

**CHEMICAL CHARACTERIZATION OF THE
NONAIRBORNE FRACTION OF THE
REPRESENTATIVE BRAKE PAD WEAR DEBRIS SAMPLE**

FINAL REPORT

Submitted to

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1515 Clay Street, Suite 1400
Oakland, CA 94612

by

Mark A. Schlautman and Ashley Haselden
School of the Environment
Clemson University
342 Computer Court, Anderson, SC 29625

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1. EXECUTIVE SUMMARY

Characterization of brake pad wear debris (BPWD) is one component of the Brake Pad Partnership's (BPP's) investigation of the environmental fate and transport of copper from automobile friction materials. In addition, environmental fate and transport models are being used to predict how copper from BPWD travels through the environment and its potential effect on the short-term and long-term concentrations of copper in the San Francisco Bay.

In a previous report to the BPP, we characterized the hypothetical airborne fraction of BPWD generated from a representative brake pad formulation (Haselden et al., 2006). The present report describes the set of experiments completed and results obtained for the nonairborne fraction of the representative BPWD. The nonairborne representative BPWD sample fraction was generated on a brake dynamometer in an independent set of tests at Link Testing Laboratories in Detroit using a standard BPWD generation protocol developed by the BPP.

The primary objective of this report is to present the results of chemical characterization tests for the nonairborne fraction of the representative BPWD sample. The characterization tests consisted of determining the total copper and iron contents of the BPWD sample as well as the solubilities and leaching potentials of copper and iron from the sample in a variety of different leaching test solutions. Although the information contained in this report cannot be used as direct input into the environmental fate and transport models, it nonetheless serves to provide guidance on the key processes involved and thus the applicability of the models themselves.

Key findings from the present study include:

- The Cu and Fe contents in the nonairborne representative BPWD sample were 7.9% ($\pm 0.2\%$) and 23.1% ($\pm 1.2\%$), respectively.
- The mean values for the Cu and Fe contents in the nonairborne representative BPWD sample were both *lower* than the values reported for a nonairborne BPWD sample previously tested in our laboratory (Hur et al., 2003). The previous sample had Cu and Fe contents of 10.8% ($\pm 0.2\%$) and 28.6% ($\pm 0.4\%$), respectively.
- The mean values for Cu and Fe contents in the nonairborne representative BPWD sample were both *higher* than the values reported for the airborne representative BPWD sample previously characterized in our laboratory (Haselden et al., 2006). The total net average Cu and Fe contents for the airborne fraction of the hypothetical representative BPWD sample were calculated as being 5.8% ($\pm 0.4\%$) and 14.8% ($\pm 2.0\%$), respectively.
- Leaching of Cu from the nonairborne representative BPWD sample was quite high (i.e., 60–100%) in the more aggressive leaching solutions. This “total Cu leaching potential” was similar to that observed previously for the one other nonairborne BPWD sample tested in our laboratory (Hur et al., 2003, 2004).
- Leaching of Fe from the nonairborne representative BPWD sample ranged from 1.4–72% in the more aggressive leaching solutions. This “total Fe leaching potential” also was similar to, or perhaps even a little higher than, that observed for the other nonairborne BPWD sample previously tested (Hur et al., 2003, 2004).
- Leaching of Cu from the nonairborne representative BPWD sample ranged from less than 1% up to 3.5% in the less aggressive leaching solutions. This indirect measure of the

“expected rate of Cu leaching” was lower than that observed previously for the one other nonairborne BPWD sample tested in our laboratory (Hur et al., 2003, 2004). The more alkaline nature of the representative BPWD sample is likely responsible for this difference.

- The “expected rate of Fe leaching” from the nonairborne representative BPWD sample in the less aggressive leaching solutions ranged from nondetectable up to 1.6%, which was similar to that previously observed for the one other tested nonairborne BPWD sample (Hur et al., 2003, 2004).

2. INTRODUCTION

The Brake Pad Partnership (BPP) is a multistakeholder effort to understand the impacts on the environment that may arise from brake pad wear debris (BPWD) generated in the use of passenger vehicles. Current efforts by the BPP are aimed at developing an approach for evaluating potential environmental impacts of copper from BPWD affecting water quality in the South San Francisco Bay as an example. Brake pad manufacturers have committed to adding this evaluation approach to their existing practices for designing products that are safe for the environment while still meeting the performance requirements demanded of these important safety-related products.

The BPP is conducting a set of interlinked laboratory, environmental monitoring, and environmental modeling studies to understand the fate and transport of copper from automobile BPWD in the environment. At the core of the Partnership’s effort are three environmental modeling studies:

- Air Deposition Modeling—to predict how much brake pad wear debris is released and deposited in the study watershed (Castro Valley).
- Watershed Modeling—to estimate how much copper from the deposited wear debris washes into streams and storm drains and eventually reaches the waters of the South San Francisco Bay.
- Bay Modeling—to determine whether and, if so, to what extent copper from BPWD affects short- and long-term concentrations of copper in the Bay.

In support of these modeling efforts, the Partnership is conducting additional studies to develop accurate input data for the models. For example, previous work conducted by Clemson University researchers characterized selected physical and chemical parameters for the airborne fraction of a BPWD sample generated from a hypothetical representative brake pad formulation (Haselden et al., 2006). These physical and chemical characteristics will then be used as direct input parameters for the air deposition model.

