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Environmental testing of dust/vegetation control, albedo, and concrete/asphalt replacement products

Jessica K. Kustas, Benjamin W. Juba, Brynal Benally, and Raymond S. Fuentes

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Name/Org: Jessica Kustas/DOE SNL/NM Date: 10/06/2020

Guidance (if applicable):

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico
87185 and Livermore,
California 94550

SUMMARY REPORT OF TERRA PAVE PRODUCTS ANALYSIS FROM SANDIA NATIONAL LABORATORIES, NEW MEXICO, USA

RELATÓRIO RESUMIDO DA ANÁLISE DOS PRODUTOS DA TERRA PAVE DOS LABORATÓRIOS NACIONAIS DA SANDIA, NOVO MÉXICO, EUA

This summary report includes the data driven from the laboratory tests conducted by the following institutes: Center for Transportation Research at the University of Texas at Austin, a National Environmental Laboratory Accreditation Program certified San Antonio Testing Laboratories, and Sandia National Laboratories (SNL), a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Este relatório inclui os dados dos testes de laboratório conduzidos pelos seguintes institutos: Center for Transportation Research da University of Texas em Austin, National Environmental Laboratory Accreditation Program certificado pelo San Antonio Testing Laboratories e Sandia National Laboratories (SNL), um laboratório multi-missão gerenciado e operado pela National Technology & Engineering Solutions de Sandia, LLC, uma subsidiária integral da Honeywell International Inc., para a Administração Nacional de Segurança Nuclear do Departamento de Energia dos Estados Unidos sob o contrato DE-NA0003525.

Terra Pave International, a "Round 2 Solar Prize Set!" contest winner of the U.S Department of Energy's American-Made Solar 2020, develops environmental-friendly and cost-effective alternatives to toxic, corrosive, and petroleum-based commercial products in the solar and pavement industries. In collaboration with Terra Pave International, the national and state laboratories stated above evaluated the environmental impact of Terra Pave products compared to current asphalt emulsion products. This included identifying and measuring levels of chemical components with environmental concerns.

Terra Pave International, vencedor do concurso "Round 2 Solar Prize Set!" do American-Made Solar 2020, do Departamento de Energia dos EUA, desenvolve alternativas ecológicas e econômicas para substituir produtos tóxicos, corrosivos e à base de petróleo nas indústrias solar e de pavimentação. Em colaboração com a Terra Pave International, os laboratórios nacionais e estaduais mencionados acima avaliaram o impacto ambiental dos produtos Terra Pave em comparação com os atuais produtos de emulsão asfáltica. Isso incluiu a identificação e medição dos níveis de componentes químicos com foco ambiental.

SAMPLE DESCRIPTIONS

DESCRIÇÕES DAS AMOSTRA

- **Top-Seal (TS) White™ and TS White Albedo™** are all-purpose liquid soil stabilizers and additives that bind and transform the base into a solid, yet flexible mass that resists fracturing. Both prevents ground base failure, vegetation control, dust pollution, and soil erosion, and it increases soil strength and reduces its permeability. Additionally Top-Seal Albedo™ has ground reflection albedo equal to snow, and thereby increases solar irradiation reflected from the ground for bi-facial solar panels.

- Top-Seal (TS) White ™ e TS White Albedo ™ são aditivos e estabilizadores líquidos para todos os fins que aderem e transformam a base do solo em uma massa sólida, porém flexível, que resiste à fratura. Ambos evitam falha da base do solo, controlam a vegetação, poluição por poeira e erosão do solo, e aumentam a resistência do solo e reduzem sua permeabilidade. Além disso, o Top-Seal Albedo ™ possui indice albedo de reflexão do solo igual ao da neve e, portanto, aumenta a irradiação solar refletida do solo para painéis solares bifaciais.

- **TS Black**™ forms a layered coating over the road base that rapidly transforms into a hardened, independent surface as an alternative to asphalt. It also increases surface friction, thereby shortening breaking distance.
- TS Black ™ forma uma camada de revestimento sobre a base da estrada que rapidamente se transforma em uma superfície endurecida e independente, sendo uma alternativa ao asfalto. Ele também aumenta o atrito da superfície, encurtando a distância de frenagem.

- **Terra Prime**™ penetrates, bonds, and stabilizes the sub-base layer of asphalt pavements, thereby waterproofing it before placing the hot mix asphalt. Terra Prime outperforms all competitor products as a replacement for MC-30.
- Terra Prime ™ penetra, cola e estabiliza a camada de sub-base de pavimentos asfálticos, impermeabilizando-a antes da colocação da mistura asfáltica a quente. Terra Prime supera todos os produtos concorrentes como um substituto para CM-30.

- **MC-30** is manufactured by adding (cutting back) petroleum solvents (also called cutter stock or diluents) to asphalt cements.
- O CM-30 é fabricado pela adição (redução) de solventes de petróleo (também chamados de cutter stock ou diluentes) ao asfálto.

- **AEP** refers to Asphalt Emulsion Product, which comprise an emulsifying agent and a suspension of asphalt cement (MC-30) in water. The Commercial Ergon Asphalt & Emulsions, Inc. product was used in SNL Lab test.
- PEA refere-se aos Produtos de Emulsão Asfáltica, que compreendem um agente emulsificante e uma suspensão de cimento asfáltico (CM-30) em água. O produto comercial da Ergon Asphalt & Emulsions, Inc. foi usado no teste de laboratório da SNL.

COMPARISON OF TERRA PAVE PRODUCTS TO AEP:
COMPARAÇÃO DOS PRODUTOS DA TERRA PAVE COM PEA:

Metallic Contaminants of Concern: One source of metal pollution are highway road bases, which when subjected to rainwater are known to leach heavy metals and contaminate water tables.
Contaminantes Metálicos de Relevância: Uma fonte de poluição por metais pesados são as bases das estradas, que, quando sujeitas à água da chuva, podem lixiviar metais pesados e contaminar os lençóis freáticos.

