Metals in Waste Foundry Sands and an Evaluation of Their Leaching and Transport to Groundwater

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Abstract While most waste foundry sands (WFSs) are not hazardous, regulatory agencies are often reluctant to permit their beneficial use in agricultural and geotechnical applications due to concerns over metal leaching. The objective of this study was to quantify total and Toxicity Characteristic Leaching Procedure (TCLP) metals in 16 waste sands from Brazilian ferrous foundries then assess their potential to leach to groundwater using a probabilistic model. Total and TCLP metal concentrations in the non-hazardous sands fell within ranges as reported in the literature, although some of the leachate concentrations were found to exceed drinking water and groundwater maximum contaminant levels (MCLs). Leachate values above the MCLs were then used in the model to estimate groundwater concentrations at hypothetical wells up to 400m downgradient from a land application unit. A conservative scenario of 1 ha of land applied WFS, and high annual rainfall totals (low evaporation) suggested that groundwater concentrations of Ba, Hg, Mn, Ni, and Pb could potentially exceed health-based MCLs at most wells. While a wet climate can exacerbate the transport of metals, land application of WFSs in areas with moderate rainfall totals or high rainfall, high evaporation was predicted to be protective of groundwater quality and human health.

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1 Introduction

Large quantities of sand are used by the metalcasting industry to create molds and cores. Sands are used because they can absorb and transmit heat while allowing gases generated during the thermal degradation of binders to pass through the grains. After the casting process is completed, resin-bound sands can be thermally reclaimed to make new molds and cores, while green sands require the addition of new bentonite clay and carbonaceous materials (Carey 2002). However, over time, the sand grains begin to break down from heat and mechanical abrasion, thus new sand must be continually added to the system to maintain proper tolerances and prevent casting defects. The sand that is removed from the system, known as discarded, spent, or waste foundry sand (WFS), is commonly

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disposed of at foundry landfills or at off-site municipal landfills.

Over the last decade or longer, a number of countries (e.g., Brazil, USA, India, Argentina) have been investigating the beneficial use of WFSs (Jing and Barnes 1993; Sota et al. 2007; Carnin et al. 2010; Singh and Siddique 2012). Diverting WFSs from landfills makes practical economic and environmental sense, since foundries can save on disposal costs, while end users decreased demand for virgin aggregate alleviates the environmental burdens associated with mining activities. Recent research has demonstrated that most waste sands from iron, steel, and aluminum foundries are a low contaminant material (Deng 2009; Dungan and Dees 2009; Miguel et al. 2012), making them safe to use in various consolidated and unconsolidated beneficial use applications. Beneficial applications include using WFSs as road subbases and embankments or to manufacture paver stones, asphalt concrete, cement, flowable fill, and soils (Partridge et al. 1999; U.S. DOT 2004; Lindsay and Logan 2005; Deng and Tikalsky 2008). Research by Lee et al. (2004a, b) suggests that waste green sands could also be used as a reactive barrier to remove zinc and trichloroethylene from contaminated groundwaters.

Brazil has nearly 1,300 foundries (Modern Casting 2010), producing approximately 3 million tons of WFS annually, with most of this material being discarded in landfills (Carnin et al. 2012). Many of the foundries are located in the southern and southeastern states of Santa Catarina, Paraná, Rio Grande do Sul, Minas Gerais, and São Paulo. Despite the success of some WFS pilot projects (Carnin et al. 2010), the environmental regulations at the federal and state levels generally do not permit their use in geotechnical and agricultural applications. Recently, the states of Santa Catarina and São Paulo have relaxed restrictions and now allow WFSs to be used as an aggregate substitute in paver stones, asphalt concrete, and non-structural concrete (CETESB 2007; CONSEMA 2008). Forward progress on the expansion of beneficial use regulations in Brazil has been slow to date, largely due to a lack of specific information on the concentration and environmental behavior of chemical constituents in WFSs.

