analytes, we can account for almost 95% of the mass of one sample (i.e., maximum %) and over 50% of all other samples.

6.5 Comparison to Background Soil Concentrations

Finally, we compared the results for the sewage sludge samples in this study to data for soils in the U.S. Table 8 compares the mean and median results from this study to data for typical soils (A Horizon) from the U.S. Geological Survey (Smith et al., 2013). The U.S. Geological study sampled 4,857 sites for various geochemical and mineralogical elements and minerals in soils of the conterminous United States.

Table 8. Comparison of Sewage Sludge to Soil Elemental Concentrations

Element	Sewage Sludge Mean %	Sewage Sludge Median %	Soil Mean %	Soil Median %
TIC	1.37	1.02	0.30	0.60
TOC	29.93	30.77	2.75	1.55
O	19.64	20.43	---	---
Si	6.47	5.13	---	---
Ca	4.46	2.75	1.61	0.74
H	3.94	4.09	---	---
N	3.84	3.97	---	---
Fe	2.39	1.42	2.19	1.99
P	2.07	1.76	0.06	0.05
S	1.32	1.18	0.06	0.03
Al	1.29	1.10	4.65	4.71

Based on the comparative data in Table 8, it can be seen that sewage sludge can be a source of essential plant nutrients. Nutrients such as calcium, nitrogen, phosphorus and sulfur are all essential plant nutrients which are low in soils and sewage sludge can provide an adequate supply for plant growth.

6.6 Total Flouride

During the original analysis of TNSSS samples, EPA included water soluble fluoride due to its widespread use in topical and systemic therapy for preventing tooth decay, as well as many other uses. Many products containing fluoride are rinsed down the drain after use. Fluoride is soluble in water, which was, in fact, the basis of the analytical results for the TNSSS. The samples were leached with reagent water as described in the original TNSSS report, and the leachate was analyzed for water extractable form of fluoride in sewage sludge. EPA's Office of Research and Development (ORD) conducted analyses of archived TNSSS samples to ascertain the levels of total fluoride.

Table 9 provides total fluoride numbers from biosolids samples from the OW (Office of Water) TNSSS (Targeted National Sewage Sludge Survey 2006) that were archived at the EPA sample repository in Baltimore, MD. In the original report, fluoride results were determined using a method that only measured water soluble fluoride. In order to get a better understanding of total soil fluoride loading and possible grazing exposure, ORD at the request of OW reanalyzed TNSSS samples to determine total fluoride concentrations. This was done by alkali fusion- Ion selective technique as defined by McQuaker and Gurney, 1977.

Data Limitations

The samples that were analyzed had been frozen at -20C for 5 years prior to processing. There should have been no effect on the fluoride concentrations but all samples were outside of normal holding times. All samples were freeze-dried prior to analysis. In the process of freeze drying, the consistency of the samples may have had an effect on the results. The samples varied from solids to liquids and sub-sampling from these may have introduced some bias in terms of fluoride analysis. All samples were run in triplicate and the mean are reported in table 9.

Table 9 Summary information comparing water soluble fluoride with total fluoride

	Water soluble F	Total Recoverable F
Mean	58	221
Median	49	188
Minimum	14	6
Maximum	234	1296

6.7 Additional Information

For more information about this report, contact Bob Brobst in EPA Region 8, 1595 Wynkoop Street, Denver, CO (telephone: 303-312-6129 or email: Brobst.bob@epa.gov) or Rick Stevens in the Health and Ecological Criteria Division, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460 (telephone: 202-566-1135 or e-mail: Stevens.rick@epa.gov).

Section 7
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