Composition, micromorphology and distribution of microartifacts in anthropogenic soils, Detroit, Michigan USA

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ABSTRACT

The composition, micromorphology and distribution of microartifacts in anthropogenic soils were studied as part of a project that was evaluating the utility of geophysical surveying techniques for mapping vacant urban land. Petrographic criteria for the identification and classification of microartifacts (MAs) were generated using a set of 25 different types of reference artifacts of known origin, and then tested on a suite of 20 urban topsoils from sites in Detroit, Michigan representing three different land use types (residential demolition, undemolished residential, and industrial). Petrographic and x-ray diffraction analyses showed that reference MAs may be classified into five basic compositional types (carbonaceous, calcareous, siliceous, ferruginous and miscellaneous). Reference MAs were generally distinguishable using optical microscopy by color, luster, fracture and microtexture, and further differentiable using scanning electron microscopy and energy-dispersive x-ray spectroscopy. MAs were found in all of the anthropogenic soils studied, but in highly variable proportions (< 15% to > 80%). Coal-related wastes were the most common types of MAs, and included unspent coal, ash (microspheres, microagglomerate), cinders and burnt shale, probably representing a legacy from the coal-burning era (~1850-1936 AD). These were associated with MAs derived from waste building materials (brick, mortar, glass), and manufacturing wastes (iron-making slag, coked coal), in demolition and industrial site soils, respectively. Urban soils impacted by airborne deposition of fly ash were widespread, including conspicuous black (10YR2/1) topsoils at undemolished residential sites located near railroads and areas of heavy industrial activity. Coal combustion products and iron-smelting slag had distinctive compositions that included magnetite-bearing aluminosilicate glass. These results support our hypothesis that there are systematic relationships between soil geophysical properties, type and abundance of microartifacts, and land use history. Hence, it seems likely that magnetic susceptibility surveying and other geophysical methods will facilitate the mapping of soils in urbanized areas.

Key Words: technosol, geophysical mapping, artifact, urban soil, fly ash

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1. Introduction

The traditional method of mapping involves delineating soils based on landscape position, and profile characteristics ascertained with a hand auger or in a hand-dug pit. This approach is difficult to apply in heavily urbanized terrain because anthropogenic soils often contain rock-like artifacts (objects of anthropogenic origin) that are difficult to penetrate with a hand auger or a shovel (Howard and Olszewska, 2011; Howard et al., 2013; Howard and Shuster, 2015). It is possible that the traditional method can be augmented by non-invasive, geophysical surveying using surface probes, but this approach has not yet been proven to be effective on urban soils. In a previous study, we found that the electrical conductivity (EC) and magnetic susceptibility (MS) signatures of soils were significantly impacted by different types of microartifacts (Howard and Orlicki, in press). We attributed these geophysical characteristics to compositional differences, but mineralogical data were sparse for many types of artifacts. We also found that the EC and MS signatures of soils were affected even when only a small quantity (< 5 – 10 wgt %) of microartifacts was present. However, the nature and geographic distributions of microartifacts generally found in urban soils were poorly known.

The purpose of this study was to better constrain the compositions and distributions of microartifacts in urban soils, and their EC and MS characteristics. We tested the hypothesis that there are systematic relationships between soil geophysical properties, type and abundance of microartifacts, and land use history. If so, we expect to be able to map urban land more efficiently with geophysical methods using land use history as a guide to ascertaining the geographic distribution of microartifact assemblages. We anticipate being able to not only distinguish between anthropogenic and native soils in urbanized terrain, but also amongst different types of anthropogenic soils. In this study, we investigated anthropogenic soils derived from Alfisols in a cool, humid-temperate climate. The study area was Detroit, Michigan, which has a long history of industrialization. We first assembled a collection of reference artifacts, and determined the compositions of selected types using optical petrography and x-ray diffraction analysis. We used the reference materials to develop a set of micromorphological criteria for the identification of

microartifacts. We then tested the method on urban soils associated with different land use types using optical and scanning electron microscopy, and energy-dispersive x-ray spectroscopy. In this paper, we synthesize compositional data to formulate an artifact classification system, and discuss the possible implications of microartifact assemblages and compositions for geophysical mapping. This study is timely, given that there is currently great interest in mapping urban soils.

2. Materials and methods

2.1 Terminology

In this paper, “anthropogenic particles” are artifacts of any size, whereas the terms “artifact” and “macroartifact” are used interchangeably for any object > 2 mm in size that was produced, modified, or transported from its source by human activity (Dunnell and Stein, 1989; IUSS Working Group, 2006; Schoeneberger et al., 2012; Soil Survey Staff, 2014). “Microartifacts” are 0.25 to 2.0 mm in size (Dunnell and Stein, 1989; Rosen, 1991; Sherwood, 2001), and “microparticles” are < 0.25 mm in size. “Charcoal” is charred wood produced by oxycombustion. Anthropogenic particles produced by iron smelting are called “ferruginous slag” and “glass slag”, whereas those produced by coal combustion are called “cinder” and “ash.” “Microspheres” are any type of spherical microparticle, “cenospheres” are hollow microspheres, and “pleurospheres” are hollow microspheres containing other smaller microspheres. “Concrete” refers to a lime-based material unless otherwise indicated. Human-altered material (HAM) is defined as parent material for a soil that has undergone *in situ* mixing or disturbance by humans. Human-transported material (HTM) is defined as parent material for a soil that has been moved horizontally onto a pedon from a source outside of that pedon by human activity, usually with the aid of earthmoving equipment (Soil Survey Staff, 2014). Hence, an anthropogenic soil is defined as a soil that has formed either in HAM or HTM.

2.2 Geologic setting

Detroit is located along the Detroit River adjacent to Windsor, Ontario, Canada (Fig. 1). The city lies on a glaciolacustrine lowland of late Wisconsinan age underlain by weakly stratified clayey diamicton and a discontinuous capping of sand or gravelly sand usually < 1 m thick (Howard, 2010). The climate is mesic, with a mean annual temperature of 9°C (49°F), 99 cm yr⁻¹ of precipitation, and a frost line at 107 cm depth. Native soils in Detroit are generally somewhat poorly drained Aqualfs developed in sandy (Metamora Series) or clayey diamicton (Blount Series) lacustrine sediments with a solum 70 to 75 cm thick (Larson, 1977). The Metamora soil (Udollic

Ochraqualf) has a sandy loam epipedon over gleyed and mottled subsoil, containing a prominent lithologic discontinuity at variable depths, depending on thickness of the lacustrine sand capping. The Blount soil (Aeric Ochraqualf) has a loamy epipedon over gleyed and mottled, silty clay to clay subsoil. These native soils are characterized by leaching of carbonate from the solum, and conversion of clay-sized chlorite to vermiculite in A horizons (Howard and Olszewska, 2011; Howard et al., 2012).

The land directly beneath Detroit is comprised almost entirely of anthropogenic surficial deposits of mixed earthy fill in which artifacts are widespread. Weakly developed soil profiles have formed in these fill deposits locally where they lie beneath lots created by building demolition that have remained vacant for many decades (Howard and Olszewska, 2011; Howard et al., 2013a). The anthropogenic soils studied are classified primarily as Anthropic or Anthropotic Udorthents, according to Soil Taxonomy (Soil Survey Staff, 2014), or as Technosols using the World Reference Base (IUSS Working Group, 2006). Detroit is mostly residential land (including schools, churches and small commercial businesses). Residential land in the inner city is a mosaic of demolished and undemolished building sites underlain by deposits of HTM produced by multiple demolition cycles, and comprised of material often dating from the 19th century. Residential land in the outer city is a similar mosaic, but undemolished buildings overlie relatively undisturbed native soils, and demolition site soils contain artifacts mainly from the 20th century. Small areas of Park Land and Cemetery Land are scattered throughout Detroit, and there are extensive areas of Industrial Land (current or former) concentrated along railroads, especially in the lower River Rouge basin near its confluence with the Detroit River.