To generate relevant and timely data, the aim of this study was to quantify total and leachable metals in waste sands from Brazilian ferrous foundries. Leaching of metals was performed using the Toxicity Characteristic Leaching Procedure (TCLP), with the results being compared to national groundwater standards (CONAMA 2009). The TCLP is the preferred leaching procedure in Brazil to determine if a solid waste exhibits the toxicity characteristic and is therefore hazardous (ABNT 2004a). It has also been used by various researchers to assess the stability of foundry sands for beneficial use applications (Deng and Tikalsky 2008; Siddique et al. 2010). Leachate metal concentrations that exceeded groundwater maximum contaminant levels (MCLs) were then used in the U.S. EPA (2002a) Industrial Waste Management Evaluation Model (IWEM) to conduct a modeling scenario to estimate groundwater concentrations at hypothetical wells up to 400m downgradient of land applied WFSs. The land application scenario was considered since unconsolidated applications of WFS represent the greatest potential risk to environmental and public health.

2 Materials and Methods

2.1 Waste Foundry Sands

Sixteen silica-based waste sands were collected at 10 ferrous foundries located in the state of Santa Catarina, Brazil (Table 1). The WFSs were a mixture of mostly molding and core sands, which were bonded with bentonite clays (i.e., green sands) or organic resins, respectively. Approximately 5 kg of WFS was collected from piles using a sampling tier, according to the method NBR 10007 (ABNT 2004b), or by releasing it from storage silos directly into clean glass or plastic sample containers. After collection, the samples were stored at 4 °C until analyzed.

2.2 Total and Leachable Metals

Prior to being analyzed, all waste sands were dried at 105 °C, homogenized, and then passed through a 2-mm sieve. For total metals, the sands were processed by microwave-assisted acid digestion using SW-846 method 3051a (U.S. EPA 2007a). The TCLP procedure was conducted according to SW-846 method 1311 (U.S. EPA 1992). In brief, the TCLP calls for the rotary agitation (30 rev. min^{-1}) of at least a 100-g sample at a 20:1 liquid-to-solid ratio with an acetic acid solution for 18 h. Following the extraction, the liquid and solid phases were separated by filtering through a glass fiber filter.

Table 1 Description of the molding and core sand systems at the ferrous foundries

Foundry	Sample ID	Molding sand	Core binder system	Metals poured	Approximate sample age	Notes
A	1	Green sand	PU[a] coldbox, Novolac	Gray iron, vermicular iron	1 day	Waste sand from bin; homogeneous sand
	2	Green sand	PU coldbox, Novolac	Gray iron, vermicular iron	1 day	Waste sand from bin; heterogeneous with core butts
	3	Green sand	PU coldbox, Novolac	Gray iron, vermicular iron	1 day	Engine block line; waste sand from bin
	4	Green sand	PU coldbox, Novolac	Gray iron, vermicular iron	1 week	Sieved waste sand (2.5 mm); stored in silo for use in paver stone manufacturing
B	5	Green sand	PU coldbox	Gray iron, vermicular iron	1 day	Foundry 1; sand from comingled waste bin
	6	Green sand	PU coldbox	Gray iron, vermicular iron	1 day	Shakeout sand from foundries 1 and 2
	7	Green sand	PU coldbox	Gray iron, vermicular iron	1 day	Foundry 2; waste sand from floor prior to silo storage
C	8	Green sand	Novolac	Gray iron, ductile iron	Few days	Waste sand from silo
D	9	Novolac	PU no-bake	Steel, white iron	1 week	Waste sand from silo. Molding sand resin contained 2 % iron oxide
E	10	PU coldbox	PU no-bake	Gray iron, Cr steel	Few days	Collected waste dust (fine sand) from storage bags
F	11	PU no-bake	PU no-bake	Gray iron, ductile iron, steel	3 days	Waste sand from silo
G	12	Green sand	PU coldbox, Novolac	Gray iron, ductile iron	1 week	Foundry 1; waste sand from bin
H	13	Green sand	PU coldbox	Gray iron	1 day	Foundry 4; waste sand from silo
	14	Green sand	No cores	Gray iron	1 day	Foundry 3; waste sand from silo
I	15	PU no-bake	PU no-bake	Gray iron, ductile iron, steel	1 week	Waste sand from silo
J	16	PU no-bake	PU no-bake	Gray iron, ductile iron, steel	1 day	Sand collected from floor at final point of disposal

[a] Phenolic urethane

The acid digests and TCLP leachates were analyzed by inductively coupled plasma–atomic emission spectroscopy for Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, V, and Zn (U.S. EPA 2007b). Mercury was analyzed using a cold-vapor atomic absorption method (U.S. EPA 2007c).

