



Chemical and Physical Analysis Methods for Characterizing Tire Crumb Rubber Used in Synthetic Turf Fields

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INTRODUCTION

- Recycled tire crumb rubber (TCR) is often used as infill material in synthetic turf playing fields.
- Concerns have been raised about the safety of this material. U.S. research studies examining crumb rubber constituents have been relatively small, restricted to a few fields or material sources, and measured a limited number of constituents.
- A multi-agency Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds was developed to investigate key factors that could impact the environment and human health.
<https://www.epa.gov/chemical-research/federal-research-recycled-tire-crumb-used-playing-fields>
- Tire crumb rubber samples from tire recycling plants will provide information on constituents in unused material while samples collected from outdoor and indoor synthetic turf fields will provide a better understanding of constituents potentially available for exposure.



GENERAL APPROACH

- TCR samples were collected from nine tire recycling plants and 40 synthetic turf fields across the U.S.
- Characterization includes direct measurement of metal and SVOC constituents of tire crumb rubber, studies of VOC and SVOC emissions and emission rates from tire crumb rubber, and bioaccessibility testing of metal and SVOC constituents.
- A combination of targeted quantitative analysis, suspect screening, and non-targeted approaches are applied for VOCs and SVOCs.
- Physical characteristics such as particle size are examined to better understand potential exposures.

SAMPLE COLLECTION

Synthetic Turf Fields				Field - Year of Installation	Number
U.S. Census Region	Outdoor Fields	Indoor Fields	Total Sampled	2004 - 2008	11
Northeast	5	4	9	2009 - 2012	19
South	11	2	13	2013 - 2016	10
Midwest	2	6	8		
West	7	3	10		
Total Number of Fields	25	15	40		

Tire Recycling Plants	Number
Ambient Process	6
Cryogenic Process	3
Total	9

Figure 1. Numbers and Types of Recycling Plants and Fields for Tire Crumb Rubber Sample Collection