2.3 Reference Artifacts

The reference materials used in this study were anthropogenic particles of known origin obtained locally from demolition sites, derelict buildings awaiting demolition, and other miscellaneous sources (Table 1). Artifact compositions are based on compilations from the literature. If published data were not available, petrographic compositions were determined by transmitted light microscopic analysis of thin sections stained for calcite, or x-ray diffraction (XRD) analysis of finely ground samples using a Bruker Phaser II diffractometer equipped with a LYNXEYE detector. Reference materials were produced by sizing with a jaw crusher, and collecting the > 2 mm, 0.25 to 2 mm (medium to very coarse sand) and 90 to 150 μ (very fine to fine sand) fractions by wet sieving. The petrographic features of microartifacts (0.25 to 2 mm) were characterized with a binocular microscope using the

criteria explained in Supplementary Table 1. Microparticles of iron-smelting slag, coal, and coal-ash were collected by hand-picking under a binocular microscope, coated in gold, and analyzed by scanning electron microscopy (SEM) using a JEOL JSM-7600F field-emission instrument. Chemical microanalyses were done by energy dispersive x-ray spectroscopy (EDS) using a Pegasus Apex 2 instrument. Chemical compositions are based on analyses of about ten individual particles per sample. Two different coal samples were analyzed and averaged together. The “average fly ash” composition was determined by averaging results from two different fly ash samples. The analyses are based on a scan of 20 to 30 densely clustered grains, repeated five times per sample. Confidence limits (error polygons) for elemental analyses were calculated as: $CI = tS/\sqrt{n}$, where CI is the confidence interval ($p = 0.05$), t is the tabulated value of Student's t -distribution, S is the standard deviation, and n is the number of particles analyzed.

2.4 Urban Soils

Topsoil samples (0 to 15 cm depth) were collected using a plastic trowel from 20 sites in metropolitan Detroit, Michigan (Fig. 1), including some of the same sites studied previously by Howard et al. (2013a). Anthropogenic soils were collected at five abandoned industrial sites, and at 15 residential sites, within 10 to 15 km of inner city Detroit. Ten of the residential samples were obtained from vacant lots at former demolition sites. Five were obtained from the front yards of abandoned derelict homes (undemolished residential). One of the industrial site soils was reassigned to the residential demolition category after microscopic analysis revealed a lack of industrial-type microartifacts. All soil samples were collected in clean polypropylene bags. Anthropogenic particles were obtained using a 35 g aliquot of < 2 mm soil, which was first dispersed in 1 N Na_2CO_3 , then soaked in a 10% solution of H_2O_2 for 4 to 7 days to remove soil organic matter, and wet-sieved to obtain the 0.25 to 2 mm and 90 to 150 μ fractions. Microartifact identifications were made using the same optical methods described above. A separate two gram sample of the 90 to 150 μ fraction of selected soils was extracted with a strong hand magnet, and weight % magnetic material determined gravimetrically. The 90 to 150 μ fractions of an undemolished industrial site soil, a demolished industrial site soil, and the magnetic fraction of soils at five undemolished residential sites, were examined by SEM-EDS analysis.

Results

3.1 Composition of Reference Artifacts

The compositions of reference artifacts are shown in Table 2. Thin sections showed that coal macroartifacts were comprised of macerals, primarily vitrinite (Fig. 2A). Asphaltic concrete was made up primarily of aggregate (95%), and only contained about 5% asphaltic binder (Fig. 2B). Petrographic and XRD analyses showed that mortar (Fig. 2C) and concrete were comprised of sand-sized or gravel-sized felsic aggregate, respectively, bound together mainly by calcite. Cinder block contained blast furnace cinders as aggregate and was characterized by very large voids (Fig. 2D). Coal cinders were characterized by a glassy vesicular microtexture with fluxion structure (Fig. 2E), and contained masses of acicular crystals which XRD analysis showed were mullite (Fig. 3), associated with magnetite and wustite. XRD analysis (Fig. 3) showed that the orange and red bricks were similar in composition. Both contained abundant quartz, and are probably comprised primarily of layer silicate minerals partially altered to glass. However, the red brick contained some cristobalite, whereas the orange brick contained carbonate minerals in greater abundance. Burnt shale, produced as an incidental byproduct of coal combustion, contained glass and mullite. Ferruginous iron-smelting slag was dense, highly vesicular (Fig. 2F), and characterized by a high temperature mineral suite including olivine, merwinite and wollastonite (Fig. 3). Glass slag produced by iron-smelting was siliceous and primarily non-crystalline, but was found to contain some silicate minerals including chlorite (Fig. 3), giving it a distinctive green color. Wrought iron nails, common in soils where buildings from the 19th century are demolished, were usually corroded and found previously to consist of a remnant ferrite nail core encased in a ferrihydrite- and goethite-cemented soil crust (Howard et al., 2013a, 2015b). XRD analysis of a sample of drywall showed that it was comprised almost entirely of gypsum.

3.2 Micromorphology of Reference Artifacts

The micromorphological characteristics of microartifacts (MAs) determined by reflected light microscopy are shown in Table 3. Wood MAs (lumber) lack luster and were brown, fibrous or platy with a splintery cleavage (Fig. 4A). Charcoal MAs retained the fibrous or platy shape and splintery cleavage of wood, but are black with a bright vitreous luster (Fig. 4B). The lamellar microstructure of wood is partially retained by coal (Fig. 4C). Hence, some of the coal MAs, with a fibrous or platy morphology and splintery cleavage, were indistinguishable from charcoal. However, coal MAs were more often angular blocky grains with a well developed conchoidal fracture, and may be distinguished by microlamination not seen in charcoal. Coked coal MAs were distinguished from charcoal and coal by their highly vesicular morphology (Fig. 4D), which contrasts sharply with the splintery fracture

of coal and charred wood. Some coke grains were iridescent, possibly due to thin microlamellar coatings of glass, or an unknown crystalline organic compound. When asphaltic concrete was crushed, the aggregate formed MAs which were indistinguishable from rock and mineral particles of natural origin. However, MAs containing the bituminous binder could be distinguished as anthropogenic. Asphaltic MAs were black and opaque (Fig. 4E) like coal and coke, but differed in being equant and subrounded with a dull earthy or resinous luster, and a granular, polymictic, aggregatic microtexture.

When lime-based concrete, mortar and brick particles were crushed for sizing, the aggregate formed MAs which were indistinguishable from natural rock and mineral particles. MAs containing the anthropogenic cement component (Fig. 4F) differed from most carbonaceous MAs in being light-colored with a polymictic granular texture (Table 3). However, it was generally not possible to distinguish between sand-sized grains of concrete, mortar and lime-brick. Asphaltic concrete had a granular aggregatic texture, but was darker and rounder than the lime-based MAs. Cinder block MAs were distinguished by a characteristic gray color, granular vesicular texture, and the presence of highly vesicular pumice-like pieces of blast furnace slag (Fig. 4G).

Coal cinder MAs were moderately to strongly magnetic and distinguishable from coal by their vesicular microtexture, and from coke by their color (multicolored black and pale brown to greenish-brown), dull vitreous luster, and conchoidal fracture (Fig. 4H). Coal ash was found to be comprised of a variety of different particle types, which can be classified generally as either spherical or non-spherical. Glassy, translucent microspheres (Fig. 4I) were common, along with light to dark-colored non-spherical, highly vesicular, pumice-like grains. Microagglomerate (Fig. 4J) was comprised of an agglutination of non-spherical or spherical microparticles. Although some coal-ash particles were in the size range of microartifacts (0.25 – 2.0 mm), most were < 0.25 mm in size. Ceramic brick MAs (Fig. 4K) had an earthy luster and granular microaggregatic texture, but were generally reddish or orangish brown in color, and contain finer grained aggregate than mortar. Terracotta and stoneware MAs, including pottery, were microscopically indistinguishable from brick MAs. The glazed ceramic pipe MAs were also similar to brick (Fig. 4L), but some grains had a slightly more vitreous luster. They were also characterized by an association of gray and reddish brown particles, the later often coated with a conspicuous glassy glaze. Window and bottle glass MAs had extreme angularity, conchoidal fracture, and were differentiated from quartz by their characteristic transparency (Fig. 4M). Glass slag MAs were similar to manufactured glass shards, but tended to be

less transparent (Fig. 4N). They ranged from darker green and opaque grains with a dull vitreous or resinous luster, to pale green translucent grains with a bright vitreous luster. Burnt shale MAs were distinguishable by their pinkish-gray color, dull vitreous luster, and platy fracture (Fig. 4O).