2.3 Probabilistic Modeling of Groundwater Concentrations

A Tier 2 analysis was conducted in IWEM using a 1-ha land application unit (LAU) with an operational life of 1 year to represent a single application of WFS that was tilled into soil. The LAU is the only no-liner scenario in IWEM, since liners are not typically used for these units. Because Ba, Cr(III), Hg, Mn, Ni, Pb, and Zn concentrations in TCLP leachates were found to exceed the MCLs (CONAMA 2009), minimum and maximum values above the groundwater MCLs were then used in the model to calculate drinking water concentrations at hypothetical wells. Wells were set downgradient from the LAU at distances of 1, 10, 25, 50, 100, 200, and 400 m

(assumes a well is located in the center line of the contaminant plume).

The following subsurface parameters were set to model defaults (i.e., "unknown"): depth to water table (5.18 m), aquifer thickness (10.1 m), hydraulic conductivity (1.89E03 m y^{-1}), regional hydraulic gradient (0.0057), groundwater pH (7), and chemical-specific decay rate (0 for metals); soil–water partition coefficients (k_d) for metals were selected from non-linear sorption isotherms estimated using the geochemical speciation model, MINTEQA2 (U.S. EPA 2002b). The "unknown" subsurface environment assumes it is a noncarbonate type. Three climates were modeled to account for a range of rainfall totals and evaporation rates in southern and southeastern states of Brazil: (1) high rainfall, low evaporation (Astoria, OR); (2) high rainfall, high evaporation (Miami, FL); and (3) moderate rainfall, moderate evaporation (Topeka, KS). The soil type selected for all model runs was the "unknown soil type".

The model runs each constituent in a probabilistic (Monte Carlo) mode for 10,000 realizations to estimate a maximum groundwater concentration that occurred

Table 2 Summary of total metal concentrations in the waste foundry sands (mg kg^{-1})

Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Ag	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Al	2,275	2,331	2,048	1,717	2,584	1,330	494	2,374	1,146	220	3,049	807	2,000	2,153	1,043	204
As	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
B	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3
Ba	28.1	28.8	30.8	39.9	32.2	48.8	<2.0	40.9	6.2	82.5	22.3	11.5	23.4	26.2	10.2	<2.0
Be	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7
Cd	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Co	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	2.2	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Cr	22.7	3.5	3.3	2.8	3.1	<2.0	<2.0	3.5	6.2	40.9	5.1	3.8	2.7	2.8	5.4	<2.0
Cu	7.0	3.5	2.3	2.5	2.7	2.4	<2.0	4.4	32.4	10.9	4.6	3.6	2.7	2.6	4.5	<2.0
Fe	5,937	2,485	1,939	1,612	2,123	3,381	475	3,240	1,249	27,081	3,133	3,563	2,007	1,926	3,813	926
Hg	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mg	665	689	545	482	784	435	25.6	818	165	1,540	966	193	679	702	76.9	16.3
Mn	168	55.6	22.3	27.3	22.7	26.2	15.7	80.7	105	401	44.2	41.0	29.3	28.8	61.1	28.5
Mo	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7
Ni	3.6	2.7	2.7	2.2	3.1	<2.0	<2.0	3.6	3.3	9.2	5.3	2.4	2.9	3.3	2.2	<2.0
Pb	3.2	<2.0	3.5	2.0	2.2	3.0	<2.0	3.7	2.8	3.1	2.6	<2.0	<2.0	<2.0	6.1	2.5
Sb	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	5.5	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Se	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
V	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	<5.3	7.4	<5.3	<5.3	<5.3	<5.3	<5.3
Zn	18.2	10.8	13.0	12.4	31.0	64.3	7.7	11.0	29.5	21.8	41.3	5.8	7.4	6.3	16.4	13.9