1.1. Of specific concern are the Resource Conservation and Recovery Act eight (RCRA8) which consists of heavy metals arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. These eight metals are extremely toxic at small concentrations. In a comparison of the RCRA8 levels

1.1.1. Terra Pave products contained lower levels of heavy metal contamination versus AEP. Please refer to Table 2-1. and 2-2 for detailed information. [2]

1.1.2. TS White Albedo contained higher levels of silver (0.16 ppm vs 0.02 ppm) than AEP, while both are below EPA allowable limits of 5.0 ppm.

1.1. De preocupação específica são o Ato 8 de Conservação e Recuperação de Recursos (RCRA8), que consistem em metais pesados arsênio, bário, cádmio, cromo, chumbo, mercúrio, selênio e prata. Esses oito metais são extremamente tóxicos em pequenas concentrações. Em uma comparação dos níveis RCRA8:

1.1.1. Os produtos Terra Pave continham níveis mais baixos de contaminação por metais pesados em comparação com PEA. Consulte a Tabela 2-1. e 2-2 para informações detalhadas.

1.1.2. O TS White Albedo continha níveis mais elevados de prata (0,16 ppm vs 0,02 ppm) do que PEA, enquanto ambos estão abaixo dos limites permitidos pela EPA de 5,0 ppm.

1.2. Regarding additional metal quantification (those metals not part of the RCRA8) Terra Pave products meet the criteria. Significant differences are outlined below. Please refer to Table 2-1 and 2-2 [2].

1.2.1. Non-toxic or low-toxic materials including magnesium, potassium, and calcium were present in higher levels in all Terra Pave products than AEP.

1.2.2. Copper, titanium, vanadium, iron, cobalt, nickel, zinc, strontium, zirconium, and molybdenum were all generally observed at much higher levels in AEP compared to the Terra Pave products.

1.2.3. The exceptions were TS White Albedo with zirconium concentrations nearly 29 ppm and titanium concentrations exceeding 5000 ppm compared to AEP. However, titanium is considered to have low toxicity and zirconium toxicity is low due to minimal solubility.

1.2. Com relação à quantificação adicional de metais (aqueles metais que não fazem parte do RCRA8), os produtos Terra Pave atendem aos critérios. As diferenças significativas são descritas abaixo. Consulte a Tabela 2-1 e 2-2.

1.2.1. Materiais não tóxicos ou de baixa toxicidade, incluindo magnésio, potássio e cálcio, estavam presentes em níveis mais elevados em todos os produtos Terra Pave do que PEA.
1.2.2. Cobre, titânio, vanádio, ferro, cobalto, níquel, zinco, estrôncio, zircônio e molibdênio foram todos geralmente observados em níveis muito mais elevados em PEA em comparação com os produtos Terra Pave.
1.2.3. As exceções foram TS White Albedo com concentrações de zircônio próximas a 29 ppm e concentrações de titânio superiores a 5000 ppm em comparação com PEA. No entanto, o titânio é considerado de baixa toxicidade e a toxicidade do zircônio é baixa devido à sua mínima solubilidade.

2. **Organic Components of Concern:** Organic contaminants are of concern with asphalt products. VOC and intermediate/semi-volatile organic compounds (I/SVOC) emissions are responsible for substantial public health effects.

2. Componentes orgânicos preocupantes: Os contaminantes orgânicos são uma preocupação com produtos de asfalto. As emissões de COV (compostos orgânicos voláteis) e de compostos orgânicos intermediários / semivoláteis (I/SCOV) são responsáveis substanciais em prejudicar a saúde pública.

2.1. Comparison of outgassing in Terra Pave products vs AEP after the samples were allowed to sit at room temperature in a sealed vial for three days. While off-gassing of compounds (solvents, product formulations, or degradation by-products) is heavily dependent on temperature, even room temperature products release substantial VOCs. Significant differences are outlined below. Please refer to Table 3-1 and 3-2 for more details[2].

2.1.1. Compounds that are highly toxic inhalation hazards were observed to outgas in high levels from AEP, while nearly no outgassing of these compounds was observed in the Terra Pave products. These compounds include benzenes, toluene, xylenes, and naphthalene.

2.1.2. Terra Pave products exhibited nearly zero outgassing of petroleum hydrocarbons.

2.1.3. Many Terra Pave products outgassed other compounds. The main components of which include alcohols (e.g., ethanol), acetaldehyde, acetic acid ethenyl ester, and ethyl acetate.

2.1. Comparação da liberação de gases em produtos Terra Pave vs PEA depois que as amostras foram deixadas em repouso em temperatura ambiente em um frasco selado por três dias. Enquanto que a liberação de gases de compostos (solventes, formulações de produtos ou subprodutos da degradação) é diretamente dependente da temperatura, mesmo à temperatura ambiente, os produtos liberam COVs substanciais. As diferenças significativas são descritas abaixo. Consulte a Tabela 3-1 e 3-2 para obter mais detalhes.

2.1.1. Observou-se que os PEA emitem elevados níveis de gases altamente tóxicos para inalação, enquanto quase nenhuma liberação desses compostos foi observada nos produtos Terra Pave. Estes compostos incluem benzenos, tolueno, xilenos e naftaleno.

2.1.2. Os produtos da Terra Pave exibiram liberação quase zero de hidrocarbonetos de petróleo.

2.1.3. Muitos produtos Terra Pave liberaram gases de outros compostos, dos quais incluem álcoois (por exemplo, etanol), acetaldeído, éster etenílico do ácido acético e acetato de etila.

2.2. Identification and quantification of semi-volatile species were performed by direct injection GC-MS. Significant differences are outlined below. Please refer to Table 1 and Table 3-3 for more details[11] [2].

2.2.1. There were no observable (<0.05 ppm) benzenes, toluene, xylenes, etc. in any of the Terra Pave products, while many of these compounds were observed in high levels (>500 ppm) in AEP.

2.2.2. As expected, AEP consisted of over 140,000 ppm of petroleum hydrocarbons while hydrocarbon levels in Terra Pave products were below the detection limit (<0.05 ppm) of the instrument and instrument parameters.