Ferruginous slag MAs were strongly magnetic with a granular vesicular texture. They were distinguishable from coal cinders by a jagged hacky fracture and a metallic luster (Fig. 4P). The corroded iron nail MAs were distinguished by a metallic luster, and the association of ferrite, goethite and ferrihydrite (Fig. 4Q). Fly ash was comprised partly of dark colored, magnetic, opaque microspheres with metallic luster (Fig. 4R). Drywall MAs were white, distinguished by very fine pores (Fig. 4S), and contained plastic fibers. In contrast, bone was characterized by very coarse cavities and pores (Fig. 4T).

3.3. Microartifacts in Urban Soils

MAs generally comprised 5 to 15% of the sand fraction of residential demolition site soils, although some samples contained as much as 30 to 40%. Undemolished residential site soils contained 20 to 40% MAs, and MAs comprised 80 to 95% of the sand fractions of industrial site soils. Coal-related wastes were the most common types of MAs (Fig. 5). They were seen in soils at sites representing all three of the land use types studied, and included unspent coal, ash (microspheres, microagglomerate), cinder and burnt shale. Although coal and charcoal MAs were indistinguishable, coal appeared to be widespread by association with cinders, microspheres and microagglomerate. Microspheres ranged from clear and translucent, to opaque brown or reddish-brown, and black. Grains of microagglomerate ranged from grayish-brown to black. Demolition site soils typically contained a mixed suite of MAs representing waste building materials and coal-related wastes (Fig. 6A). Glass, brick, mortar and cinder were the most common MAs in residential demolition site soils (Fig. 5), which is consistent with the observed abundances of macroartifacts (Howard, 2014; Howard et al., 2015ab). Undemolished residential site soils contained only microspheres and microagglomerate grains, suggesting that they had been impacted by airborne deposition of fly ash. These soils were mainly associated with abandoned derelict homes located near railroads or areas of heavy industrial activity. MAs in industrial site soils were dominantly coal-related wastes (coal, cinder and ash) in a mixture with MAs unique to manufacturing operations such as coked coal and ferruginous slag (Fig. 6B). Thus, the results in Figure 5 suggest that distinctive MA assemblages correspond to differences in land use history.

An association was noted between low-value/low-chroma topsoils and weight % magnetic microparticles in the study area. Topsoils at residential demolition sites ranged from brown (10YR5/4) to black (10YR3/1) with increasing soil age from ~3 to 68 years, and about 1 to 4% of the fine sand fraction was magnetic (Fig. 5). In contrast, industrial site topsoils were all very black (10YR2/1), and 25-35% of the fine sand fraction was magnetic. Fly ash-impacted, undemolished residential topsoils were also black (10YR3/1), but only 1 to 4% of the fine sand fraction was magnetic. Removal of the magnetic fraction with a hand magnet resulted in a striking increase in the value and chroma of these soils, suggesting that much of the black color was caused by an abundance of iron microspheres.

3.4. SEM-EDS Analyses

SEM-EDS analyses of individual grains (Fig. 6; Supplementary Table 2) showed that reference coal, iron-smelting slag and coal (fly) ash microparticles were distinguishable on the basis of Fe, Si and C content (Fig. 7). Fly ash ranged widely in composition from carbonaceous, to siliceous and ferruginous, corresponding to micromorphological differences. The black opaque microspheres were ferruginous, whereas the clear translucent microspheres were siliceous. Non-spherical, vesicular, pumice-like microparticles varied from carbonaceous (dark colored) to siliceous (light colored). When clusters of grains from the two different fly ash samples were scanned simultaneously (i.e. the “average fly ash”), both were found to be very similar in composition to each other, and to the carbonaceous fly ash particles analyzed individually. This suggests that, on average, carbonaceous fly ash particles were most abundant.

Microparticle assemblages in the industrial site soils were complex, and some of the grains were difficult to distinguish using optical microscopy alone. Hence, a suite of microparticles from a representative sample were analyzed by SEM-EDS (Supplementary Table 3). Some particles plotted in the field of the reference coal sample, others plotted in, and around, the fly ash fields, and a few plotted near the iron slag field on the ternary diagram (Fig. 7). Thus, the variable compositions of grains in the industrial site soil seem to reflect the fact that it is comprised of a mixture of microparticle types, which is consistent with observations made using optical microscopy (Fig. 6B). Some dark-colored vesicular grains from a former industrial demolition site soil, which had a bright luster, were found to plot in close association with the carbonaceous fly ash field (Fig. 7). Hence, these grains were identified as coal cinder MAs using SEM-EDS. The microagglomerate grains from the undemolished residential site soils mainly

plotted in, and around, the fly ash fields, which verified that these soils had been impacted by fly ash. Ferruginous microspheres, siliceous microspheres, and non-spherical siliceous microparticles from a fly ash-impacted soil in Roosevelt Park (Fig. 1; site 3), adjacent to the historic Michigan Central train station, also plotted in, or near, the fields of reference fly ash microparticles (Fig. 7).

SEM-EDS analyses suggest that two types of microagglomerate MAs were present in the fly ash-impacted soils. Type A was comprised of microspheres embedded in an agglutinated matrix of non-spherical microparticles, and was only sparsely abundant. The microspheres are comprised of Fe and O, and are inferred to be magnetite (Fig. 6C and D), based on observations using optical microscopy that the microspheres are magnetically attracted to each other, thus forming long chains and clusters. The matrix of non-spherical grains is interpreted as aluminosilicate glass containing trace amounts of Cu, Ti, and Zn (Fig. 6E and F). Type B microagglomerate was comprised entirely of non-spherical grains, and was the predominant type of microagglomerate particle in the fly ash-impacted soils. EDS analyses showed that type B grains were of very similar composition in each of the five soils studied (Supplementary Table 3). Types A and B are similar in composition to the non-spherical siliceous fly ash particles in Roosevelt Park (Fig. 7).

Overall, the average elemental compositions of reference coal, iron slag and fly ash were distinctive (Table 4). Iron-smelting slag was characterized by very high values of Ca and Fe, and very low C and Si. It was distinguished by the presence of Mn and a very high O/C ratio. Coal was characterized by very high C, and hence the lowest O/C ratio. It was distinguished by the presence of S and occasionally P. Fly ash showed a similar pattern of increasing O/C ratio with increasing Fe content, and decreasing O/C ratio with increasing C content. Carbonaceous and siliceous fly ash microparticles were generally highest in bases and Ti. In general, carbonaceous microparticles had an $O/C < 1.0$, whereas siliceous and ferruginous types were > 1.0 . Microparticles from the industrial site soil were distinguished by high Fe values, and high levels of Cu, Ti and Zn (Table 4). The fly ash-impacted soils had lower levels of Fe, despite being magnetic, but also contained elevated levels of Cu, Ti and Zn.

4. Discussion

The results of this study suggest that anthropogenic particles may be classified into five basic compositional types (Table 2). Carbonaceous particles are comprised primarily of organic compounds, calcareous

types of calcite, siliceous types of silicate minerals and glass, ferruginous types of Fe-oxides, and miscellaneous types of sulfate and phosphate minerals. Many of the observed compositional and micromorphological characteristics are related to heating or combustion as a result of human activity. For example, wood (comprised of cellulose and lignin) undergoes partial thermal decomposition at $\sim 250^{\circ}$ to 400°C . Thus, charcoal is comprised of hydrocarbons and black carbon (Rutherford et al., 2005; Brodowski et al., 2005), mixed with remnant laminar structures of parent plant materials (Cornelissen et al., 2005; Forbes et al., 2006). Coal is comprised of vitrinite macerals, which also retain the laminar microstructure of wood (Petrakis and Grandy, 1980; ICCP, 1998; Suarez-Ruiz, 2012). This explains the splintery fracture of wood, charcoal and coal MAs (Table 3). The coking process involves heating bituminous coal to $\sim 1100^{\circ}\text{C}$ or more (Suarez-Ruiz, 2012). As coal is heated, it softens into a plastic mass, devolatilizes and vesiculates, often with considerable foaming. This accounts for the vesicular microtexture of coked coal MAs (Table 3). Coal cinders are formed by combustion of coal at $\sim 1200^{\circ}$ to 1500°C (Ward and French, 2005) when ash particles derived from the inorganic constituents of coal fuse together. Hence, the vesicularity of the typical coal cinder can be attributed to degassing in a molten state. Similarly, ferruginous slag represents the vesiculated molten inorganic waste left after heating iron ore and other additives at $\sim 2000^{\circ}\text{C}$ in a blast furnace (Proctor et al., 2000). The vitreous luster of cinders and certain ceramic artifacts reflects the presence of glass produced by decomposition of phyllosilicates above $\sim 900^{\circ}\text{C}$ (Livingston et al., 1998; Cultrone et al., 2004, 2005).