The primary objective of the present study was to characterize the nonairborne fraction of the representative BPWD sample. The characterization tests performed here consisted of determining the total copper and iron contents of the BPWD sample as well as the solubilities and leaching potentials of copper and iron from the sample in a variety of different leaching test solutions. A secondary objective of the present work was to determine how the characteristics of

the nonairborne representative BPWD compared to those of the airborne fraction of the representative BPWD (Haselden et al., 2006), as well as to those of a nonairborne BPWD sample previously tested for the BPP (Hur et al., 2003, 2004). Results from this study will be used by the BPP to inform our efforts to model the transport and fate of BPWD in the environment. For example, although the information contained in this report cannot be used as direct input into the environmental fate and transport models, it nonetheless serves to provide guidance on the key processes involved and thus the applicability of the models themselves.

3. EXPERIMENTAL

3.1 Representative BPWD Sample

The representative BPWD sample used in this study was generated through the cooperative efforts of the Brake Manufacturers Council-Product Environmental Committee (BMC-PEC) and the BPP. The methodology used to generate the representative sample has been documented in a companion report (Generating a Representative Sample of Brake Pad Wear Debris, BMC-PEC, 2006) and therefore is only briefly summarized here.

Because a variety of forms of copper are used in brake pad formulations, including but not limited to copper fiber, copper powder, brass fiber, brass powder, copper with organic complexes, and copper sulfide, the BMC surveyed PEC member companies with respect to their copper usage in original equipment manufacturer (OEM) automobile brake pads for the model year 2002. The PEC member companies submitted information on the forms of copper used in each OEM application to the BMC. A pareto analysis of the data allowed the BMC to select three materials comprising greater than 90% of the copper usage in OEM automobile brake pads. The BMC then requested three member companies to prepare samples of their respective brake pad formulations for use in generating BPWD.

The three material samples were run in succession on a brake dynamometer at Link Testing Laboratory, Inc. (Detroit, MI) in October/November 2004 to generate and collect BPWD, generally following an established protocol (Trainor, 2001; Trainor et al., 2002). Each material was run for a period of time proportionate to the volume of the material sold on vehicles in 2002, without cleanout of the dynamometer between tests. Upon completion of the third material run, the nonairborne fractions of the BPWD from the three materials were collected, sent to Huron Valley Laboratories, Inc. (Romulus, MI) for processing, returned to Link, and then ultimately shipped to Clemson University. Upon receipt, a visual inspection and mass inventory of the shipped samples were conducted, and then the various samples were combined to create one composite sample (hereafter referred to as the nonairborne representative BPWD sample) for use in the subsequent digestion and leaching experiments.

3.2 Materials and Reagents

Details regarding the materials and reagents used in the present study have been previously reported (Hur et al., 2003, 2004), and so are only summarized here. All solutions were prepared using distilled, deionized water (DDW) (Millipore Milli-Q System) having a resistivity > 18.0

M Ω -cm. Low metals-containing reagents (hydrochloric acid [HCl]: 30%, EM Omnitrace; nitric acid [HNO₃]: 70%, EM Omintrace); hydrogen peroxide [H₂O₂]: 30%, Mallinckrodt) were used for the microwave-assisted digestion tests. All other commercially-available chemical reagents used were analytical grade or better. Eight different leaching solutions/procedures were tested: Toxicity Characteristic Leaching Procedure (TCLP) solution, Waste Extraction Test (WET) solution, Synthetic Precipitation Leaching Procedure (SPLP) solution, a synthetic rainwater solution, an inorganic synthetic rainwater solution, a concentrated synthetic rainwater solution, a solution containing 3 mg C/L of Suwannee River Fulvic Acid (SRFA), and a solution containing 80 μ M ethylenediamine tetraacetic acid (EDTA). All leaching solutions had a nominal initial pH value of 5.0 except for the TCLP solution which had a nominal initial pH of 4.9 (Hur et al., 2003, 2004). New high-density polyethylene (HDPE) plastic bottles (Wheaton, Millville, NJ) were used without further treatment for each extraction. As necessary, all other bottles and glassware were soaked in 10% HNO₃ overnight and then rinsed with copious amounts of DDW before use.

3.3 Total Cu and Fe Determinations using Microwave-Assisted Digestion

Details regarding total Cu and Fe determinations in BPWD samples using microwave-assisted digestion have been reported previously (Hur et al., 2003, 2004). Briefly, replicate subsamples (1 or 10 mg nominal mass) of the nonairborne representative BPWD were placed into Teflon microwave digestion vessels. The digestion reagents were then added to the vessels (10 mL total nominal volume) and the contents were gently swirled to completely contact the sample with the digestion solution. The Teflon vessels were then sealed with their Teflon covers and placed into the microwave (Ethos Plus, Milestone Inc.) for digestion using a manufacturer-recommended digestion program. After the digestions were completed and the samples had cooled down, the solutions were quantitatively transferred to 100 mL volumetric flasks and diluted to volume with DDW to dilute the strong acid matrix and bring the Cu and Fe concentrations into an appropriate range. The diluted solutions were filtered and aliquots transferred to clean 15-mL plastic bottles (Wheaton HDPE bottle) which were then sent to the Clemson Agricultural Services Laboratory (Clemson, SC) for analysis. A blank control solution was processed similarly to quantify the background levels of Cu and Fe in the samples.