2.2.3. Levels of acetonitrile were between 14,000 – 285,000 ppm in Terra Pave products.

2.2. A identificação e quantificação das componentes semivoláteis foram realizadas por injeção direta de sistemas de cromatografia de gás - espectrometria de massa (GC-MS). As diferenças significativas são descritas abaixo. Consulte a Tabela 1 e a Tabela 3-3 para obter mais detalhes.

2.2.1. Não foram observados (<0,05 ppm) benzenos, tolueno, xilenos, etc. em nenhum dos produtos Terra Pave, enquanto muitos desses compostos foram observados em níveis elevados (> 500 ppm) em PEA.

2.2.2. Como esperado, PEA consistia em mais de 140.000 ppm de hidrocarbonetos de petróleo, enquanto os níveis de hidrocarbonetos nos produtos Terra Pave estavam abaixo do limite de detecção do instrumento e de seus parâmetros (<0,05 ppm).

2.2.3. Os níveis de acetonitrila estavam entre 14.000 - 285.000 ppm nos produtos Terra Pave.

3. Additional test results are stated below. Please refer to Table 4-1 for more details [2].

3.1.1. Terra Pave products contained higher levels of natural sodium content compared to AEP. Considering the vastly different base composition of Terra Pave products compared to the petroleum-based AEP, this was not unexpected. Terra Pave products have a maximum of 0.6 gallons per square yard application rate. Terra Pave layers can be ground up and mixed in with the existing soil. Because of the maximum application rate, the non-toxic sodium content of the Terra Pave layer is not going to be a concern when recycling the treated soil.

3. Resultados de testes adicionais estão indicados abaixo. Consulte a Tabela 4-1 para obter mais detalhes.

3.1.1. Os produtos Terra Pave continham níveis mais elevados de conteúdo de sódio natural em comparação com PEA. Considerando a vasta diferença da composição de básica dos produtos Terra Pave em comparação com o PEA à base de petróleo, isso não era inesperado. Os produtos Terra Pave têm uma taxa de aplicação máxima de 0,6 galões por metro quadrado. As camadas do Terra Pave podem ser trituradas e misturadas com o solo existente. Por causa da taxa de aplicação máxima, o conteúdo atóxico de sódio da camada Terra Pave não será uma preocupação ao reciclar-se o solo tratado.

CONCLUSION

CONCLUSÃO

Based on the inorganic content of these products, Terra Pave products exhibited far less to no heavily metal contaminants, while many exhibited high levels of titanium, magnesium, potassium, and calcium. These are generally considered safe and ion chromatography revealed far less calcium and potassium leaching into the water than the total content observed in the products. Furthermore, the volatile organic analysis revealed extremely low petroleum hydrocarbon content and outgassing in the Terra Pave products, while AEP revealed extremely high levels.

In conclusion, Terra Pave products reduce the risks of CM-30 and AEP while they match or exceed these traditional petroleum-based materials in strength, permeability, and penetration tests [3]. Instead of adding a petroleum agent to lower the prime coat's viscosity — which causes VOC emissions and their associated risks — Terra Pave Products are water-based emulsions comprising emulsifiers and polymers that makes them environmentally-conscientious choice for solar and pavement industries.

Com base no conteúdo inorgânico desses produtos, os produtos Terra Pave exibiram muito menos ou nenhum contaminante fortemente metálico, enquanto muitos exibiram altos níveis de titânio, magnésio, potássio e cálcio. Estes são geralmente considerados seguros e a cromatografia de íons revelou muito menos cálcio e potássio lixiviado para a água do que o conteúdo total observado nos produtos. Além disso, a análise orgânica volátil revelou conteúdo de hidrocarbonetos de petróleo extremamente baixo e liberação de gases dos produtos Terra Pave, enquanto PEA revelou níveis extremamente altos.

Em conclusão, os produtos Terra Pave reduzem os riscos dos MC-30 e PEA enquanto eles igualam ou excedem esses materiais tradicionais à base de petróleo em testes de resistência, permeabilidade e penetração. Em vez de adicionar um agente de petróleo para reduzir a viscosidade do revestimento primário - o que causa emissões de COV e seus riscos associados - os produtos Terra Pave são emulsões à base de água que compreendem emulsificantes e polímeros que os tornam uma escolha ambientalmente consciente para as indústrias solar e de pavimentação.

http://www.ecoestates.us/tp.html

Terra Pave products

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ABSTRACT

The U.S Department of Energy's American-Made Solar Prize competition supports the growth of solar manufacturing through cash prizes and national laboratory support, condensing the timeline between concepts, prototype, and commercialization of eco-friendly products. The Terra Pave team, a "Round 2 Solar Prize Set!" contest winner and part of Ecological Estates LLC, develop environmentally-friendly and cost-effective alternatives to toxic, corrosive, and petroleum-based commercial products in the solar and pavement industries. In collaboration with Terra pave and through a national laboratory program voucher prize, SNL evaluated the environmental impact of Terra pave products compared to current asphalt emulsion products. This included identifying and measuring levels of chemical components with environmental concerns.

ACKNOWLEDGEMENTS

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ACRONYMS AND DEFINITIONS

Abbreviation	Definition
SNL	Sandia National Laboratories
AEP	asphalt elusion product
VOCs	volatile organic compounds
PV	photovoltaic
TS	Top-Seal
HR-TS	Haul Road Top-Seal
RCRA	Resource Conservation and Recovery Act
ICP-MS	inductively coupled plasma mass spectrometry
I/SVOC	intermediate/semivolatile organic compounds

1. STATEMENT OF WORK

Sandia National Laboratories (SNL) proposes as time and budget allow, to design and perform environmental testing of Terra Pave products, as well as, current asphalt emulsion products, to determine and compare the levels of hazardous, corrosive, and petroleum components. This will be completed through a suite of analytical techniques, including inductively coupled plasma mass spectrometry/ optical emission spectroscopy, ion chromatography, and gas chromatography mass spectrometry. SNL will specifically perform the following test and/or analysis:

- **Comparison with asphalt emulsion product (AEP) and other samples**
  Quantification of constituents of concern present in AEP and other samples, including metal ions, petroleum components, and other solvents. A comparison between these samples will provide information on the environmental impacts of the Terra Pave products compared to well-known products.