Most previous studies of microartifacts were done by archaeologists (Dunnell and Stein, 1989; Rosen, 1991; Sherwood, 2001), typically to infer human behavior at prehistoric sites in non-urban areas, e.g., identifying activity areas, assessing tool technology, etc. The results of this study suggest that a wider variety of informative microartifacts is potentially present at historic sites in urban areas. Microartifacts usually can be distinguished readily by their micromorphological characteristics using an optical microscope. However, there were some uncertainties in differentiating charcoal from coal, clay brick MAs from pottery sherds and, in some cases, coal cinders from iron-smelting slag. Although this may not be serious problem at prehistoric sites, it may confound geoarchaeological analyses of historic sites. Our data suggest that most such microartifacts of questionable affinity can be identified successfully using a combination of optical microscopy and SEM-EDS analyses. However, it is unclear if this approach is effective for distinguishing clay brick MAs from pottery sherds.

Our previous work demonstrates that some microartifacts are characterized by high abrasion pHs, which was attributed to the hydrolysis of basic cations released from the abraded surfaces of minerals (Howard and Orlicki, in press). The results of this study are consistent with that interpretation. The data in Figures 2 and 3 suggest that concrete, mortar, coal cinders, orange brick and ferruginous slag MAs have high abrasion pHs because they contain significant amounts of carbonate minerals or portlandite. High values of electrical conductivity were observed in association with mortar, concrete, orange brick and ferruginous slag artifacts (Howard and Orlicki, in press). The results herein suggest that this is explained by ionic conduction via cations released from the abraded surfaces of carbonate minerals or portlandite. In the case of clay bricks, variations in electrical conductivity can be explained further by differences in firing temperature. Bricks from the 19th century were typically fired at temperatures < 900°C because of technological limitations (Reedy, 2008). At temperatures above ~900°C, dolomite and calcite begin to decompose to CaO, and phyllosilicates are altered to non-crystalline material (Cultrone et al., 2004, 2005). Hence, because glass is an insulator, the much higher electrical conductivity of the 19th century orange unglazed brick (compared with the 20th century red glazed brick) is attributed to the presence of phyllosilicates which were still relatively intact. Ionic conduction was probably affected by these phyllosilicates because the diffuse double layer has a higher conductivity than the soil solution (Telford et al., 1990; Wightman et al., 2003).

MAs were widespread in the anthropogenic soils studied, and varied as a function of land use history (Table 5). The presence of MAs explains why anthropogenic soils can be distinguished from native soils on the basis of elevated values of pH, electrical conductivity and magnetic susceptibility (Howard and Orlicki, in press). Elevated values of pH and electrical conductivity are generally attributable to the presence of carbonate- or portlandite-bearing MAs, particularly brick, mortar and glass, whereas elevated magnetic susceptibilities are explained by magnetite-bearing fly ash, cinder or ferruginous slag MAs. Although MAs were widespread, they generally comprised < 30% of sand fractions. However, our previous work has shown that the geophysical signatures of soils are affected even when only small quantities (< 5-10%) of microartifacts are present (Howard and Orlicki, in press). Compared with the diverse artifact types reported previously in the > 2 mm fraction (Howard and Olszewska, 2011; Howard et al., 2013a), there were far fewer different types of artifacts seen in the < 2 mm fraction (Fig. 5). On the other hand, some anthropogenic particle types (e.g., fly ash) were only seen in the sand-sized and finer fractions. Some waste building materials which were expected, but not seen as microartifacts, included plaster (or drywall) and paint. However, the results of Dubay's (2012) simulated weathering experiment suggest that these

materials may have decomposed after more than 30 years of weathering. This is also in accordance with artifact stability sequences previously observed, and weathering rates predicted by the solubility products of principal mineral components of artifacts (Howard and Olszewska, 2011; Howard et al., 2013ab).

The micromorphological characteristics of fly ash particles like those seen in the anthropogenic soils studied are similar to those reported previously. Microsphere and microagglomerate particles are typical of fly ash (Fisher et al., 1976, 1978) which, along with cenospheres and pleuroospheres, are commonly 20 to 150 μ in size (Smith et al., 1979; Ngu et al., 2007). Fisher et al. (1976, 1978) previously described eleven different morphological types of fly ash microparticles, including microagglomerate. They also noted that microparticles with similar morphology often have different chemical compositions. Fly ash particles are generally formed by condensation of gas bubbles blown off from the surface of burning coal (Fisher et al., 1976; Smith et al., 1979). Anthropogenic magnetite microspheres and agglomerate have been reported from soils elsewhere, and may be generated from various industrial combustion processes (Yang et al., 2010a; Lu et al., 2011; Lanteigne et al., 2012). Magnetite “ferrospheres” are known to be derived by molten iron and coal combustion (Fisher et al., 1978; Sharonova et al., 2013).

The large quantities of magnetic fly ash particles found in the anthropogenic soils of the study area were surprising. However, there have been anecdotal references to the airborne deposition of black anthropogenic dust from industrial sources for many years in Detroit City (Detroit Free Press, 2010), particularly before the advent of air pollution control measures. It is also likely that this material is partly a legacy from the coal-burning era in Detroit (~1850 to 1936 A.D.). SEM-EDS analyses showed that the microagglomerate particles in the fly ash-impacted soils were more ferruginous than the reference fly ash samples obtained from coal-fired power plants. This may indicate that these microparticles were produced by iron-smelting. The observed increase in the abundance of ferruginous fly ash particles in soils with increasing age also accounts for the utility of the ΔA horizon-Darkening-Index of Howard et al. (2013a) as a relative soil age indicator in urban settings. Soils impacted by airborne deposition of fly ash is a well known phenomenon in Europe. Although most airborne deposition generally takes place at distances of < 5 to 10 km (Hartmann et al., 2010), significant levels of fly ash deposition have been measured locally at 10 to 30 km (Schmidt et al., 2000; Koschke et al., 2011), from the source. Very fine fly ash particles are probably able to travel for many tens of km (Rose, 1996). Excessive airborne deposition and

accumulation of black fly ash microparticles is significant from the standpoint of Soil Taxonomy because fly ash-contaminated topsoils with very low chromas can be easily mistaken in the field for mollic epipedons.

The data in Table 2 show that anthropogenic particles commonly found as artifacts are often comprised of artificial minerals (or mineraloids) not normally found in rocks and native soil parent materials. For example, fly ash contains glass and mullite (Ward and French, 2005), concrete contains ettringite, belite, and portlandite (Marchand et al., 2001), and steel-making slag contains merwinite, melilite, etc. (Proctor et al., 2000). Our previous work showed that weathering of artifacts affected the chemistry and mineralogy of urban soil chronosequences in Detroit, Michigan. Alteration of calcareous (mortar) and ferruginous (nails) artifacts resulted in measurable increases in carbonate and Fe-oxide contents, respectively, after only 35 years of weathering (Howard and Olszewska, 2011; Howard et al., 2013a). Further study is needed to determine what impacts the weathering of artificial minerals may have on soil health, the biogeochemical cycling of nutrients and pollutants, and perhaps other characteristics affecting the future use and management of anthropogenic soils. Artificial minerals may also potentially affect the taxonomic classification of anthropogenic soils at the family level.

5. Conclusions

The results of this study show that microartifacts may be classified into carbonaceous, calcareous, siliceous, ferruginous, and miscellaneous compositional types. Most can be identified by their micromorphological characteristics using optical microscopy alone, but some require additional SEM-EDS analyses. Many of the observed compositional and micromorphological characteristics of microartifacts are related to heating or combustion as a result of human activity. Microartifacts are widespread in the anthropogenic soils studied, and varied with land use type. Coal-related wastes were the most common types of microartifacts, and soils impacted by fly ash were widespread. Coal ash, cinders and certain other artifacts were found to be highly magnetic. Compositional differences explain why many artifacts have unique geophysical signatures. These results support our hypothesis that urban soils contain microartifacts of distinct composition which vary systematically as a function of land use history. Hence, it seems likely that magnetic susceptibility surveying and other geophysical methods will be effective for mapping soils in urbanized terrain. Further studies are underway to test these methods in the field. We recognize that the results of this study may only be applicable to cities with a long industrial history, and where anthropogenic soils are derived from Alfisols formed glacial parent materials in a cool-humid temperate

climate. Further studies are needed to determine if these results are applicable to other soil orders in different settings.