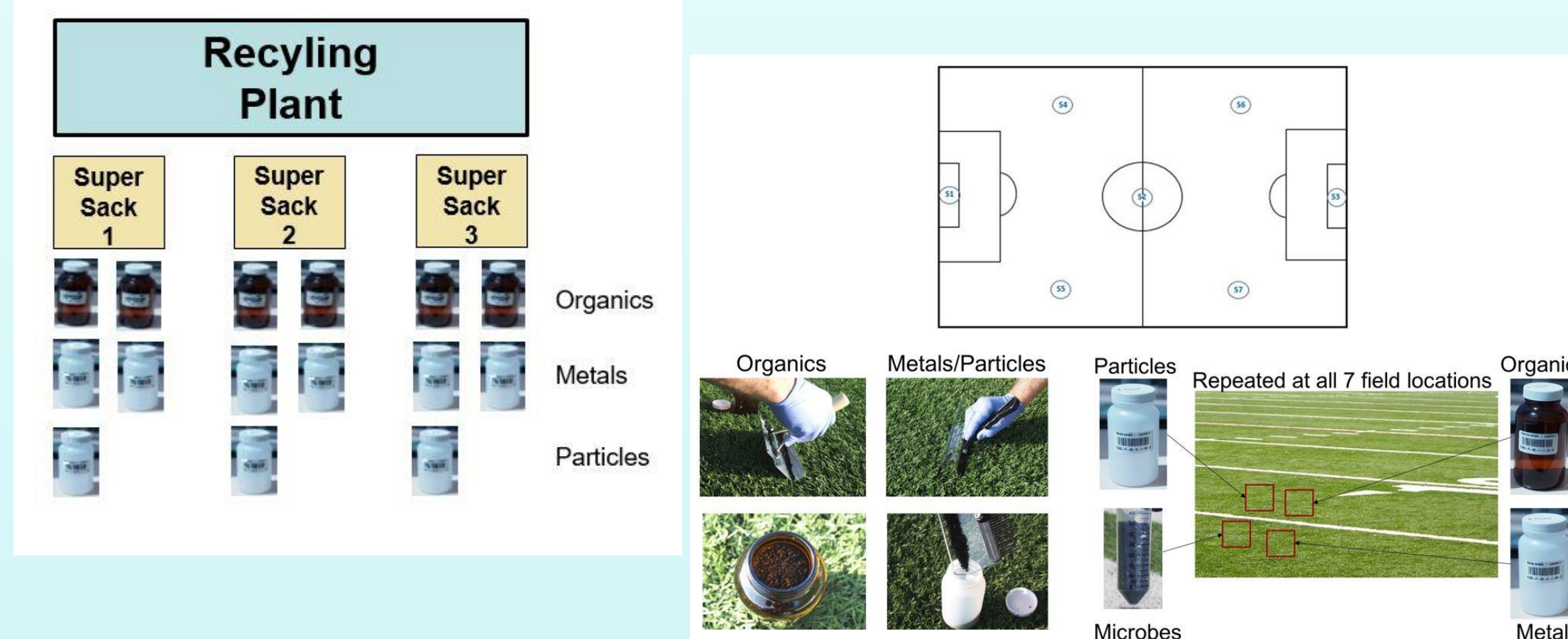


Figure 2. Sample Collection at Recycling Plants and Synthetic Turf Fields

SAMPLE PREPARATION

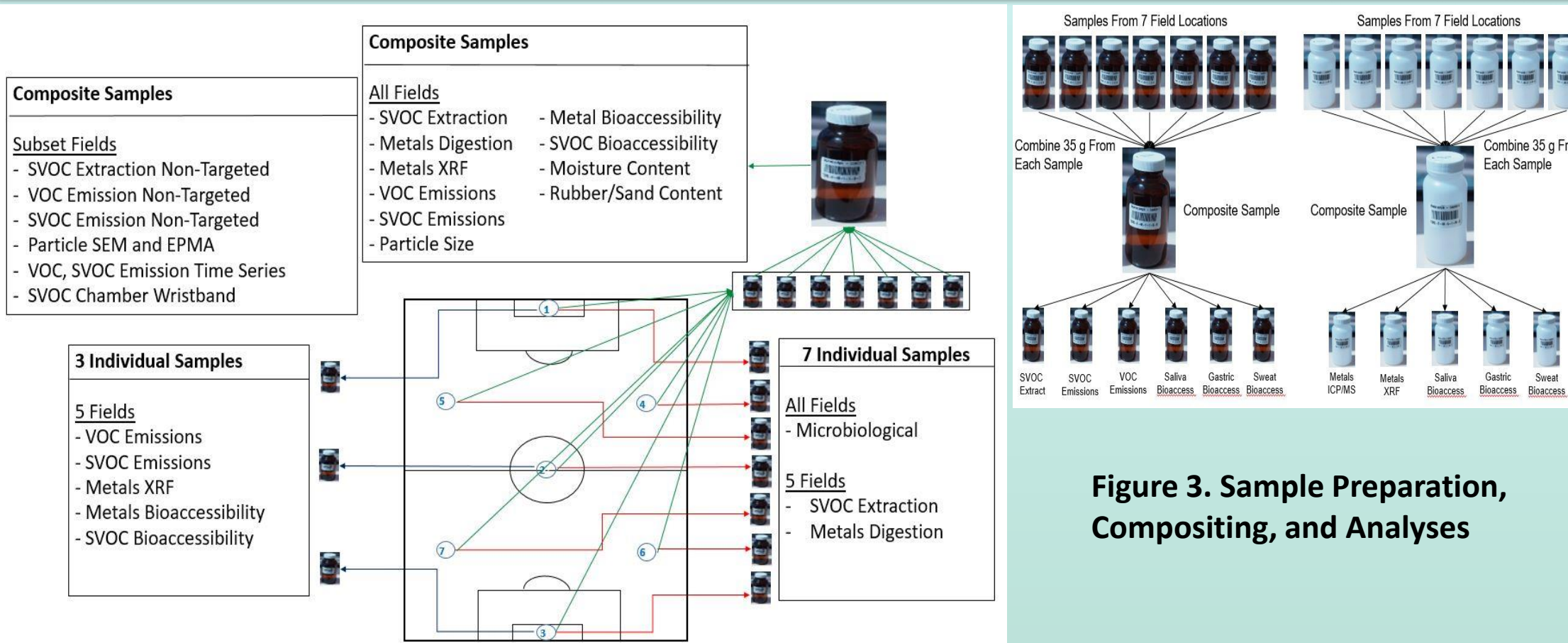


Figure 3. Sample Preparation, Compositing, and Analyses

SAMPLE ANALYSIS

Characterization Analysis Summary

Solvent Extraction
SVOCs – GC/MS/MS
SVOCs – LC/TOFMS

Acid Digestion
Metals – ICP/MS

Spectrometry
Metals – XRF
Metals – ED - EPMA

Particle Characterization
Particle Size – Gravimetric
Morphology/Size - SEM
Moisture Content
Rubber/Sand Content

Microbial Characterization
Targeted Species - ddPCR
Non-Targeted Species - PCR

Small Chamber Emissions
@ 25° and 60° C
Formaldehyde – HPLC/UV
VOCs – GC/TOFMS

Micro Chamber Emissions
@ 25° and 60° C
SVOCs – GC/MS/MS
SVOCs – LC/TOFMS

Bioaccessibility
SVOCs – Sweat - GC/MS
SVOCs – Saliva – GC/MS
SVOCs – Gastric – GC/MS

Bioaccessibility
Metals – Sweat - ICP/MS
Metals – Saliva – ICP/MS
Metals – Gastric – ICP/MS

Direct TCR and Constituent Analyses

- SVOCs – GC/MS/MS**
 - Vortex extract 1g TCR w/ 10 mL 1:1 acetone:hexane in duplicate
 - Analyze extract, 10-fold dilution, and 100-fold dilution
- SVOCs – LC/TOFMS**
 - Solvent exchange TCR extract (above) into methanol