- **Identification of volatile organic compounds (VOCs)**
  Typical petroleum-based asphalt generates and releases high levels of volatile organic compounds (VOCs), often harmful, into the environment during production, application, and curing. Identification of the VOCs produced through mild heating will provide insight into the atmospheric emissions that may be produced from the asphalt emulsion sealant.

- **Water leaching environmental effects**
  Asphalt and asphalt emulsion sealants have also been known to pollute water sources and, therefore, analyses to determine ions or molecules that are water-soluble will provide insight into potential water leaching environmental effects.

1.1. Background

Terra Pave International provides eco-friendly (non-toxic, non-hazardous, non-corrosive, non-petroleum based) materials for dirt/dust control, vegetation control, improving roadways, airfields, solar reflective surfaces for bifacial solar panels, and roof protection. The following are current fields with challenges relating to these types of products:

- **Photovoltaic (PV) Systems**

  Energy losses in PV systems due to soiling have been the subject of considerable research spanning decades. With limited options for preventing soiling, reduced output from these types of losses ranges from 5% to 50%. Currently, solar panels required regular, labor-intensive cleaning with freshwater, which is neither eco-friendly nor cost-effective. Also important for ground-mounted PV systems is weed or vegetation management. Tall weeds growing around the installation create shading, negatively impacting system production. They can also cause hot spot heating — if a part of the solar cell is shaded, the cell can heat up to such extreme temperatures that a module can burn out, causing permanent damage. Solutions include mowing, spraying herbicide, and relying on herbivorous animals or covers. Unfortunately, these solutions are labor-intensive, not eco-friendly, nor cost-effective.

- **Bi-facial Panels**

  Bi-facial panels can capture solar irradiation from the front and back. This means they can generate power from the sun by capturing the sunlight reflected from the ground, as well as direct sunlight, therefore increasing total energy generation. Currently, there is no eco-friendly or cost-effective product to increase albedo from ground surfaces.

- **Road and Roof Construction/Maintenance**

  Asphalt, a petroleum hydrocarbon-based product, is used extensively in road paving, roofing, siding, and concrete work. When hot asphalt is applied in a molten state, it generates toxic fumes. Workers exposed to asphalt fumes are at risk of developing headaches, rashes, cough, and possibly cancer. These hydrocarbon-based products also contain chemicals unfriendly to the soil and which impact stormwater runoff.

1.2. Sample Descriptions

The following are product descriptions as reported on the Ecological Estates LLC company website:

- **Top-Seal (TS) White™ and TS White Albedo™** are all-purpose liquid soil stabilizers and additives that bind and transform the base into a solid, yet flexible mass that resists fracturing. Top-Seal Albedo™ increases solar irradiation reflected from the ground for bi-facial solar panels, prevents ground base failure, vegetation control, dust pollution, and soil erosion, and it increases soil strength and reduces its permeability. It is non-petroleum-based and eco-friendly, evaporating only water during the curing process and emitting no VOCs. It does not contain solvents or cause damage to solar farm equipment, roads, or vehicles. It is easily applied, requiring no special equipment or handling procedures. Top-Seal Albedo is a product for solar farms with bi-facial solar panels. Top-Seal Albedo has ground reflection albedo equal to snow.

- **TS Black™** forms a layered coating over the road base that rapidly transforms into a hardened, independent surface. It also increases surface friction, thereby shortening braking distance. After it has been applied and has hardened (polymerized), it creates a thick membrane coating, which prevents the penetration of water and air into the pavement. Top-Seal Black is a polymer-based emulsion that requires water dilution. It is non-petroleum-based and eco-friendly asphalt replacement pavement, evaporating only water during the curing process and emitting no VOCs. It does not contain solvents or causes damage to roads or vehicles. It is easily applied, requiring no special equipment or handling procedures.

- **Haul Road Top Seal™ (HR-TS)** was internationally recognized for its excellent performance in controlling vegetation, dirt/dust pollution at ground-mount mono-facial utility solar farms, and major haul roads. HR-TS™ is composed of a water-based and 100% environmentally friendly polymer compound. HR-TS™ sits on the leading edge of technology for products specifically designed with vegetation control, dust control, fugitive

dust, road dust control, soil stabilization, erosion control, and soil permeability enhancement as the end objective.

- **Terra Roof™** is a high-quality, environmental-friendly, and cost-effective solution for improving performance and extending service life in commercial & residential roofs.

- **Terra Prime™** penetrates, bonds, and stabilizes the sub-base layer of asphalt pavements, thereby waterproofing it before placing the hot mix asphalt. Terra Prime outperforms all competitor products as a replacement for MC-30, SS1 Tack Coat.

- **Terra Fog™** is a high-quality, environmental-friendly, and cost-effective solution for improving performance and extending service life in chip seals. Chip seals, also known as seal coats, are an inexpensive way to preserve asphalt pavements and prevent further deterioration of their structure. Terra Fog™ reinforces the chip seal by reducing asphalt oxidation, preventing brittleness and weakness.

- **AEP** commercial Ergon Asphalt & Emulsions, Inc. product.

2. METALLIC CONTAMINANTS OF CONCERN

While heavy metals are naturally occurring, the large quantities polluted into the environment threatens and compromises animal and human health. Due to the nondegradable state of metals, there can be bioaccumulation of these pollutants in the food chains, with remediation typically requiring extensive physical and chemical sequestrations in soil, air, and/or water. One source of metal pollution are highway road bases, which when subjected to rainwater are known to leach heavy metals and contaminate water tables.[1] Of specific concern are the Resource Conservation and Recovery Act eight (RCRA8) which consists of heavy metals arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. These eight metals are extremely toxic at small concentrations. In order to determine concentrations of not just the RCRA8, SNL utilized inductively coupled plasma mass spectrometry (ICP-MS) to identify the metallic elements present in the products and measure their concentration. Sections 2.1- 2.2 describe the specific protocols developed for metallic quantification.