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References

- Asami, K., Kikuchi, M., 2002. Characterization of rust layers on weathering steels air-exposed for a long period. *Materials Trans.* 43, 2818-2825.
- Bayless, E.R., Bullen, T.D., Fitzpatrick, J.A., 2004. Use of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$ to identify slag-affected sediment in southern Lake Michigan. *Environ. Sci. Tech.* 38, 1330-1337.
- Berna, F., Matthews, A., Weiner, S. 2004. Solubilities of bone mineral from archaeological sites: the recrystallization window. *J. Archaeol. Sci.* 31, 867-882.
- Brodowski, S., Amelung, W., Haumaier, L., Abetz, C., Zech, W., 2005. Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy dispersive x-ray spectroscopy. *Geoderma* 128, 116-129.
- Brown, J.L., 2013. Rocky road: The story of asphalt pavement. *Civil Eng.* 83, 40-43.
- Carlson, C.L., Adriano, D.C., 1993. Environmental impacts of coal combustion residues. *Jour. Environ. Qual.* 22, 227-247.

- 399 Choudhury, N., Mohanty, D., Boral, P., Kumar, S., Hazra, S.K., 2008. Microscopic evaluation of coal and coke for
400 metallurgical usage. *Current Science* 94, 74-81.
- 401 Cornelissen, G., Gustafsson, O., Bucheli, T.D, Jonker, M.T.O., Koelmans, A.A., van Noort, P.C.M., 2005. Extensive
402 sorption of organic compounds to carbon black, coal, and kerogen in sediments and soils: Mechanisms and
403 consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Tech.* 39, 6881-6895.
- 404 Cultrone, G., Sebastian, E., Elert, K., de la Torre, M. J., Cazalla, O., Rodriguez-Navarro, C., 2004. Influence of
405 mineralogy and firing temperature on the porosity of bricks: *Journal of the European Ceramic Society* 24, 547-564.
406
- 407 Cultrone, G., Sebastian, E., de la Torre, M.J., 2005. Mineralogical and physical behavior of solid bricks with
408 additives: *Construction and Building Materials* 19, 39-48.
409
- 410 Detroit Free Press, 2010. 48217: Life in Michigan's most polluted zip code, illness is just as pervasive as metallic
411 dust cover. June 10, 2010.
- 412 Diamant, R. M. E. 1970. *The chemistry of building materials*. Business Books, London.
- 413 Doolittle, J.A., Indorante, S.J, Potter, D. K., Hefner, S.G., McCauley, W. M. 2002. Comparing three geophysical
414 tools for locating sand blows in alluvial soils of southeast Missouri. *Jour. Soil Water Conserv.* 57, 175-182.
- 415 Doolittle, J.A., Brevik, E.C., 2014. The use of electromagnetic induction techniques in soils studies. *Geoderma* 223-
416 225, 33-45.
- 417 Dubay, B.R., 2012. Urban soil genesis, weathering of waste building materials, and bioavailability of lead in a
418 chronosequence at former demolition sites, Detroit, Michigan. M.S. thesis, Dept. of Geology, Wayne State
419 University, Detroit, MI, 107 pp.
- 420 Dunnel, R.C., Stein, J.K., 1989. Theoretical issues in the interpretation of microartifacts: *Geoarchaeology* 4, 31-42.
- 421 Effland, W.R., Pouyat, R.V., 1997. The genesis, classification, and mapping of soils in urban areas. *Urban*
422 *Ecosystems* 1, 217-228.

- 423 Fisher, G.L., Chang, D.P.Y., Brummer, M., 1976. Fly ash collected from electrostatic precipitators: Microcrystalline
424 structures and the mystery of the spheres. *Science* 192, 553-555.
- 425 Fisher, G.L., Prentice, B.A., Silberman, D., Ondov, J.M., Biermann, A.H., Ragaini, R.C., McFarland, A.R., 1978.
426 Physical and morphological studies of size-classified coal fly ash. *Envir. Sci. Tech.* 12, 447-451.
- 427 Forbes, M.S., Raison, R.J., Skjemstad, J.O., 2006. Formation, transformation and transport of black carbon
428 (charcoal) in terrestrial and aquatic systems. *Sci. Total Env.* 370, 190-206.
- 429
- 430 Fredericci, C.; Zanutto, E.D.; Ziemath, E.C., 2000. Crystallization mechanism and properties of a blast furnace slag
431 glass. *Journal of Non-Crystalline Solids* 273, 64–75.
- 432
- 433 Fromm, J., 2013. Xylem development of trees: From cambial divisions to mature wood cells. In: Fromm, J. (Ed.),
434 Cellular aspects of wood formation. *Plant Cell Monographs* Vol. 20, Springer-Verlag, Berlin, pp. 3-40.
- 435
- 436 Gray, R.J., 1991. Some petrographic applications to coal, coke and carbons. *Org. Geochem.* 17, 535-555.
- 437 Hartmann, P., Fleige, H. Horn. R., 2010. Changes in soil physical properties of forest floor horizons due to long-
438 term deposition of lignite fly ash. *Jour. Soils Seds.* 10, 231-239.
- 439 Howard, J.L. 2010, Late Pleistocene glaciolacustrine sedimentation and paleogeography of southeastern Michigan,
440 USA. *Sedim. Geol.* 223, 126-142.
- 441 Howard, J.L., Olszewska. D., 2011. Pedogenesis, geochemical forms of heavy metals, and artifact weathering in an
442 urban soil chronosequence, Detroit, Michigan. *Envir. Poll.* 159, 754-761.
- 443 Howard, J.L., Clawson, C.R., Daniels, W.L., 2012. A comparison of mineralogical techniques and potassium
444 adsorption isotherm analysis for relative dating and correlation of late Quaternary soil chronosequences. *Geoderma*
445 179-180, 81-95.
- 446 Howard, J.L., Dubay, B.R., Daniels, W. L., 2013a. Artifact weathering, anthropogenic microparticles, and lead
447 contamination in urban soils at former demolition sites, Detroit, Michigan. *Envir. Poll.* 179: 1-12.

- 448 Howard, J.L., Dubay, B.R., McElmurry, S.P., Clemence, J., Daniels, W.L., 2013b. Comparison of sequential extraction and
 449 bioaccessibility analyses of lead using urban soils and reference materials. *Water Air Soil Pollut.* 224: 1678-1691.
 450
- 451 Howard, J.L., Putnam, S., Moorhead, S., Schooch, R., 2013c (unpub.), Preliminary Quaternary geologic map of the
 452 Detroit, Michigan quadrangle. Scale: 1:24,000.
- 453 Howard, J.L., 2014. A proposal to add anthrostratigraphic and technostratigraphic units to the stratigraphic code for
 454 classification of anthropogenic Holocene deposits. *The Holocene* 24, 1856-1861.
- 455 Howard, J.L., Shuster, W.B., 2015a . Experimental order 1 soil survey of vacant urban land, Detroit, Michigan.
 456 *Catena* 126, 220-230.
- 457 Howard, J.L., Ryzewski, K., Dubay, B.R., Killion, T.K., 2015b. Artifact preservation and post-depositional site-
 458 formation processes in an urban setting: A geoarchaeological study of a 19th century neighborhood in Detroit,
 459 Michigan. *Jour. Archaeol. Sci.* 53, 178-189.
- 460 Howard, J.L., Orlicki, K. M., in press . Effects of anthropogenic particles on the chemical and geophysical
 461 properties of urban soils, Detroit, Michigan. *Soil Science*.
- 462 ICCP (International Committee for Coal and Organic Petrology), 1998. The new vitrinite classification (ICCP
 463 System 1994). *Fuel* 77, 349-358.
- 464 IUSS Working Group, 2006. World Reference Base for Soil Resources 2006: World Soil Resources Report 103,
 465 Food and Agriculture Organization United Nations, Rome, Italy, 145 p.
- 466 Kapper, K.L., Anesin, D., Donadini, F., Angelucci, D.E., Cavulli, F., Pedrotti, A., Hirt, A.M., 2014. Linking site
 467 formation processes to magnetic properties. Rock and archaeomagnetic analysis of the combustion levels at Riparo
 468 Gaban (Italy). *Jour. Archaeol. Sci.* 41, 836-855.
- 469 Kosmatka, S.H., Kerkoff, B., Panerese, W.C., 2002. Design and control of concrete mixtures. 14th ed., Skokie, IL.,
 470 Portland Cement Assoc., 358 pp.