3.4 Leaching Tests

For consistency with our previous leaching tests (Hur et al., 2003, 2004), a low solid-to-liquid ratio (1:10⁴) was maintained for all leaching experiments. All of the leaching procedures were conducted for a standard 18 hour time period, except for the WET procedure which has a standard extraction time of 48 hours. An appropriate mass (2.5 mg) of the nonairborne representative BPWD sample was weighed out in each bottle-point reactor (30 mL, Wheaton HDPE bottles) before transferring a fixed volume (25 mL) of leaching solution to each bottle. All tests were conducted in triplicate using three separate reactors containing the same leaching solution, and a blank control solution was processed for each leaching condition tested. All reactor bottles were equilibrated in the dark at room temperature (21 \pm 2 $^{\circ}$ C) on an end-over-end tumbler rotating at approximately 25 rpm. At the end of the leaching tests, particulate materials were removed from sample aliquots using an acid- and water-washed syringe filter (Gelman Laboratory). The first 2 to 3 mL of each filtrate was discarded before collecting a filtered sample aliquot in a clean 15 mL plastic bottle (Wheaton HDPE bottle), measuring its final pH, and then

acidifying it to pH 3 with 0.1 N nitric acid and conducting Cu and Fe analyses. The pH of each filtered sample aliquot was measured to monitor pH changes that occurred during the leaching process (Hur et al., 2004). Aliquots of the remaining unfiltered samples were then taken for total Cu and Fe determinations following the digestion procedures described above and by Hur et al. (2003, 2004). These follow-up digestions enabled us to determine the total Cu and Fe contents for each tested sample and allowed us to close the mass balance on each sample. For heterogeneous samples, including this one which had been composited from the wear debris generated from three different brake pad formulations, closing the mass balance on each sample aids in obtaining better experimental results. Additional information on the leaching tests used here is available in our previous reports (Hur et al., 2003, 2004).

3.5 Analytical Methods

All filtered samples were analyzed for total Cu and Fe by inductively coupled plasma atomic emission spectrometry (ICP-AES). Operational parameters and conditions for the ICP analyses and quality control/assurance procedures have been reported previously (Hur et al., 2003).

4. RESULTS AND DISCUSSION

4.1 Total Cu and Fe Contents of the Nonairborne Representative BPWD Sample

Independent digestion tests and analyses for total Cu and Fe for the nonairborne representative BPWD sample were conducted following the Clemson digestion procedure (Hur et al., 2003). The same solid to water ratio ($1:10^4$) was used here for consistency with the previous digestion tests and with the subsequent leaching tests. For a digesting solution volume of 10 mL in these tests, the target mass for each subsample was thus 1 mg. Because that relatively small mass of material raised the concern of adverse sample heterogeneity effects, particularly for this material which was generated by compositing the wear debris from three different brake pad formulations, we also decided to test a higher ($1:10^3$) solid to water ratio. In general, using larger subsample masses should result in lower experimental errors because they are 1) more likely to cover the full range of components contained in heterogeneous samples, and 2) more accurately weighed with a conventional four decimal place balance such as the one used in this study. Therefore, in addition to digesting 1 mg subsamples of the material we also tested 10 mg subsamples. Triplicate digestion tests were performed for each solid to water ratio, plus a blank sample to use for background subtraction if needed. Results for the background subtracted samples are shown in Table 1. One outlier value for copper (shown in red in Table 1) was excluded from the mean value determination because it deviated significantly from the other values (Barnett and Lewis, 1984).

Estimating the “true” mean Cu content in the nonairborne representative BPWD sample can be made by two alternative procedures (Hur et al., 2003). The first approach, based on the assumption that each subsample (excluding the outlier) tested in Table 1 is representative of the composite sample itself (i.e., each subsample a representative measure of the “universe”), merely calculates the average value from the five individual Cu content measurements. Using this assumption and procedure results in an estimated mean Cu content of 7.9%, with a standard error

Table 1. Copper and Iron Contents of the Nonairborne Representative BPWD Sample.

Sample Number	Sample Mass (mg)	Copper Mass (mg)	% Copper	Iron Mass (mg)	% Iron
201	1.0	0.04379	4.38	0.20817	20.82
202	1.1	0.08584	7.80	0.28177	25.62
203	1.4	0.11142	7.96	0.31947	22.82
205	12.9	1.03442	8.02	2.97647	23.07
206	9.6	0.83112	8.66	2.60647	27.15
207	11.2	0.81162	7.25	2.17247	19.40
Mean Value (\pm Standard Error)			7.9% ^a (\pm 0.2%)	23.1% (\pm 1.2%)	

^a Excluding the outlier shown in red.

of 0.2% and a 95% confidence range of 7.3 to 8.6% for the mean value. The second approach, which is not limited by the assumption of each subsample being representative, calculates the mean value by dividing the sum of the measured copper masses from the six subsamples (including the outlier) by the sum of the six subsample total masses. Using the second approach results in an estimated mean copper content of 7.8%, which is essentially the same value as calculated by the first procedure. Note that omitting the outlier sample in the second calculation approach also results in a mean Cu content of 7.9%. Therefore, we conclude that a reasonable estimate of the copper content of the nonairborne representative BPWD sample is 7.9% (g/g).

Iron is often observed as being the largest constituent element present in BPWD, despite the fact that some brake pad formulations contain little to no iron (Hur et al., 2003, and references therein). For brake pads containing little to no iron, the iron found in brake wear debris then presumably comes from the associated wear of the rotor during the braking process. Since the ICP-AES analytical procedure simultaneously gave us total iron as well as copper concentrations in all of our samples, we applied the same copper data analysis procedures described above to iron (Table 1). Based on the first approach, we calculated a total Fe content of 23.1%, with a standard error of 1.2% and a 95% confidence range of 20.1 to 26.2% for the mean value. Using the second approach results in an estimated mean Fe content of 23.0%, again essentially the same value as calculated by the first procedure. Therefore, we conclude that a reasonable estimate of the Fe content of the nonairborne representative BPWD sample is 23.1% (g/g).