 - Analysis with both positive and negative electrospray ionization
- Metals – HR-ICP/MS**
 - 0.25g TCR microwave extraction w 3:1 nitric:hydrochloric acid
 - Hydrogen peroxide added, dilution to 50 mL with water
- Metals – XRF**
 - 5 – 10g samples in HDPE cups with Mylar membrane
 - Test stand; 300 sec for heavy metals; 300 sec for light elements
- Particle Size**
 - Sieving and gravimetric analysis; sizes: >4.75; >2–4.75; >1–2; >0.25–1; >0.125–0.25; >0.063–0.125; and <0.063 mm
- Particle Characterization**
 - SEM 150 & 1200 magnification; back scatter detector
 - Energy dispersive microprobe analysis for selected elements

Emissions Testing/Analysis

- VOCs**
 - Dynamic emissions testing in small chambers (53 L) at 1 h⁻¹ ACH
 - 25°C, 46 % Relative Humidity (RH) and 60°C, 6.6 % RH
 - Samples collected on DNPH and Carbopack X tubes at 24 h
 - Formaldehyde analysis by HPLC-UV; VOCs by GC/TOFMS
- SVOCs**
 - Dynamic emissions testing in micro chambers (114 or 44 mL)
 - Ventilation ranging from 28 – 82 h⁻¹ ACH
 - 25°C, 45% Relative Humidity (RH) and 60°C, 7% RH
 - Samples collected on PUF cartridges at 24 h
 - Extraction using 1:1 acetone:hexane; GC/MS/MS analysis
 - Solvent exchange into methanol; LC/TOFMS analysis