within a period of 10,000 years after leaching began. After the model runs were completed, the estimated 90th percentile well water concentrations were compared to the groundwater MCLs. If the 90th percentile constituent concentration was at or below the MCL, then the land application scenario of WFS was considered protective of human health. To develop an understanding of model sensitivity to leaching concentration inputs and maximum possible concentrations that could be used in IWEM without exceeding the groundwater MCLs, the model was also run for each climate at an assumed well distance of only 1 m. Complete details about IWEM can be found in the *User's Guide* (U.S. EPA 2002a) and *Technical Background Document* (2002b).

3 Results and Discussion

Of the foundry sands investigated in this study, the majority of the molding sands (11 of 16) were green sands, with all of the core binder systems being phenol–formaldehyde-based resins (Table 1). Compared to the core, the exterior mold is by far the largest portion of the complete metalcasting mold, thus the combined WFS generally takes on the characteristic of the molding sand. Chemically bound molds and cores contain residual binder, much of which is thermally degraded during the casting process resulting in the formation of volatile and semi-volatile organics (Dungan and Reeves 2005). Similarly, carbonaceous additives (e.g., seacoal, gilsonite) in green sands are also thermally degraded, producing a number of volatile hydrocarbons (Dungan and Reeves 2007). While the focus of this manuscript is on metal contaminants, organics of environmental concern can be detected in WFSs, but they are usually at relatively low concentrations (Dungan 2006; Dungan et al. 2009).

The total metal concentrations for each of the WFSs are presented in Table 2. As expected, the metals at the highest concentrations in the waste sands were Al, Ba, Fe, Mg, Mn, and Zn. While these elements are found within the silica sand matrix or bentonite clay, they can also become elevated in the WFSs when they are transferred during the metalcasting process. Evidence also suggests that the metal concentrations within the sands become increasingly elevated each time they are reclaimed (Miguel et al. 2012). The remainder of the metals analyzed in the WFSs were at substantially lower concentrations, with most elements being lower than the

method detection limit (MDL). Metals that were below the MDL for all sand samples were Ag, As, B, Be, Cd, Co, Hg, Mo, and Se, while Sb and V were only slightly above the MDL in one sand. The concentrations of the remaining metals (i.e., Cr, Cu, Ni, and Pb) were mostly at the same order of magnitude as the MDL; however, in some sands, it was 10-fold higher. For example, the MDL for Cr and Cu was 2.0 mg kg^{-1}, but sand 10 from a gray iron and chrome steel foundry contained the highest concentrations at 40.9 and 10.9 mg kg^{-1}, respectively. Regardless of these elevated concentrations, the maximum values reported in this study fell within concentration ranges reported in other studies (Table 3). In addition, the metal concentrations were at levels similar to those found in native soils (Dungan and Dees 2009) and do not impede the growth of agronomic crops (Dungan and Dees 2007; Dayton et al. 2010).

In Brazil, a waste is hazardous if any inorganic and organic analyte in the leachate exceeds the maximum

Table 3 Comparison of metal concentrations in waste foundry sands (mg kg^{-1})

Element	This study (n=16)	Dayton et al. 2010 (n=39)	Miguel et al. 2012 (n=96)
Ag	<2.0		<0.70
Al	204–3,049	193–11,700	281–15,074
As	<2.0	0.13–7.8	
B	<5.3		
Ba	<2.0–82.5		7.1–115
Be	<2.7	<0.1–0.60	<0.07–0.64
Cd	<1.3	<0.04–0.36	<0.20–0.97
Co	<2.0–2.2	<0.5–6.6	<0.70–77.1
Cr	<2.0–40.9	<0.5–115	297–931
Cu	<2.0–32.4	<0.5–137	<0.5–303
Fe	475–27,081	1,280–64,400	4,769–18,217
Hg	<0.2		
Mg	16.3–1,540	50–3,200	<0.20–4,002
Mn	15.7–401	5.7–707	34.2–202
Mo	<2.7	<1.0–22.9	0.99–20.8
Ni	<2.0–9.2	1.1–117	40.8–260
Pb	<2.0–6.1	<1.0–22.9	<4.20–647
Sb	<1.3–5.5		<3.2–4.4
Se	<1.5	<0.04–0.10	
V	<5.3–7.4	<1.0–11.3	3.5–25.7
Zn	5.8–64.3	<10–245	6.1–171