2.1. Product Digestion

In alignment with US EPA microwave digestion method 3051, Terra Pave products and AEP were digested with minimal changes to ensure total digestion. In brief, 0.5 g of sample was weighed into a Teflon digestion vessel and 10 mL nitric acid was added. Terra Pave product TS White Albedo required the use of a hydrofluoric acid (8 mL): nitric acid (2 mL) mixture due to the titanium oxide and zirconium oxide content. Samples were allowed to outgas for approximately 15 min before sealing the vessel. Utilizing a MARS6 microwave digestion system (CEM Corporation, Matthew, North Carolina, US), samples were digested according to the following heating program: Ramp to 200 °C over 15 min using 900-1800 W power, hold 15 min at 200 °C, followed by cooling to room temperature.

2.2. Instrument Parameters

The metallic impurities of the products were determined with a NexIon model 350D ICP-MS (Perkin Elmer, Groton, CT, US) equipped with a PFA concentric nebulizer and baffled cyclonic spray chamber. The plasma conditions were optimized before analysis with a standard solution of analytes. Samples were analyzed along with standard elemental reference materials (Inorganic Ventures, Christiansburg, VA, US). First, solutions were run in semi-quantitative mode on the ICP-MS using a 10-ppb calibration solution to determine analytes of interest for full quantification, *i.e.,* those analytes above 10-ppb in any of the samples, in addition to, the RCRA8. In full quantification mode, the sample analyte signal was compared to a known standard signal which used relative instrument response factors to calculate the concentration of those elements detected in the sample. Diluted samples and standards were aspirated directly into the instrument without modification. Quality control samples, using separate source standards, were analyzed to verify the calibration curve and instrument function.

2.3. Comparison of Terra Pave products to AEP

In addition to measuring the levels of the RCRA8, metal ions determined to be above 10 ppb in any of the products were also quantified. These results were compared to measured AEP levels in Tables 2-1 and 2-2. Those values determined to be significantly higher in comparison to other products were bolded in red. In a comparison of the RCRA8 levels, Terra Pave products contained lower or similar levels of heavy metal contamination versus AEP, with two exceptions. First, while the levels of selenium were below 0.25 ppm for all Terra Pave products, the levels were above that of AEP (<0.0001 ppm). Second, TS White Albedo contained higher levels of silver (0.16 ppm vs 0.02 ppm) than AEP, while both are below EPA allowable limits of 5.0 ppm.

Additional metal quantification (those metals not part of the RCRA8) revealed a distinct difference when comparing the Terra Pave products with AEP. Specific significant differences are outlined below.

- Magnesium, potassium, and calcium were present in much higher levels in all Terra Pave products, in some cases over 18x that observed in AEP (potassium, TS White Albedo).
- Titanium was observed in higher concentrations in AEP compared to the Terra Pave Products, apart from TS White Albedo. This albedo product contained very high concentrations (exceeding 5000 ppm) of titanium. However, titanium is generally considered to have low toxicity.[2]
- Vanadium, iron, cobalt, nickel, and zinc were all observed at much higher levels in AEP compared to the Terra Pave products. Again, the one exception was TS White Albedo which exhibited slightly higher zinc content compared to AEP.
- Copper levels were generally low for all samples, while TS White Albedo reach a concentration just above 1 ppm.
- Overall, concentrations of strontium, zirconium, and molybdenum were low, with nearly all below 0.3 ppm. The exceptions were TS White Albedo with zirconium concentrations nearly 29 ppm and AEP with molybdenum levels at 2.27 ppm. While zirconium toxicity is low due to minimal solubility, molybdenum toxicity has been linked in animals to kidney failure, infertility, and reduced growth.[3]

Table 2-1. Comparison of metal ion concentrations (ppm) in Asphalt Emulsion Product (AEP) to multiple Top Seal (TS) products. Standard deviations are provided in parenthesis.

Metal	AEP	TS White	TS White Albedo	TS Black	HRTS
Magnesium	2.26 (0.57)	***33.47 (2.27)***	***18.20 (0.65)***	***23.74 (1.91)***	***34.59 (0.45)***
Potassium	3.96 (1.93)	***9.65 (0.07)***	***73.20 (4.00)***	***11.13 (0.71)***	***11.53 (0.17)***
Calcium	9.92 (2.50)	***37.29 (0.33)***	***19.81 (0.90)***	10.70 (0.78)	***133.64 (0.87)***
Titanium	1.37 (0.97)	0.06 (0.02)	***5214.07 (295.82)***	0.12 (0.02)	0.05 (0.01)
Vanadium	***260.26 (34.53)***	0.008 (0.001)	0.06 (0.01)	0.018 (0.002)	0.008 (0.001)
*Chromium	***1.09 (0.83)***	0.22 (0.01)	0.82 (0.23)	0.49 (0.004)	0.14 (0.01)
Iron	***14.69 (4.39)***	2.91 (0.30)	2.35 (0.80)	2.85 (0.64)	2.94 (0.83)
Cobalt	***0.11 (0.08)***	0.0008 (0.0003)	0.01 (0.004)	0.002 (0.0002)	0.004 (0.003)
Nickel	***56.75 (7.27)***	0.008 (0.003)	0.17 (0.08)	0.02 (0.005)	0.02 (0.002)
Copper	0.12 (0.01)	0.05 (0.004)	***1.17 (0.25)***	0.10 (0.01)	0.04 (0.0009)
Zinc	***21.66 (3.23)***	0.08 (0.01)	***27.72 (1.39)***	0.60 (0.04)	0.06 (0.02)
*Arsenic	0.06 (0.01)	0.002 (0.0004)	0.01 (0.004)	0.003 (0.0007)	0.002 (0.000001)
*Selenium	<0.0001	0.05 (0.006)	<0.0001	0.06 (0.03)	0.04 (0.01)
Strontium	0.10 (0.004)	0.22 (0.001)	0.14 (0.03)	0.16 (0.02)	0.22 (0.002)
Zirconium	0.06 (0.02)	0.001 (0.0002)	***28.99 (1.71)***	0.04 (0.02)	0.002 (0.0005)
Molybdenum	***2.27 (0.52)***	0.003 (0.0005)	0.007 (0.003)	0.003 (0.0008)	0.003 (0.0004)
*Silver	0.02 (0.01)	0.0004 (0.00003)	***0.16 (0.03)***	0.0007 (0.00008)	0.0003 (0.00007)
*Cadmium	0.003 (0.002)	<0.0001	0.007 (0.002)	<0.0001	<0.0001
*Barium	***0.26 (0.07)***	0.02 (0.0004)	***0.21 (0.04)***	0.04 (0.005)	0.02 (0.002)
*Mercury	0.002 (0.0006)	0.0005 (0.0002)	0.004 (0.002)	0.005 (0.002)	0.002 (0.0007)
*Lead	0.07 (0.003)	0.002 (0.001)	0.005 (0.0007)	0.005 (0.001)	0.01 (0.01)