The mean values for the Cu and Fe contents of the nonairborne representative BPWD sample from Table 1 were both lower than the values reported for the nonairborne sample previously tested in our laboratory (Hur et al., 2003; Hur et al., 2004). That sample had a Cu content of 10.8% (with a 95% confidence range of 10.3–11.2%) and Fe content of 28.6% (with a 95% confidence range of 27.6–29.6%). However, because the purpose of the previous brake pad formulation and resulting BPWD sample was to help develop the BPWD generation protocol (Trainor, 2001; Trainor et al., 2002), it was purposely chosen to have a copper content of approximately 10% and thus never was intended to be representative of the entire mass of BPWD entering the environment. The mean copper content observed here for the representative

BPWD sample is, in fact, much closer to the value of 6.5% that can be calculated from the information provided in the Copper Use Monitoring Report for brake pad formulations for the model year 2002 (Brake Pad Partnership, 2004).

The mean values from Table 1 can be compared to the estimated Cu and Fe contents that we previously calculated for the hypothetical airborne fraction of the same representative BPWD sample (Haselden et al., 2006). In that companion study, we calculated the total net average Cu and Fe contents for the hypothetical airborne fraction of the representative BPWD to be 5.8% ($\pm 0.4\%$) and 14.8% ($\pm 2.0\%$), respectively. These calculated values for the airborne fraction are thus lower than the nonairborne fraction values (i.e., differences of about 2% and 8% for the Cu and Fe contents, respectively). These differences suggest that some Cu and Fe fractionation may have occurred between the airborne versus nonairborne BPWD, although unresolved complications associated with the dynamometer tests used to generate the representative sample cannot be completely ruled out.

Finally, estimates of the total Cu and Fe contents of the nonairborne representative BPWD sample also can be obtained from the leaching tests described in more detail below. As part of those leaching tests, total Cu and Fe determinations were made for each replicate sample at the end of each leaching test to close the mass balance and account for any potential sample heterogeneity. This procedure thus generated 24 separate measurements of the total Cu and Fe contents in the representative sample. The results determined following this approach were (mean \pm standard error): 5.5% ($\pm 0.4\%$) Cu content and 18.6% ($\pm 1.9\%$) Fe content. These values ended up being lower (i.e., differences of about 2% and 5% for the Cu and Fe contents, respectively) versus the independent digestion measurements shown in Table 1. Because these follow-up digestion tests are more difficult to perform than the independent digestion tests, and thus are subject to more experimental error propagation, comparing their resulting values may not be all that beneficial. However, the value of the follow-up digestions for more accurate determinations of the percent Cu and Fe leaching is very clear (Appendix A).

4.2 Cu and Fe Leaching in Model Environmental Solutions

The purpose of this set of tests was to determine whether copper and iron leaching from the nonairborne representative BPWD sample would be consistent with the results obtained previously for a different nonairborne BPWD sample (Hur et al., 2003, 2004) in a variety of model environmental test solutions. For the present study, background subtracted replicate sample values that resulted in negative Cu/Fe masses were assigned the value of zero because of the physical impossibility of negative mass present. Such results merely reflect the low mass of Cu/Fe present in a particular replicate sample relative to the background levels in the blank samples (Appendix A).

A wide variation in the leaching of Cu from the representative sample was observed, with leaching percentages ranging from essentially 0 to 100% (Table 2). The highest Cu leaching resulted from the WET procedure, which was the most aggressive leaching procedure tested here and requires exposure of the solid phase to a 0.2 M citrate solution for 48 hours (Hur et al., 2003). The other aggressive leaching procedures (i.e., TCLP, concentrated synthetic rainwater, EDTA) only had 18 hour contact times but also had high Cu leaching efficiencies (~ 60 to 75%).

Table 2. Leaching test results for the representative nonairborne BPWD sample.^a

Leaching Solution ^b	Cu recovery (%)	Fe recovery (%)	Final pH
TCLP	72.7 ± 3.9	16.8 ± 1.8	4.9
WET	101.0 ± 1.9	71.7 ± 3.1	4.9
SPLP	2.5 ± 1.1	BD ^c	6.5
Inorganic synthetic rainwater	0.6 ± 0.1	BD	7.7
Synthetic rainwater	0.1 ± 0.1 ^d	BD	7.1
Concentrated synthetic rainwater	70.5 ± 1.0	1.4 ± 0.9	5.3
SRFA (3 mg C/L)	3.5 ± 0.1	1.6 ± 0.4	6.4
EDTA (8 × 10 ⁻⁵ M)	63.5 ± 3.7	2.9 ± 0.9	7.1

^a Recovery percentages (mean ± standard error) were calculated based on background subtracted leaching and total Cu/Fe determinations for each replicate sample. Background subtracted samples values that resulted in negative numbers were assigned the value of zero in these calculations. ^b All test solutions used a solid-to-liquid ratio of 1:10⁴ (g/g) and had a nominal initial pH of 4.9 (TCLP) or 5.0 (all other leaching solutions). Leaching times for all tests were 18 h, except for the 48-h standard WET test. ^c BD, below detection. For these samples, the background concentrations were greater than or equal to all replicate sample values. ^d The mean and standard error values shown are based on one replicate value of 0.44% recovery and two replicate values that were BD and therefore set to zero.

Conversely, the less aggressive 18-hour leaching tests (SPLP, SRFA, synthetic rainwater with and without organic acids present) resulted in less than 5% Cu leaching from the representative sample.

As expected (Hur et al., 2003, 2004), the leaching of Fe from the representative sample was less than Cu, although the same qualitative trends were generally observed (Table 2). As for Cu, the highest Fe leaching (~70%) occurred in the WET procedure. The TCLP test was next highest with ~17% Fe leaching, while the other 18-hour tests all had less than 3% Fe leaching.