- 471 Koschke, L., Lorz, C., Furst, C., Glaser, G., Makeschin, F., 2011. Black carbon in fly-ash influenced soils of the
 472 Dubener Heide region, central Germany. *Water Air Soil Pollut.* 214, 119-132.
- 473 Lane, D.S., 2004. Petrographic methods of examining hardened concrete: A petrographic manual. U.S. Dept. of
 474 Transp. Pub. FHWA-HRT-04-150, 324 pp.
- 475 Lanteigne, S., Schindler, M., McDonald, A.M., Skeries, K., Abdu, Y., Mantha, N.M., Murayama, M., Hawthorne,
 476 F.C., Hochella, M. F., Jr., 2012. Mineralogy and weathering of smelter-derived spherical particles in soils:
 477 Implications for the mobility of Ni and Cu in the surficial environment. *Water Air Soil Pollut.* 223, 3619-3641.
- 478 Larson, J. D. 1977. Soil survey of Wayne County area, Michigan. U.S. Gov. Printing Office, 83 pp.
- 479 Livingston, R.A., Stutzman, P.E., Schumann, I., 1998. Quantitative x-ray diffraction analysis of handmolded brick.
 480 In: Baer, N. S., Fritz, S., and Livingston, R. A. (Eds.), *Conservation of historic brick structures*. Donhead Pub. Ltd.,
 481 Shafesbury, UK., pp. 105-116.
- 482
- 483 Lu, S.G., Wang, H.Y., Guo, J.L., 2011. Magnetic enhancement of urban roadside soils as a proxy of degree of
 484 pollution by traffic-related activities. *Environ. Earth Sci.* 64, 359-371.
- 485 Marchand, J., Bentz, D.P., Samson, E., Maltais, Y., 2001. Influence of calcium hydroxide dissolution on the
 486 transport properties of hydrated cement systems. *Materials science of concrete*, American Ceramic Society, 113-129.
- 487 McGill, J.T., 1964. Growing importance of urban geology. *USGS Circular* 487, 4 pp.
- 488 Miller, F.P., 1978. Soil survey under pressure: The Maryland experience. *Jour. Soil Water Conserv.* 33, 104-111.
- 489 Moffatt, I., Wallis, L.A., Hounslow, M.W., Niland, K., Domett, K., Trevorrow, G., 2010. Geophysical prospection
 490 for late Holocene burials in coastal environments: Possibilities and problems from a pilot study in south Australia.
 491 *Geoarchaeology* 25, 645-665.
- 492 Mukherjee, S., 2011. *Applied mineralogy – applications in industry and environment*. Springer, Dordrecht, 575 pp.
- 493 Nearing, G.S., Tuller, M., Jones, S.B., Heinse, R., Meding, M.S., 2013. Electromagnetic induction for mapping
 494 textural contrasts of mine tailings deposits. *Jour. of Applied Geophy.* 89, 11-20.

- 495 Neff, D., Dillman, P., Bellot-Gurlet, L., Beranger, G., 2005. Corrosion of iron archaeological artefacts in soil:
496 characterization of the corrosion system. *Corros. Sci.* 47, 515-535.
- 497 Ngu, L.N., Wu, H., Zhang, D.K., 2007. Characterization of ash cenospheres in fly ash from Australian power
498 stations. *Energy and Fuels* 21, 3437-3445.
- 499 Petrakis, L., Grandy, D.W., 1980. Coal analysis, characterization and petrography. *Jour. Chem. Ed.* 57, 689-694.
- 500 Piatak, N.M., Seal, R.R., II, 2012. Mineralogy and environmental geochemistry of historic iron slag, Hopewell
501 Furnace National Historic Site, Pennsylvania, USA. *Appl. Geochem.* 27, 623-643.
- 502 Price, S. J., Ford, J. R., Cooper, A. H., Neal, C., 2011. Humans as major geological and geomorphological agents in
503 the Anthropocene: the significance of artificial ground in Great Britain: *Philosophical Transactions of the Royal*
504 *Society (Series A)* 369, 1056-1084.
- 505 Proctor, D.M., Fehling, K.A., Shay, E.C., Wittenborn, J. L., Green, J.J., Avent, C., Bigham, R.D., Connolly, M.,
506 Lee, B., Shepker, T.O., Zak, M.A., 2000. Physical and chemical characteristics of blast furnace, basic oxygen
507 furnace, and electric arc furnace steel industry slags. *Envir. Sci. Tech.* 34, 1576-1582.
- 508 Rapp, G., 2009. *Archaeomineralogy*. Springer, Dordrecht.
- 509
- 510 Reedy, CL. 2008. *Thin-section petrography of stone and ceramic cultural materials*. Archetype Pub. Ltd., London,
511 256 pp..
- 512 Rose, N. L., 1996. Inorganic fly-ash spheres as pollution tracers. *Environ. Pollut.* 91, 245-252.
- 513 Rosen, A. R., 1991. Guide to artifacts: Microartifacts and the study of ancient societies: *Biblical Archaeol.* 54, 97-
514 103.
- 515 Rosenbaum, M.S., McMillan, A.A., Powell, J.H., Cooper, A.H., Culshaw, M.G., Northmore, K.J., 2003,
516 *Classification of artificial (man-made) ground*: *Eng. Geol.* 69, p. 399-409.
- 517 Rutherford, D.W., Wershaw, R.L., Cox, L.G., 2005. Changes in composition and porosity occurring during the
518 thermal degradation of wood and wood components. *USGS Special Inv. Rept.* 2004-5292, 79 pp.

- 519 Schmidt, M.W.I., Knicker, H., Hatcher, P.G., Kogel-Knabner, I., 2000. Airborne contamination of forest soils by
520 carbonaceous particles from industrial coal processing. *Jour. Environ. Qual.* 29, 768-777.
- 521 Schoeneberger, P.J., Wysocki, D.A., Benham, E. C., Soil Survey Staff., 2012. Field book for describing and
522 sampling soils, Version 3.0. Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE.
- 523 Sharonova, O. M., Anshits, N.N., Anshits, A. G., 2013. Composition and morphology of narrowly sized
524 ferrospheres isolated from various types of fly ash. *Inorg. Mat.* 49, 586-594.
- 525 Sherwood, S.C., 2001. Microartifacts. In: Goldberg, P., Holliday, V. T. and Ferring, C. R., *Earth sciences in*
526 *archaeology*, Kluwer Academic, New York, pp. 327-351.
- 527 Singh, V., Pande, P.C., Jain, D.K., 2010. *Text Book of Botany: Structure Development and Reproduction in*
528 *Angiosperms*; Rastogi Publications, 220 pp.
- 529
- 530 Smith, R.D., Campbell, J.A., Nielson, K.K., 1979. Concentration dependence upon particle size of volatilized trace
531 elements in fly ash. *Envir. Sci. Tech.* 13, 553-558.
- 532
- 533 Soil Survey Staff, 2014. *Keys to Soil Taxonomy* (12th ed.). USDA-NRCS, U.S. Govt. Print. Office, Washington,
534 DC.
- 535 Stoltman, J. B., 2001. The role of petrography in the study of archaeological ceramics. In: Goldberg, P., Holliday, V.
536 T., Ferring, C.R. (Eds.), *Earth sciences and archaeology*. Plenum Pub., New York, pp. 297-326.
- 537 Suarez-Ruiz, I., 2012. Organic petrology: An overview. In: Al-Juboury, A. (Ed.), *Petrology – New perspectives and*
538 *applications*, Intech Pub., Shanghai, pp. 199-224.
- 539 Telford, W.M., Geldart, L.P., Sheriff, R.E., 1990. *Applied geophysics* (2nd ed.), Cambridge Univ. Press, pp. 283-
540 292.
- 541