*RCRA 8 metals

Metals with concentrations significantly higher than other samples have been bolded and highlighted in red.

Table 2-2. Comparison of metal ion concentrations (ppm) in Asphalt Emulsion Product (AEP) to multiple Terra products. Standard deviations are provided in parenthesis.

Metal	AEP	Terra Roof	Terra Prime	Terra Fog
Magnesium	2.26 (0.57)	***25.15 (1.32)***	***32.52 (1.51)***	***28.88 (0.52)***
Potassium	3.96 (1.93)	***10.25 (0.40)***	***10.50 (1.19)***	***9.99 (0.43)***
Calcium	9.92 (2.50)	13.57 (1.36)	16.46 (6.92)	13.25 (1.11)
Titanium	***1.37 (0.97)***	0.08 (0.008)	0.04 (0.005)	0.22 (0.15)
Vanadium	***260.26 (34.53)***	0.007 (0.0008)	0.01 (0.001)	0.02 (0.0007)
*Chromium	***1.09 (0.83)***	0.60 (0.01)	0.14 (0.02)	0.45 (0.10)
Iron	***14.69 (4.39)***	2.60 (0.14)	2.69 (0.33)	3.96 (0.90)
Cobalt	***0.11 (0.08)***	0.001 (0.0001)	0.001 (0.0005)	0.002 (0.001)
Nickel	***56.75 (7.27)***	0.02 (0.003)	0.03 (0.01)	0.06 (0.04)
Copper	0.12 (0.01)	0.06 (0.007)	0.07 (0.01)	0.13 (0.05)
Zinc	***21.66 (3.23)***	0.19 (0.05)	0.15 (0.02)	0.39 (0.05)
*Arsenic	0.06 (0.01)	0.002 (0.0006)	0.001 (0.0002)	0.003 (0.0003)
*Selenium	<0.0001	***0.22 (0.02)***	0.007 (0.0008)	0.03 (0.01)
Strontium	0.10 (0.004)	0.20 (0.01)	0.30 (0.09)	0.20 (0.004)
Zirconium	0.06 (0.02)	0.006 (0.003)	0.02 (0.008)	0.05 (0.01)
Molybdenum	***2.27 (0.52)***	0.003 (0.0008)	0.002 (0.0005)	0.006 (0.003)
*Silver	0.02 (0.01)	0.001 (0.0007)	0.0007 (0.0001)	0.05 (0.004)
*Cadmium	0.003 (0.002)	<0.0001	<0.0001	<0.0001
*Barium	***0.26 (0.07)***	0.02 (0.002)	0.02 (0.0004)	0.03 (0.004)
*Mercury	0.002 (0.0006)	0.003 (0.001)	0.002 (0.0005)	0.0004 (0.0001)
*Lead	0.07 (0.003)	0.001 (0.0003)	0.005 (0.003)	0.005 (0.002)

*RCRA 8 metals

Those metals with concentrations significantly higher than other samples have been bolded and highlighted in red.

3. ORGANIC CONTAMINANTS OF CONCERN

In addition to metal pollution, organic contaminants are of concern with asphalt products. Freshly paved roads and tar roofs are a significant source of air and water pollution.[4] VOC and intermediate/semivolatile organic compounds (I/SVOC) emissions are responsible for substantial public health effects.[5] While off-gassing of compounds (solvents, product formulations, or degradation by-products) is heavily dependent on temperature, even room temperature products release substantial VOCs.

3.1. Instrument Parameters

3.1.1. Entech headspace focuser GC-MS

Volatile organic species outgassing from the Terra Pave and AEP products were analyzed using an Entech Instruments (Simi Valley, CA) model 7650 Headspace CTS system coupled to an Agilent (Santa Clara, CA) 7890B GC and 5977B HES mass spectrometer. A Restex RXI-5ms 60 m x 0.32 mm id x 1 μm capillary column was used for this analysis. An aliquot of approximately 0.5 mL (0.25 mL for AEP) of the sample was added to a 40 cc headspace vial as gaseous vapors were allowed to collect and equilibrate at room temperature for 3 days. Following the incubation period, a 20 cc (10 cc for AEP) headspace volume was aspirated into the Entech cyro focuser where VOCs were concentrated and injected into a 120 ˚C inlet with a 100:1 split mode. Oven parameters were as followed: hold at 35 ˚C for 5 min, ramp to 100 ˚C at 5 ˚C/min, ramp to 220 ˚C at 12.5 ˚C/min, hold 5 min. Identification and quantification of compounds within the samples were performed using the NIST Mass Spectral Search Program and Automated Mass Spectral Deconvolution and Identification System (AMDIS).