The Cu/Fe leaching results obtained for the nonairborne representative BPWD sample can be compared to the nonairborne BPWD sample previously tested in our laboratory (Hur et al., 2003, 2004). As shown by the results compiled in Table 3, the highest leaching of Cu and Fe occurred with the WET procedure, followed by the TCLP, concentrated synthetic rainwater and then EDTA tests. Copper leaching in the less aggressive tests was lower, but still significant and ranged from ~10 to 40%. The amount of Fe leaching in the less aggressive tests, however, were all well below 1%.

One possible interpretation of the different leaching tests is that the more aggressive leaching solutions (WET, TCLP, concentrated synthetic rainwater, EDTA) are in fact qualitative metrics of the “total leaching potential” of Cu and Fe from the solid particulate phase. Conversely, the less aggressive leaching tests (SPLP, SRFA, synthetic rainwater with and without organic acids present) can be considered qualitative metrics for the “expected rate of leaching” of Cu and Fe from the BPWD samples. Such an interpretation would be consistent with the overall trends observed in our previous studies of both the rates and extents of Cu and Fe leaching in these types of tests (Hur et al., 2003, 2004). Although no doubt overly simplistic, these qualitative

Table 3. Leaching test results for the previous nonairborne BPWD sample.^a

Leaching Solution ^b	Cu recovery (%)	Fe recovery (%)	Final pH
TCLP	84.80 ± 5.94	4.45 ± 0.47	4.9
WET	102.58 ± 0.46	37.67 ± 1.28	5.0
SPLP	13.15 ± 0.46	0.034 ± 0.008	6.2
Inorganic synthetic rainwater	30.74 ± 0.56	0.026 ± 0.004	5.8
Synthetic rainwater	40.07 ± 1.66	0.034 ± 0.002	5.8
Concentrated synthetic rainwater	71.67 ± 1.57	1.21 ± 0.06	5.3
SRFA (3 mg C/L)	23.89 ± 0.83	0.078 ± 0.006	6.0
EDTA (8 × 10 ⁻⁵ M)	55.00 ± 1.57	1.02 ± 0.29	6.0

^a Results compiled from Hur et al., J. Environ. Monit., 2003, 5, 837-843 and Hur et al., J. Environ. Monit., 2004, 6, 89-94. Recovery percentages (mean ± standard error from triplicate samples) are based on total Cu and Fe contents of 10.8 and 28.6% (g/g), respectively, in the BPWD. ^b All test solutions used a solid-to-liquid ratio of 1:10⁴ (g/g) and had a nominal initial pH of 4.9 (TCLP) or 5.0 (all other leaching solutions). Leaching times for all tests were 18 h, except for the 48-h standard WET test.

metrics can provide a useful means of interpreting the effects that would be expected when the BPWD materials come into contact with environmental aqueous solutions.

Upon comparing the results shown in Tables 2 and 3, one can readily see that the “total Cu leaching potential” of the nonairborne representative BPWD appears to be similar to that of the nonairborne BPWD previously tested (Figure 1). The “total Fe leaching potential” of the representative material also appears to be similar to, or perhaps even higher than, the previous material (Figure 1). Conversely, the “expected rate of Cu leaching” from the representative material appears to be lower than that of the previous material (Figure 1). Presumably, such a difference could be the result of some inherent difference(s) in the copper contained in the representative sample, in the original brake pad formulations, in the physical structure of the BPWD particles, etc. Note that the “expected rate of Fe leaching” was low in every case.

Examining the final solution pH values for the different leaching tests provides some insight into the differences observed in the leaching of the two BPWD samples. As can be seen in Tables 1 and 2 and Figure 2, the final pH values for the less aggressive leaching solutions were higher for the representative sample than for the sample previously tested. Detailed studies of the effects of pH on the leaching of Cu and Fe from BPWD have clearly shown the importance of pH in the leaching process, with higher extents and faster rates of leaching always being observed at lower pH values regardless of the particular leaching solution background composition (Hur et al., 2004). Therefore, the higher final pH values observed here suggest that the more alkaline nature of the representative BPWD is likely responsible for the lower expected rate of Cu leaching versus the previous BPWD material.