Table 4 Summary of metal concentrations in TCLP leachates from the waste foundry sands (mg L^{-1})

Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Ag	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Al	2.8	3.0	2.6	2.0	4.8	10.0	4.3	4.2	1.5	<0.03	0.67	0.32	2.0	0.59	2.0	0.18
As	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B	1.9	0.21	1.6	0.08	2.7	0.64	1.2	0.90	0.61	<0.02	0.56	1.5	0.70	1.4	0.15	0.94
Ba	0.76	0.93	0.39	0.22	3.9	2.0	0.97	1.5	1.3	1.1	1.2	1.6	1.7	2.2	0.76	2.2
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Co	0.02	0.01	0.01	0.01	<0.005	0.02	<0.005	0.01	<0.005	0.04	<0.005	<0.005	<0.005	<0.005	<0.005	0.03
Cr	0.02	0.02	0.02	<0.01	0.01	0.21	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.10	0.10	0.03	0.23
Cu	0.06	0.04	0.03	<0.009	0.05	0.05	0.04	0.07	0.04	<0.009	0.02	0.02	0.11	0.02	0.02	0.08
Fe	12.9	6.3	1.9	0.62	3.3	224	5.5	8.4	2.9	384	1.5	10.5	75.8	0.61	34.2	199
Hg	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Mg	5.8	5.4	4.6	4.6	7.6	9.5	7.9	5.9	3.7	55.7	0.61	4.4	1.4	5.4	1.3	0.33
Mn	0.64	0.57	0.46	0.65	0.41	1.8	0.63	0.56	0.36	6.1	0.07	0.42	0.57	0.29	0.39	1.5
Mo	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Ni	0.03	0.03	0.02	0.02	0.03	0.10	0.03	0.03	<0.005	<0.005	<0.005	0.02	0.05	0.01	0.03	0.12
Pb	<0.009	<0.009	<0.009	<0.009	0.17	0.04	<0.009	<0.009	<0.009	<0.009	<0.009	0.08	<0.009	<0.009	0.04	<0.009
Sb	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Se	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009
V	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Zn	3.0	0.38	1.9	0.14	3.9	5.4	1.7	1.5	1.2	0.76	1.1	2.5	1.3	2.1	0.95	1.9

Table 5 Comparison of the TCLP results with groundwater maximum contaminant levels (mg L^{-1})

Element	TCLP[a]				
	Min	Max	Mean	Median	MCL[b]
Ag	<0.005				0.05
Al[c]	<0.03	10.0	2.6	2.0	3.5
As	<0.01				0.01[d]
B[c]	0.01	2.7	0.94	0.80	0.5
Ba[c]	0.22	3.9	1.4	1.3	0.7[d]
Be	<0.01				
Cd	<0.004				0.005[d]
Co	0.0025	0.04	0.01	0.01	0.07
Cr[c]	<0.01	0.23	0.06	0.05	0.05[d]
Cu	<0.009	0.11	0.04	0.04	2.0[d]
Fe[c]	0.61	384	60.7	7.4	2.45
Hg[c]	<0.006				0.001[d]
Mg	0.33	55.7	7.7	5.0	
Mn[c]	0.07	6.1	0.97	0.56	0.4
Mo	<0.015				0.07
Ni[c]	<0.005	0.12	0.03	0.03	0.02[e]
Pb[c]	<0.009	0.17	0.02	0.005	0.01[d]
Sb	<0.005				0.005[d]
Se	<0.009				0.01[d]
V	<0.015	0.03	0.01	0.008	
Zn[c]	0.14	5.4	1.9	1.6	1.05

[a] Calculations based on setting sample concentrations<MDL at one half that value

[b] Groundwater maximum contaminant level (MCL) under CONAMA (2009)