3.1.2. Direct injection GC-MS

Higher temperature volatile organic species from the Terra Pave and AEP products were analyzed via direct injection using an Agilent 6890N Gas Chromatograph with a Mass Selective Detector (5973MSD). The GC is used with a J&W DB-5MS capillary column (60 m x 0.32 mm x 0.25 μm film). Injection volumes were 1 μL. Instrument parameters were as followed: inlet temperature 300C, 0.3 mL/min helium flow, oven ramp 1- 50 ˚C/min up to 200 ˚C followed by 2 min hold, ramp 2- 10 ˚C/min up to 300 ˚C followed by 2 min hold. Identification and quantification of compounds within the samples was performed using the NIST Mass Spectral Search Program and Automated Mass Spectral Deconvolution and Identification System (AMDIS).

3.2. Comparison of outgassing in Terra Pave products vs AEP

Prior to the identification and quantification of outgassing species from the AEP and Terra Pave products, samples were allowed to sit at room temperature in a sealed vial for three days. Concentrations of highly volatile compounds of interest and petroleum hydrocarbons are provided in Tables 3-1 and 3-2, with differences between samples highlighted in red text. Significant differences are outlined below.

- Compounds that are highly toxic inhalation hazards were observed to outgas in high levels from AEP, while nearly no outgassing of these compounds was observed in the Terra Pave products. These compounds include benzenes, toluene, xylenes, and naphthalene.
- Terra Pave products exhibited nearly zero outgassing of petroleum hydrocarbons.
- Many Terra Pave products outgassed "other" compounds. The main components of which include alcohols (e.g., ethanol), acetaldehyde, acetic acid ethenyl ester, and ethyl acetate.

Table 3-1. Select organic constituents of concern and comparisons of their concentrations (ppm) in Asphalt Emulsion Product (AEP) and multiple Terra products.

	AEP	TS White	TS White Albedo	TS Black	HRTS	Terra Roof	Terra Prime	Terra Fog
Benzenes	***7.43***	n.a.	n.a.	n.a.	0.03	n.a.	n.a.	n.a.
Toluene	***5.95***	n.a.	0.01	n.a.	n.a.	n.a.	n.a.	n.a.
Ethylbenzene	***1.60***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Xylenes	***4.55***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fluorene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Naphthalene	***0.44***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Phenanthrene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Pyrene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = no peak observed

Those compounds with concentrations significantly higher than other samples have been bolded and highlighted in red.

Table 3-2. Comparison of the total concentrations (ppm) of petroleum hydrocarbons outgassed from Asphalt Emulsion Product (AEP) and multiple Terra products. All other non-hydrocarbon-based species are grouped and identified as "other".

	AEP	TS White	TS White Albedo	TS Black	HRTS	Terra Roof	Terra Prime	Terra Fog
Total petroleum hydrocarbons	***169.67***	0.05	0.04	0.08	0.01	0.01	n.a.	0.02
C6-C12	***158.37***	0.05	0.04	0.08	0.01	0.01	n.a.	0.02
C13-C28	***11.30***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
C29-35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Other (not hydrocarbons)	***49.09***	12.52	***94.81***	***48.67***	4.70	***36.11***	1.38	***35.80***

n.a. = no peak observed

Groups with concentrations significantly higher than other samples have been bolded and highlighted in red.

3.3. Comparison of Terra Pave products to AEP

Identification and quantification of semi-volatile species was performed by direct injection GC-MS. Concentrations of specific compounds of interest and petroleum hydrocarbons are provided in Tables 3-3 and 3-4, with differences between samples highlighted in red text. Significant differences are outlined below.

- There was no observable (<0.05 ppm) benzenes, toluene, xylenes, etc. (Table 3) in any of the Terra Pave products, while many of these compounds were observed in high levels (>500 ppm) in AEP.
- As expected, AEP consisted of over 140,000 ppm of petroleum hydrocarbons while hydrocarbon levels in Terra Pave products were below the detection limit (<0.05 ppm) of the instrument and instrument parameters.
- Levels of acetonitrile were between 14,000 – 285,000 ppm in Terra Pave products.

Table 3-3. Select organic constituents of concern and comparisons of their concentrations (ppm) in Asphalt Emulsion Product (AEP) and multiple Terra products.

	AEP	TS White	TS White Albedo	TS Black	HRTS	Terra Roof	Terra Prime	Terra Fog
Benzenes	***500***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Toluene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ethylbenzene	***1700***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Xylenes	***420***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fluorene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Naphthalene	***2300***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Phenanthrene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Pyrene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = no peak observed

Those compounds with concentrations significantly higher than other samples have been bolded and highlighted in red.

Table 3-4. Comparison of the total concentrations (ppm) of petroleum hydrocarbons and acetonitrile in Asphalt Emulsion Product (AEP) and multiple Terra products. All other non-hydrocarbon-based species are grouped and identified as "other".

	AEP	TS White	TS White Albedo	TS Black	HRTS	Terra Roof	Terra Prime	Terra Fog
Total petroleum hydrocarbons	***145,500***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
C6-C12	***33,400***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
C13-C28	***111,300***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
C29-35	***800***	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Acetonitrile	n.a.	***285,000***	***190,000***	***184,000***	***14,700***	***200,000***	***135,400***	***158,600***
Other (not hydrocarbons)	***30,100***	***3,500***	***14,900***	***10,600***	10.8	***7700***	820	***2,000***

n.a. = no peak observed

Groups with concentrations significantly higher than other samples have been bolded and highlighted in red.

4. WATER POLLUTION

Aside from organic pollution, water pollution can also occur from leaching of salts into the environment. Some fresh bodies have become so salty that they are ~25% the level of seawater.[6] Increased salinity can have lethal and sublethal effects on aquatic plants and invertebrates, including making freshwater non-potable for human consumption.[7] One indication of salinity is chloride elevation as this is a common anion in salts. Chloride is also a well-known metal corrosion initiator.