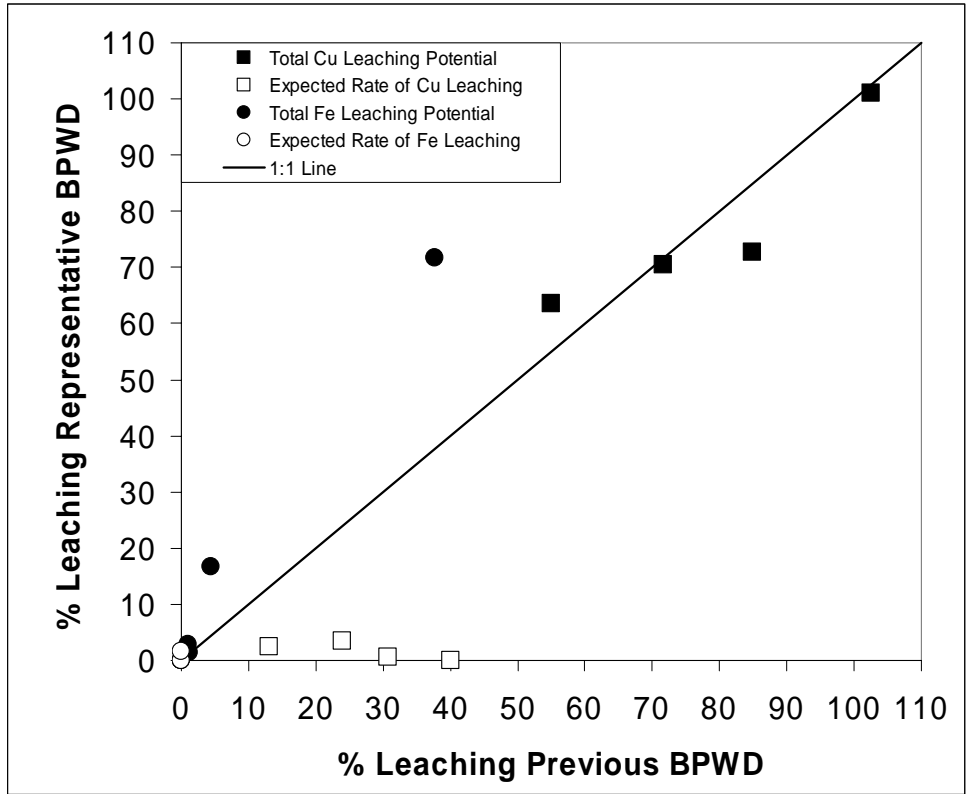


Figure 1. Comparison of leaching test results for the two nonairborne BPWD samples.

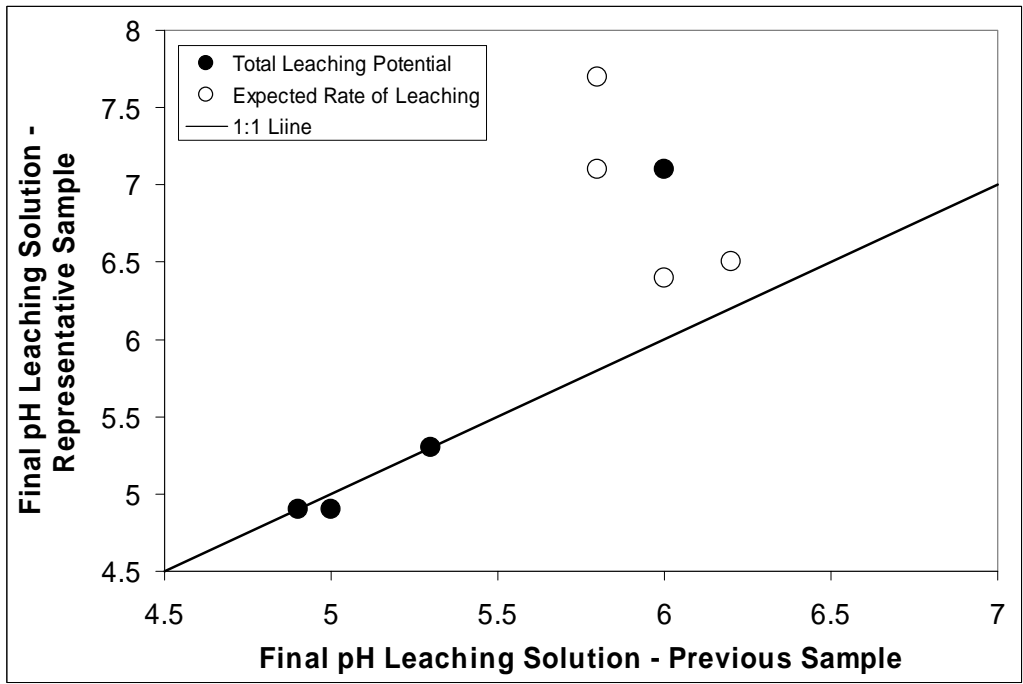


Figure 2. Comparison of final leaching solution pH values for the two nonairborne BPWD samples.

5. CONCLUSIONS

The total copper and iron mass contents (7.9% and 23.1%, respectively) of the nonairborne fraction of the representative BPWD were determined by microwave-assisted digestion followed by total metals analysis using ICP-AES. These values were higher than the ones we reported previously for the airborne fraction of the same representative BPWD sample, but lower than the ones measured for a different nonairborne BPWD sample previously tested in our laboratory.

Total dissolved copper and iron concentrations were determined in a variety of different leaching test solutions to better understand the leaching characteristics of the two metals from the nonairborne representative BPWD sample. In the more aggressive tests, the leaching of Cu was quite high, ranging from 60 to 100%. These Cu leaching results were similar to those for the previous nonairborne BPWD sample tested. Leaching of Fe from the nonairborne representative BPWD sample ranged from 1.4 to 72% in the more aggressive leaching solutions, which was greater than or equal to that observed for the other nonairborne BPWD sample. In the less aggressive tests, leaching of Cu from the nonairborne representative BPWD sample ranged from less than 1% up to 3.5%, which was lower than the results for the previous nonairborne sample. Although characterizing the differences between the two nonairborne samples has not been pursued, it is expected that the more alkaline nature of the representative BPWD sample is at least partly responsible for the observed differences. In all cases, leaching of Fe in the less aggressive tests was low for both BPWD samples tested to date.

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Appendix A

Digestion/Leaching Data for the Nonairborne Representative BPWD Sample

Independent BPWD Digestions

Sample #	Sample Mass (mg)	Copper			Iron		
		(ppm)	(mg)	% total mass	(ppm)	(mg)	% total mass
201	1.0	0.4437	0.04437	4.44	2.097	0.2097	20.97
202	1.1	0.8642	0.08642	7.86	2.833	0.2833	25.75
203	1.4	1.12	0.112	8.00	3.21	0.321	22.93
204	0.0	0.0058	0.00058	(background)	0.0153	0.00153	(background)
205	12.9	10.35	1.035	8.02	29.78	2.978	23.09
206	9.6	8.317	0.8317	8.66	26.08	2.608	27.17
207	11.2	8.122	0.8122	7.25	21.74	2.174	19.41
201-204	1.0	0.4379	0.04379	4.38	2.0817	0.20817	20.82
202-204	1.1	0.8584	0.08584	7.80	2.8177	0.28177	25.62
203-204	1.4	1.1142	0.11142	7.96	3.1947	0.31947	22.82
205-204	12.9	10.3442	1.03442	8.02	29.7647	2.97647	23.07
206-204	9.6	8.3112	0.83112	8.66	26.0647	2.60647	27.15
207-204	11.2	8.1162	0.81162	7.25	21.7247	2.17247	19.40

NOTE: Sample # 201 is an outlier for the copper determination, but not for the iron determination.