Analytes – Target, Suspect Screening, Non-Targeted Analysis

- Metals**
 - 21 ICP/MS target analytes; examples: Pb, Zn, Cr, Cd, As, Ni
- VOCs**
 - 31 target analytes; examples: MIBK, benzothiazole, formaldehyde, benzene, styrene, 1,3-butadiene
 - Non-targeted analysis in subset of samples
- SVOCs**
 - 42 target analytes across GC/MS and LC/MS methods
 - PAHs, phthalates, thiazoles, other rubber-related chemicals
 - Examples: pyrene, benzo(a)pyrene, di-ethylhexyl phthalate, benzothiazole, 2-mercaptobenzothiazole
 - ~90 chemicals for suspect screening by LC/TOFMS
 - Non-targeted analysis in subset of samples

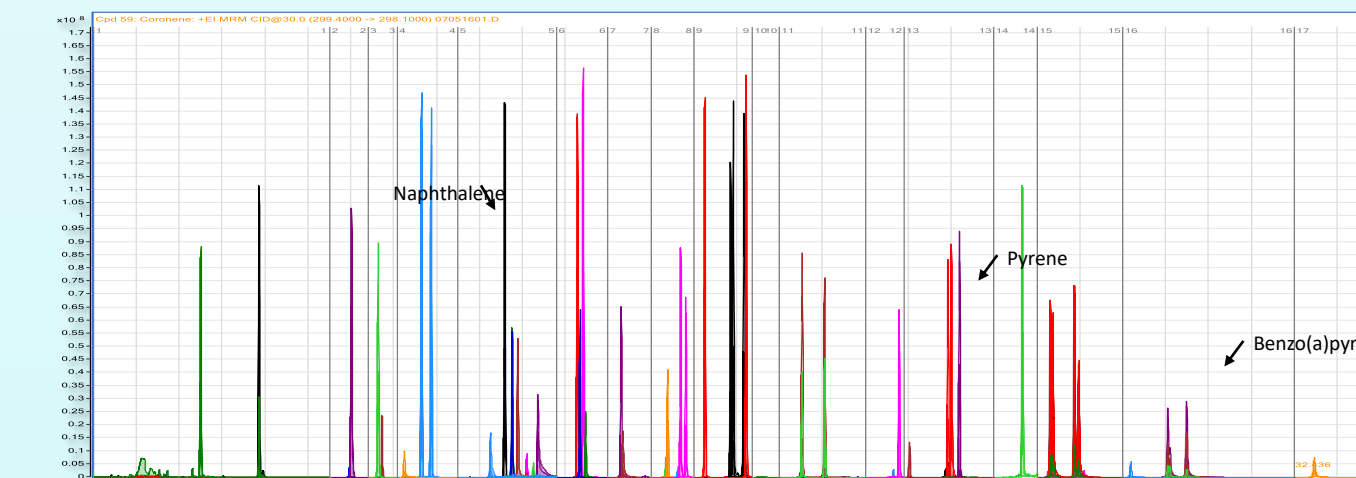


Figure 4. Example MRM Chromatogram for SVOCs in TCR Extract

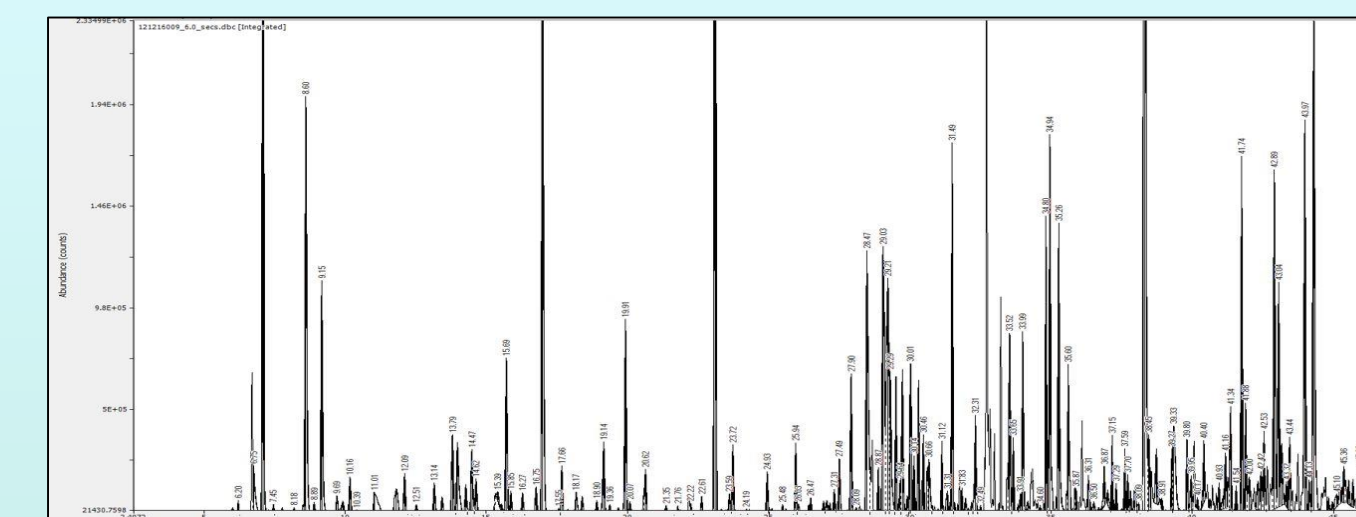


Figure 5. Example Chamber VOC Emission 60°C Chromatogram

Bioaccessibility Analyses

- Prep of Biofluids**
 - Saliva, sweat, sebum, gastric fluids
- Bioaccessibility Testing**
 - TCR 'extraction' using modified EPA Method 1340
 - 2g TCR rotated in 8 mL biofluid at 37°C for 1 h
 - SVOCs: extract biofluid w 3 x 2 mL at pH 2, 7, and 12
 - Sebum coated tubes used with artificial sweat
- Analyses**
 - Metals: ICP-AES and ICP-MS
 - Mercury: Digested and analyzed by cold vapor atomic adsorption procedure
 - SVOCs: GC/MS

DISCUSSION

Status

- >80% of over 2900 analyses completed.

Observations

- Tire crumb rubber is a complex matrix requiring careful choices of analytical approaches.
- Organic chemical analyses result in complex mixtures requiring substantial data processing.