- 542 Van Oss, H.G., 2005. Background facts and issues concerning cement and cement data. U. S. Geological Survey
 543 Open File Report 2005-1152, 44 pp.
- 544 Ward, C. R., 2002. Analysis and significance of mineral matter in coal seams. *Int. Jour. Coal Geol.* 50, 135-168.
- 545 Ward, C.R., French, D., 2005. Relation between coal and fly ash mineralogy, based on quantitative x-ray diffraction
 546 methods. *Proc. World of Coal Ash Conf.*, Lexington, KY, 14 pp.
- 547 Wightman, W.E., Jalinoos, E.F., Sirles, P., Hanna, K.,. 2003. Application of Geophysical Methods to Highway
 548 Related Problems. Federal Highway Administration, Central Federal Lands Highway Division, Lakewood, CO,
 549 Publication No. FHWA-IF-04-02.
- 550 Yang, T., Liu, Q., Li, H., Zeng, Q., Chan, L., . 2010a. Anthropogenic magnetic particles and heavy metals in the
 551 road dust: Magnetic identification and its implications. *Atmos. Envir.* 44, 1175-1185.
- 552 Yang, Y., Mahler, B.J., Van Metre, P.C., Ligouis, B., Werth, C. J., 2010b. Potential contributions of asphalt and coal
 553 tar to black carbon quantification in urban dust, soils, and sediments. *Geochim. Cosmo. Acta* 74, 6830-6840.
- 554 Yildirim, I. Z., Prezzi, M., 2011. Chemical, mineralogical, and morphological properties of steel slag. *Adv. Civil*
 555 *Eng. Article* 463638, 13 pp.

556

557 **FIGURE CAPTIONS**

558 **Figure 1.** Study area in the Detroit, Michigan 7.5 minute topographic quadrangle, and surrounding areas, showing
 559 locations of anthropogenic soils sampled.

560 **Figure 2.** Selected photomicrographs (transmitted light microscopy) of reference artifacts: A, coal showing vitrinite
 561 macerals; B, asphaltic concrete showing bituminous binding material; C, mortar; D, cinder block; E, coal cinder; F,
 562 ferruginous iron-making slag. All samples in plane polarized light. a, aggregate; c, calcite; v, void; g, glass; o,
 563 merwinite; m, magnetite.

Figure 3. Selected x-ray powder diffractograms showing mineralogical compositions of various types of reference artifacts.

Figure 4. Photomicrographs (reflected light microscopy) of reference microartifacts. Carbonaceous: A, wood (lumber); B, charcoal; C, coal; D, coked coal; E, asphaltic concrete. Calcareous: F, lime-based mortar; G, cinder block containing dark gray blast furnace cinders. Siliceous: H, coal cinder; I, clear siliceous microspheres comprising fly ash; J, microagglomerate comprising fly ash; K, red brick; L, glazed ceramic pipe (stoneware); M, window glass; N, iron-making glass slag; O, burnt shale. Ferruginous: P, iron-making ferruginous slag; Q, corroded iron (nail); R, black magnetitic microspheres comprising fly ash. Miscellaneous: S, drywall; T, bone.

Figure 5. Microartifacts in anthropogenic topsoils of different land use types, Detroit, Michigan. See Fig. 1 for sample locations.

Figure 6. Characteristics of microartifacts in anthropogenic topsoils, Detroit, Michigan: A, microartifact assemblage in a demolition site soil; B, microartifact assemblage in an industrial site soil; C, scanning electron micrograph of microagglomerate grain (compare Fig. 4J) showing spot analyzed by EDS analysis; D, elemental composition suggesting that sphere in C is magnetite; E, scanning electron micrograph showing another spot analyzed by EDS analysis; F, elemental composition suggesting that other microparticles are aluminosilicate glass. br, brick; mo, mortar; cd, coal cinder; co, coal; cc, coked coal; ag, microagglomerate; gl, glass or glass slag; fm, ferruginous microsphere.

Figure 7. Means (solid circles) and 95% confidence limits (error polygons) of elemental compositions of reference coal, iron-smelting slag and fly ash microparticle samples. Error boxes of ferruginous microspheres (fm), siliceous microspheres (sm), and siliceous non-spherical microparticles (sn) are from fly ash-impacted train station site soil (after Howard et al., 2013a). The identities of microparticles from soils at undemolished industrial sites (solid triangles), demolished industrial sites (open circles), and fly ash-impacted undemolished residential sites (solid squares) can be inferred from the compositions of reference samples.

589

590 **Table 1.** Origin and types of anthropogenic particles examined in this study.

Origin	Type of Anthropogenic Particle
Coal-related wastes	Unspent coal, cinders, ash, burnt shale
Waste building materials	Wood (lumber), charcoal, asphaltic concrete, lime concrete, mortar, cinder block, lime brick, ceramic brick, other ceramics (pipe, tile, etc.), window glass, nails, drywall
Industrial wastes	Coked coal, glass slag, ferruginous slag
Archaeological materials	Ceramic pottery sherds, bottle glass, bone

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Table 2. Composition and classification of anthropogenic particles found in urban soils in Detroit, Michigan.

	Type of Artifact	Description	Source	Composition	References
Carbonaceous	Wood (lumber)	The hard fibrous xylem of trees	Used in wood-frame construction	A natural composite of cellulose and hemi-cellulose fibers embedded in a matrix of lignin	Singh et al. (2010); Fromm (2013)
	Charcoal	A residue of plant remains and carbonaceous materials produced by the incomplete combustion of wood	Incidentally related to use of wood as a fuel or building material	Aromatic hydrocarbons, black carbon, some remnant lignin	Brodowski et al. (2005); Forbes et al. (2006)
	Coal	An organic sedimentary rock comprised of carbonized plant fossils and trace amounts of mineral matter	Domestic, commercial fuel source	Organic macerals of various types depending on rank, and minor quartz, illite, kaolinite, feldspar, calcite, dolomite, pyrite, galena	Petrakis and Grandy (1980); ICCP (1998); Ward (2002); Suarez-Ruiz (2012); This study
	Coked coal	A hard, dark gray or black carbonaceous fuel produced by heating coal to > 300°C	Used as a fuel for smelting iron and in coal-fired power plants	Inertinite macerals and black carbon	Gray (1991); Choudhury et al. (2008)
	Asphaltic concrete	An artificial rock-like material comprised of gravel-sized rock and mineral particles (aggregate) and a bituminous binder	Used primarily as road pavement	Bituminous hydrocarbons	Yang et al. (2010b); Brown (2013); This study
Calcareous	Lime concrete	An artificial rock-like material comprised of gravel- and sand-sized rock and mineral particles (aggregate), and a lime-based cement	Used for road pavement, sidewalks and building construction	Various mixtures of calcite, portlandite, belite, alite, tobermorite, ettringite, etc. with variable rock and mineral fragment types	Kosmatka et al. (2002); Lane, 2004; Van Oss (2005); This study
	Mortar	An artificial rock-like material comprised of sand-sized rock and mineral particles (aggregate), and a lime-based cement	Used in masonry	Various mixtures of calcite, portlandite, belite, alite, tobermorite, ettringite, etc. with variable rock and mineral fragment types	Kosmatka et al. (2002); Van Oss (2005); This study
	Cinder block	A type of concrete masonry unit in which some of the aggregate is comprised of blast furnace cinders	Used in masonry to construct walls and foundations	Similar composition to concrete, but containing blast furnace slag and possibly fly ash	This study
	Lime brick	A block of rock-like material comprised of sand-sized rock and mineral particles (aggregate), and a lime-based cement	Used in masonry	Various mixtures of calcite, portlandite, belite, alite, tobermorite, ettringite, etc. with variable rock and mineral fragment types	This study
Siliceous	Coal cinders	The gravel-sized solid waste material left after coal is burned at 1200° to 1500°C	Domestic stoves, steam locomotives; power plants; iron smelting	Aluminosilicate glass, mullite, quartz, magnetite, hematite	Ward and French (2005); This study
	Coal ash	Sand-sized and finer microspheres and agglomerate produced by coal combustion	Incidentally related to coal combustion	Aluminosilicate glass, mullite, quartz, magnetite, hematite, calcite, gypsum	Fisher et al., 1976; Carlson and Adriano, 1993; Ward and French (2005); Lanteigne et

Table 3. Petrographic characteristics of reference microartifacts, as observed with reflected-light optical microscopy.