Leaching Test ICP Results

Sample #	Leaching Solution	Sample Mass in 25 mL (g)	Sample Mass in 10 mL (g)	Volume after adding acid (mL)	Copper			Iron	
					conc. after digestion ppm	mass in digested sample µg	leached mass entire sample mg	conc. after digestion ppm	mass in digested sample µg
1	TCLP	0.0025	0.001	10.2	6.22	63.44	0.1586	9.84	100.37
2	TCLP	0.0027	0.00108	10.3	8.53	87.86	0.2196	3.615	37.23
3	TCLP	0.0022	0.00088	10.2	5.22	53.24	0.1331	3.135	31.98
4	TCLP	0	0	10.3	0.1984	2.04	0.0051	0.1625	1.67
5	WET	0.0025	0.001	10.1	7.57	76.46	0.1911	15.09	152.41
6	WET	0.0023	0.00092	10.1	6.05	61.11	0.1528	14.31	144.53
7	WET	0.0026	0.00104	10.1	8.34	84.23	0.2106	18.54	187.25
8	WET	0	0	10.1	0.4061	4.10	0.0103	0.927	9.36
9	SRFA	0.0029	0.00116	10.1	0.717	7.24	0.0181	0.4026	4.07
10	SRFA	0.0028	0.00112	10.1	0.683	6.90	0.0172	0.3389	3.42
11	SRFA	0.0025	0.001	10.1	0.523	5.28	0.0132	0.1036	1.05
12	SRFA	0	0	10.1	0.4628	4.67	0.0117	0.013	0.13
13	EDTA	0.0027	0.00108	10.1	3.749	37.86	0.0947	0.568	5.74
14	EDTA	0.0025	0.001	10.1	3.534	35.69	0.0892	0.875	8.84
15	EDTA	0.0029	0.00116	10.1	4.113	41.54	0.1039	0.4144	4.19
16	EDTA	0	0	10.1	0.3744	3.78	0.0095	0.046	0.46
17	SPLP	0.0024	0.00096	10.1	0.1058	1.07	0.0027	0.0029	0.03
18	SPLP	0.0023	0.00092	10.1	0.0408	0.41	0.0010	0.0049	0.05
19	SPLP	0.0022	0.00088	10.1	0.0206	0.21	0.0005	0.0046	0.05
20	SPLP	0	0	10.1	0.0025	0.03	0.0001	0.0069	0.07
21	inorganic synthetic rainwater	0.0029	0.00116	10.1	0.0357	0.36	0.0009	0.0054	0.05
22	inorganic synthetic rainwater	0.0027	0.00108	10.1	0.0339	0.34	0.0009	0.0046	0.05
23	inorganic synthetic rainwater	0.0021	0.00084	10.1	0.0486	0.49	0.0012	0.0029	0.03
24	inorganic synthetic rainwater	0	0	10.1	0.0164	0.17	0.0004	0.0068	0.07
25	synthetic rainwater	0.0028	0.00112	10.1	0.0796	0.80	0.0020	0.0052	0.05
26	synthetic rainwater	0.0027	0.00108	10.1	0.0394	0.40	0.0010	0.0065	0.07
27	synthetic rainwater	0.0029	0.00116	10.1	0.0281	0.28	0.0007	0.0057	0.06
28	synthetic rainwater	0	0	10.1	0.0553	0.56	0.0014	0.0063	0.06
29	concentrated synthetic rainwater	0.0023	0.00092	10.1	5.96	60.20	0.1505	0.508	5.13
30	concentrated synthetic rainwater	0.0029	0.00116	10.1	6.38	64.44	0.1611	0.1496	1.51
31	concentrated synthetic rainwater	0.0023	0.00092	10.1	4.567	46.13	0.1153	1.787	18.05
32	concentrated synthetic rainwater	0	0	10.1	0.4123	4.16	0.0104	0.0263	0.27