- Multiple solvents tested for SVOC extraction; acetone and hexane worked well without TCR dissolution.
- For SVOCs, there was a large range in target analyte concentrations requiring multiple dilutions.
- For VOCs, there was a large range in target analyte concentrations requiring careful selection of analysis parameters and programmed signal attenuation.

Challenges

- Lack of suitable reference materials for QA/QC.
- Differences in methods across studies may affect comparability.
- Further non-targeted assessment needed to fully elucidate chemical mixtures relevant for exposure assessment.

Conclusions

- The research will help fill data gaps regarding the types and concentrations of the chemical constituents in TCR and their potential availability for human exposure.
- The research will provide information on variability of TCR across recycling plants and synthetic turf fields in the U.S.
- TCR characterization data must be put into an exposure context to assess potential for exposure via inhalation, dermal adsorption, and ingestion.

ACKNOWLEDGEMENTS

EPA/ORD	Steve Gardner	CDC/ATSDR	NIOSH
Annette Guiseppi-Elie	Ed Heithmar	Angela Ragin-Wilson	Brandon Law
Jose Zambrana	Xiaoyu Liu	Zheng Li	Aleksandr Sefaniak
Matthew Clifton	Nichole Brinkman	Kelsey McCall Benson	
Mark Strynar	Christine Alvarez	David Chambers	
Donald Whitaker	Carry Croghan		
Karen Oliver	Tammy Jones-Lepp		
Kasey Kovalick	Brian Schumacher		
Myriam Medina-Vera			
Georges-Marie Momplaisir			

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