Sample	Color	Clarity	Luster	Fracture	Texture	Shape
Carbonaceous						
Wood (lumber)	light to dark brown and black	opaque	earthy	splintery to fibrous	agranular	angular platy to rod-like and fibrous
Charcoal	black	opaque	bright vitreous	splintery to fibrous	agranular	angular blocky to prismatic
Coal	black	opaque	bright vitreous	splintery to hacky jagged and conchoidal	agranular, possible microlamination	angular to very angular blocky
Coked coal	black	opaque	dull to bright vitreous; some iridescence	jagged hacky	agranular vesicular	very angular blocky
Asphaltic concrete	black	opaque	earthy to resinous	smooth hacky	polymictic granular, aggregatic	subangular to subrounded equant
Calcareous						
Lime concrete	white	opaque	earthy	smooth hacky	polymictic granular aggregatic	subangular to subrounded equant
Lime brick	grayish-white	opaque	earthy	smooth hacky	polymictic granular aggregatic	subangular to subrounded equant
Mortar 1	white	opaque	earthy	smooth hacky	polymictic granular aggregatic	subangular to subrounded equant
Mortar 2	pinkish white	opaque	earthy	smooth hacky	polymictic granular aggregatic	subangular to subrounded equant
Cinder block	grayish-white to dark gray	opaque	earthy	jagged hacky	polymictic granular aggregatic vesicular	angular blocky
Siliceous						
Coal cinders	black to pale brown	opaque to semi-translucent	dull to bright vitreous	conchoidal to jagged hacky	agranular vesicular	angular to very angular blocky
Coal ash (microspheres)	gray	translucent	bright vitreous	none	granular	Very well rounded
Coal ash (agglomerate)	gray to grayish-brown	semi-translucent	dull vitreous	none	granular aggregatic	Well rounded to subangular
Burnt shale	pale pinkish gray to pinkish brown	opaque	Dull vitreous	platy	agranular	subangular to very angular
Red brick	dark brownish orange to reddish brown	opaque	earthy	smooth hacky	polymictic granular aggregatic	subrounded equant to blocky
Orange brick	brownish orange	opaque	earthy	smooth hacky	polymictic granular aggregatic	subangular to subrounded equant
Yellow brick	pale yellowish brown	opaque	earthy		polymictic granular aggregatic	
Terracotta	reddish orange	opaque	earthy	jagged hacky	polymictic granular aggregatic	very angular to subangular blocky
Glazed ceramic	light grayish brown to brownish orange	opaque	earthy to vitreous	Smooth hacky	polymictic granular aggregatic	angular to subrounded blocky

Table 4. Elemental compositions of microparticles in anthropogenic soils compared with reference materials determined by SEM-EDS analysis. X, mean; S, standard deviation. bdl, below detection limit.

Element	Sample Type																	
	Reference Material												Anthropogenic Soil Type					
	Ferruginous Slag		Coal		Carbonaceous Fly Ash		Siliceous Fly Ash		Ferruginous Fly Ash		Average Fly Ash		Undemolished Residential		Undemolished Industrial		Demolished Industrial	
	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S
	Wgt %																	
Ca	22.9	6.5	0.4	0.7	0.31	0.07	bdl	bdl	bdl	bdl	0.25	0.15	4.1	5.6	1.7	1.2	3.3	2.1
Mg	3.2	1.7	0.05	0.10	0.30	0.14	0.61	0.29	bdl	bdl	0.27	0.09	1.2	0.9	0.5	0.4	0.6	0.3
K	0.02	0.09	0.08	0.17	0.75	0.24	2.16	1.18	bdl	bdl	0.81	0.33	1.6	0.6	0.4	0.3	0.9	0.2
Na	0.04	0.10	0.6	1.4	bdl	bdl	0.17	0.12	bdl	bdl	bdl	bdl	0.5	0.4	0.2	0.2	bdl	bdl
Fe	24.6	9.4	0.3	0.6	0.98	0.51	1.82	0.65	62.0	5.0	2.76	2.36	7.9	3.3	18.1	27.2	4.7	1.8
Al	1.2	0.6	0.5	1.0	6.75	3.9	16.46	2.36	3.0	1.7	6.86	1.8	7.4	2.5	5.7	5.1	3.2	0.7
Si	6.9	3.1	1.2	2.0	8.4	5.0	22.7	2.2	4.6	2.71	8.51	2.2	19.7	5.1	7.8	5.4	6.5	2.3
O	32.3	4.4	16.5	6.7	25.1	7.4	44.5	1.9	25.8	2.0	32.5	2.62	30.7	6.6	20.4	7.5	28.8	3.3
C	5.6	3.3	79.1	11.3	56.2	16.6	10.5	2.5	4.46	0.77	47.5	5.56	21.8	7.9	40.5	19.6	50.3	10.1
Cu	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.2	1.6	2.1	1.2	bdl	bdl
Ti	0.2	0.3	bdl	bdl	0.45	0.23	0.96	0.54	bdl	bdl	0.48	0.19	0.8	1.1	0.3	0.2	bdl	bdl
Zn	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.1	1.4	1.7	1.0	bdl	bdl
V	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Mn	3.0	1.6	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
P	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S	bdl	bdl	0.7	0.6	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
O/C	4.2	2.3	0.22	0.13	0.66	0.90	4.5	1.36	6.0	1.43	0.70	0.14	1.33	0.43	0.69	0.48	0.60	0.17
Sample Size	12		14		10		10		9		10		13		9		7	

Table 5. Main types of microartifacts, and range of geophysical characteristics (Howard and Orlicki, in press), as a function of soil and land use type, Detroit, Michigan.

Soil Type	Land Use Type	Microartifacts	pH		Electrical Conductivity ($\mu\text{S cm}^{-1}$)		Mass Magnetic Susceptibility ($10^{-8} \text{ m}^3 \text{ kg}^{-1}$)		Sample Size
			Ave.	Range	Ave.	Range	Ave.	Range	
Native	Park	None	6.6	4.6 to 7.0	86	75 to 110	39	13 to 83	5
Anthropogenic	Residential Demolition	Brick, mortar, glass, cinders, microagglomerate, microspheres	7.8	7.4 to 8.2	680	222 to 1138	140	30 to 250	10
Anthropogenic	Undemolished Residential	Microagglomerate, microspheres	7.6	7.1 to 8.0	374	209 to 540	196	91 to 302	6
Anthropogenic	Industrial	Unspent coal, coked coal, cinders, slag, microagglomerate, microspheres	8.3	7.7 to 8.8	302	169 to 434	1253	70 to 2436	5

figure 1

figure 2

figure 3

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figure 5

Type of Microartifact	Type of Site																			
	Residential Demolition											Industrial				Undemolished Residential				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Wood	0	0	0	0	0	0	0	0	0	●	0	0	0	0	0	0	0	0	0	0
Charcoal	0	0	0	0	●	0	0	0	0	●	0	0	0	0	0	0	0	0	0	0
Coal	●	0	■	0	●	0	●	●	●	■	●	■	●	■	■	0	0	0	0	0
Coked coal	0	0	0	0	0	0	0	0	0	0	0	0	●	●	●	0	0	0	0	0
Coal cinders	●	■	●	●	●	●	●	■	■	■	●	■	●	●	■	0	0	0	0	0
As. Concrete	●	0	0	0	0	0	0	0	0	0	0	●	0	0	0	0	0	0	0	0
Brick	●	●	●	■	0	■	●	0	■	●	■	●	●	●	●	0	0	0	0	0
Mortar	●	■	●	■	■	■	●	●	●	0	■	●	●	●	●	0	0	0	0	0
Bone	0	0	●	0	0	0	0	0	0	0	0	●	0	0	0	0	0	0	0	0
Glass	■	0	0	●	0	●	●	●	0	●	0	0	0	●	0	0	0	0	0	0
Glass-slag	0	0	0	0	0	0	0	0	0	0	0	0	0	●	0	0	0	0	0	0
Metal. slag	0	0	0	0	0	0	0	0	●	●	0	0	●	●	■	0	0	0	0	0
Corroded iron	0	0	●	●	0	0	0	0	0	0	0	0	0	●	0	0	0	0	0	0
Microspheres	●	●	●	●	●	●	●	0	●	●	0	0	●	●	■	●	■	●	■	●
Microagglomerate	●	■	■	●	0	●	0	■	■	■	0	0	0	●	0	■	■	■	■	■
Wgt. % Magnetic	4.3	4.0	15.3	3.2	0.2	0.5	0.6	1.1	1.5	2.6	2.7	33.7	19.1	12.3	22.2	3.0	3.2	2.9	1.4	1.4

figure 7

Graphical abstract