4.1. Instrument Parameters

Polypropylene specimen containers were coated with 10 mL of the individual products and allowed to dry. Once dry, 10 mL of deionized H_2O was pipetted onto the dry samples and capped. The mixture sat for 25 days at room temperature. Water was then decanted and collected. Cations and anion concentrations in the water were then measured using a Dionex ICS 5000+ system. The cation system was equipped with an EGC 500 MSA Eluent Generator, a CERS 500 2 mm, a CTC-RC 500 Continuously Regenerated Cation Trap, and an IonPac CS16-4 μm 2 x 250 mm analytical column with an IonPac CG16-4 μm 2 x 50 mm Guard Column. The anion system was equipped with an EGC 500 KOH Eluent Generator, an AERS 500 2 mm, a CR-ATC 500 Continuously Regenerated Anion Trap, and an AS24 2 x 250 mm analytical column with an IonPac AG24 2 x 50 mm Guard Column. All standards were made in deionized H_2O. All reported ions were calibrated between 2.485743 ppm to 10.043080 ppm. A blank of deionized H_2O was run and subtracted from all chromatograms before integration. All samples were prepared and analyzed in triplicate.

4.2. Comparison of Terra Pave products to AEP

4.2.1. Cations

In comparing the concentrations of cations which leached from Terra Pave products vs that which leached from AEP, significant differences were identified and highlighted in red text. These results were compared to measured AEP levels in Table 4-1. Generally, Terra Pave products contained higher levels of salts compared to AEP. Considering the vastly different base composition of Terra Pave products compared to the petroleum-based AEP, this was not unexpected. Specific significant differences are outlined below.

- Sodium leaching was greater in all Terra Pave products with the largest (Terra Fog) exhibiting 37x the leached sodium as AEP.
- TS White Albedo exhibited at least 3x more ammonium leaching than all other samples.
- Magnesium and calcium leaching observed in HRTS and Terra Prime was ~1.75x or greater than the rest of the samples analyzed.

Table 4-1. Comparison of cation concentrations (µg/cm²) in Asphalt Emulsion Product (AEP) to multiple Terra products. Standard deviations are provided in parenthesis.

	AEP	TS White	TS White Albedo	TS Black	HRTS	Terra Roof	Terra Prime	Terra Fog
Lithium	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Sodium	2.07 (0.55)	***62.21 (1.52)***	***66.63 (10.97)***	***78.11 (17.43)***	***45.15 (0.94)***	***35.65 (3.85)***	***57.26 (4.38)***	***77.40 (6.71)***
Ammonium	n.a.	3.60 (0.17)	***12.48 (1.48)***	4.91 (1.57)	1.71 (0.03)	2.35 (0.14)	n.a.	4.41 (0.31)
Potassium	0.04 (0.004)	1.93 (0.06)	2.63 (0.41)	0.85 (0.23)	2.12 (0.03)	0.42 (0.04)	3.73 (0.33)	1.46 (0.13)
Magnesium	0.34 (0.008)	***1.78 (0.06)***	0.57 (0.03)	0.77 (0.30)	***3.38 (0.16)***	0.44 (0.02)	***7.34 (0.70)***	1.20 (0.03)
Calcium	0.44 (0.01)	2.37 (0.06)	1.50 (0.17)	1.13 (0.40)	***4.25 (0.21)***	0.61 (0.04)	***8.89 (0.67)***	1.85 (0.08)

n.a. = no peak observed

Those cations with concentrations significantly higher than other samples have been bolded and highlighted in red.

4.2.2. Anions

In comparing the concentrations of anions which leached from Terra Pave products vs that which leached from AEP, significant differences were identified and highlighted in red text. These results were compared to measured AEP levels in Table 4-2. Again, Terra Pave products contained higher levels of salts compared to AEP. Specific significant differences are outlined below.

- Chloride leaching was significantly higher in all Terra Pave samples, with TS White, HRTS, Terra Prime, and Terra Fog samples exhibiting between 2.5-109x the leaching levels than the remaining samples.
- Sulfate leaching was significantly higher in all Terra Pave samples compared to AEP leaching (up to 110x).
- TS White Albedo exhibited higher levels of both bromide and nitrates compared to the remaining samples.

Table 4-2. Comparison of anion concentrations (µg/cm^2) in Asphalt Emulsion Product (AEP) to multiple Terra products. Standard deviations are provided in parenthesis.

	AEP	TS White	TS White Albedo	TS Black	HRTS	Terra Roof	Terra Prime	Terra Fog
Fluoride	0.17 (0.04)	0.10 (0.06)	n.a.	0.07 (0.04)	0.26 (0.02)	0.05 (0.03)	0.57 (0.05)	0.00009 (0.00001)
Chloride	0.21 (0.05)	***19.76 (0.60)***	3.54 (0.78)	6.17 (1.13)	***21.96 (0.32)***	2.61 (0.27)	***42.55 (3.28)***	***12.65 (1.49)***
Sulfate	0.55 (0.10)	***60.77 (1.67)***	***69.60 (13.88)***	***57.81 (10.95)***	***44.14 (1.30)***	***31.05 (4.24)***	***51.68 (3.05)***	***59.77 (5.39)***
Bromide	n.a.	1.24 (0.08)	***2.72 (0.55)***	n.a.	0.78 (0.02)	0.54 (0.05)	n.a.	n.a.
Nitrite	0.08 (0.06)	1.46 (0.07)	***2.67 (0.51)***	1.87 (0.45)	0.82 (0.03)	0.86 (0.05)	n.a.	***2.02 (0.14)***
Phosphate	n.a.	0.35 (0.20)	n.a.	n.a.	n.a.	n.a	n.a.	n.a.

n.a. = no peak observed

Those anions with concentrations significantly higher than other samples have been bolded and highlighted in red.

5. CONCLUSION

Through NREL and the American-Made Solar Prize contest, we have evaluated the eco-friendliness of Terra Pave products compared to that of heavily used AEP. This consisted of inorganic and organic pollutants of concern, as well as salt leaching. Based on the inorganic content of these products, Terra Pave products exhibited far less to no heavily metal contaminants, while many exhibited high levels of titanium, magnesium, potassium, and calcium. These are generally considered safe and ion chromatography revealed far less calcium and potassium leaching into the water than the total content observed in the products. Ion chromatography did however exhibit significant sodium and sulfate leaching. The volatile organic analysis revealed extremely low petroleum hydrocarbon content and outgassing in the Terra Pave products, while AEP revealed extremely high levels.

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