Digestion Test ICP Results

Sample #	Leaching Solution	Total Sample Mass in 25 mL (g)	Volume of Digested Sample* determined gravimetrically (mL)	Copper			Iron	
				conc. after digestion ppm	mass in digested sample µg	total mass entire sample mg	conc. after digestion ppm	mass in digested sample µg
1	TCLP	0.0025	5.1918	0.4636	46.36	0.2232	2.564	256.40
2	TCLP	0.0027	5.1213	0.555	55.50	0.2709	1.291	129.10
3	TCLP	0.0022	5.2878	0.4091	40.91	0.1934	1.064	106.40
4	TCLP	0	5.2171	0.0086	0.86	0.0041	0.0366	3.66
5	WET	0.0025	5.3499	0.3337	33.37	0.1559	1.143	114.30
6	WET	0.0023	5.3647	0.3206	32.06	0.1494	1.136	113.60
7	WET	0.0026	5.3533	0.429	42.90	0.2003	1.282	128.20
8	WET	0	5.2624	0.0119	1.19	0.0057	0.0546	5.46
9	SRFA	0.0029	5.1717	0.3851	38.51	0.1862	0.961	96.10
10	SRFA	0.0028	5.0348	0.3163	31.63	0.1571	0.919	91.90
11	SRFA	0.0025	5.0394	0.2051	20.51	0.1017	0.617	61.70
12	SRFA	0	5.1405	0.0033	0.33	0.0016	0.0421	4.21
13	EDTA	0.0027	5.1435	0.3085	30.85	0.1499	1.61	161.00
14	EDTA	0.0025	5.1650	0.2769	27.69	0.1340	0.972	97.20
15	EDTA	0.0029	5.2027	0.2866	28.66	0.1377	0.833	83.30
16	EDTA	0	5.2775	0.0087	0.87	0.0041	0.0299	2.99
17	SPLP	0.0024	5.2342	0.1241	12.41	0.0593	0.437	43.70
18	SPLP	0.0023	5.0262	0.1038	10.38	0.0516	0.3765	37.65
19	SPLP	0.0022	5.3007	0.1236	12.36	0.0583	0.424	42.40
20	SPLP	0	5.2432	0.0049	0.49	0.0023	0.0275	2.75
21	inorganic synthetic rainwater	0.0029	5.3475	0.187	18.70	0.0874	0.729	72.90
22	inorganic synthetic rainwater	0.0027	5.2874	0.1773	17.73	0.0838	0.614	61.40
23	inorganic synthetic rainwater	0.0021	5.1760	0.2369	23.69	0.1144	0.594	59.40
24	inorganic synthetic rainwater	0	5.2407	0.0098	0.98	0.0047	0.0262	2.62
25	synthetic rainwater	0.0028	5.2934	0.3035	30.35	0.1433	2.195	219.50
26	synthetic rainwater	0.0027	5.3339	0.2029	20.29	0.0951	0.779	77.90
27	synthetic rainwater	0.0029	5.3990	0.3818	38.18	0.1768	1.326	132.60
28	synthetic rainwater	0	5.0962	0.0108	1.08	0.0053	0.036	3.60
29	concentrated synthetic rainwater	0.0023	5.3158	0.4448	44.48	0.2092	1.138	113.80
30	concentrated synthetic rainwater	0.0029	5.1355	0.4402	44.02	0.2143	1.184	118.40
31	concentrated synthetic rainwater	0.0023	5.3240	0.3278	32.78	0.1539	0.788	78.80
32	concentrated synthetic rainwater	0	5.1867	0.0113	1.13	0.0054	0.0264	2.64

* "Volume of Sample" based on 1g solution = 1mL

Overall Leaching Test Results

Sample #	Leaching Solution	Total Sample Mass (mg)	Total Copper (mg)	Leached Copper (mg)	Total Iron (mg)	Leached Iron (mg)	pH after leaching
1	TCLP	2.50	0.2232	0.1586	1.2346	0.2509	4.92
2	TCLP	2.70	0.2709	0.2196	0.6302	0.0931	4.92
3	TCLP	2.20	0.1934	0.1331	0.5030	0.0799	4.93
4	TCLP	0.00	0.0041	0.0051	0.0175	0.0042	5.03
5	WET	2.50	0.1559	0.1911	0.5341	0.3810	4.93
6	WET	2.30	0.1494	0.1528	0.5294	0.3613	4.94
7	WET	2.60	0.2003	0.2106	0.5987	0.4681	4.93
8	WET	0.00	0.0057	0.0103	0.0259	0.0234	4.92
9	SRFA	2.90	0.1862	0.0181	0.4645	0.0102	6.52
10	SRFA	2.80	0.1571	0.0172	0.4563	0.0086	6.31
11	SRFA	2.50	0.1017	0.0132	0.3061	0.0026	6.40
12	SRFA	0.00	0.0016	0.0117	0.0205	0.0003	5.45
13	EDTA	2.70	0.1499	0.0947	0.7825	0.0143	7.07
14	EDTA	2.50	0.1340	0.0892	0.4705	0.0221	7.10
15	EDTA	2.90	0.1377	0.1039	0.4003	0.0105	7.04
16	EDTA	0.00	0.0041	0.0095	0.0142	0.0012	4.60
17	SPLP	2.40	0.0593	0.0027	0.2087	0.0001	6.50
18	SPLP	2.30	0.0516	0.0010	0.1873	0.0001	6.41
19	SPLP	2.20	0.0583	0.0005	0.2000	0.0001	6.68
20	SPLP	0.00	0.0023	0.0001	0.0131	0.0002	5.02
21	inorganic synthetic rainwater	2.90	0.0874	0.0009	0.3408	0.0001	7.74
22	inorganic synthetic rainwater	2.70	0.0838	0.0009	0.2903	0.0001	7.80
23	inorganic synthetic rainwater	2.10	0.1144	0.0012	0.2869	0.0001	7.56
24	inorganic synthetic rainwater	0.00	0.0047	0.0004	0.0125	0.0002	5.10
25	synthetic rainwater	2.80	0.1433	0.0020	1.0367	0.0001	7.04
26	synthetic rainwater	2.70	0.0951	0.0010	0.3651	0.0002	7.10
27	synthetic rainwater	2.90	0.1768	0.0007	0.6140	0.0001	7.05
28	synthetic rainwater	0.00	0.0053	0.0014	0.0177	0.0002	4.99
29	concentrated synthetic rainwater	2.30	0.2092	0.1505	0.5352	0.0128	5.23
30	concentrated synthetic rainwater	2.90	0.2143	0.1611	0.5764	0.0038	5.36
31	concentrated synthetic rainwater	2.30	0.1539	0.1153	0.3700	0.0451	5.40
32	concentrated synthetic rainwater	0.00	0.0054	0.0104	0.0127	0.0007	4.90
BLUE	Sample Values <= Bkgd						
RED	Sample Outlier						