[c] At least one TCLP extract with metal concentrations above the MCL

[d] Values are the same as the Brazilian drinking water standards (Ministério da Saúde 2011)

[e] Drinking water standard for Ni is 0.07 mg L^{-1}

limits of classification standards present in NBR 10004 (ABNT 2004a). Just considering metals in the TCLP leachates (Table 4), none of the WFSs examined in this study would be classified as hazardous waste. The TCLP test has been applied to numerous WFSs; and in almost all cases, sands from iron, steel, and aluminum foundries were not determined to be toxic (Deng 2009; Miguel et al. 2013). The leaching results were also compared to groundwater MCLs (Table 5), which are environmental cleanup standards for contaminated sites (CONAMA 2009). The groundwater MCLs are the same as the Brazilian drinking water standards (Ministério da Saúde 2011) or are more restrictive, but only in the case of Ni at 0.02 versus 0.07 mg L^{-1} (Table 5). Of all of the metals analyzed, the following metals were higher than the MCL in at least one TCLP leachate: Al, B, Ba, Cr, Fe, Hg, Mn, Ni, Pb, and Zn. While not conclusive, the TCLP results suggest that all of the WFSs could potentially leach elevated quantities of one or more of the metals if beneficially used in an unconsolidated manner (e.g., land application, road subbase). However, the TCLP test was designed to assess leaching from mixed industrial and municipal wastes in the presence of organic acids (Kendell 2003). Because the TCLP simulates conditions within an environment (i.e., landfill) that is different from beneficial use scenarios, the values presented in Table 5 are higher than would have been obtained using a non-buffered extractant such as distilled water (Baba and Kaya 2004). The added benefit of using these values in our modeling scenarios is that there is built in conservatism.

Compared to consolidated applications (e.g., asphalt, concrete), the direct application of WFS to land clearly represents the greatest risk for the transport of contaminants to surface and groundwaters. Table 6 lists the IWEM groundwater modeling results at the 90th percentile. Conservative exposure estimates were developed using the minimum and maximum TCLP values that initially exceeded the groundwater MCL. As a result, the only elements that were considered in the probabilistic model were Ba, Cr(III), Hg, Mn, Ni, Pb, and Zn (Al, B, and Fe cannot be modeled in IWEM). Under the high rainfall and low evaporation scenario, modeled values for Ba, Hg, Ni, Pb, and Mn (highest TCLP values only) exceeded the MCLs at hypothetical well distances of 1 to 400 m from the LAU. At leachate concentrations of 1.1 and 5.4 mg L^{-1} for Zn, none of the modeled exposure levels were found to exceed the MCLs. When the rate of evaporation was high, Ba, Hg, and Mn exceeded the MCL at well distances up to 50 m. Under moderate rainfall and evaporation, only Mn exceeded the MCL of 1.05 mg L^{-1} at well distances up to 25 m. Since TCLP leachate values were used in IWEM, along with other conservative model inputs, the 90th percentile modeled exposure levels likely represent an overestimation of actual risks of land applied WFSs.

To determine the maximum leachate concentrations that could be modeled without exceeding the groundwater MCLs, we reran IWEM multiple times under the

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Table 6 Modeled groundwater exposure concentrations for land applied waste foundry sands (mg L^{-1})

Element	Leachate conc. tested	90th Pecentile modeled exposure level							MCL[a]
		1 m	10 m	25 m	50 m	100 m	200 m	400 m	
		High rainfall, low evaporation							
Ba	0.76	0.510	0.464	0.406	0.329	0.233	0.171	0.162	0.7
	3.9	*2.477*	*2.240*	*1.953*	*1.575*	*1.122*	*0.801*	*0.821*	
Cr(III)	0.1	6.0E-04	3.0E-04	1.0E-04	6.1E-05	3.1E-05	2.3E-05	9.8E-06	0.05
	0.23	0.001	0.001	3.0E-04	2.0E-04	1.0E-04	7.0E-05	3.9E-05	
Hg	0.006	*0.003*	*0.003*	*0.003*	*0.003*	*0.002*	0.001	0.001	0.001
Mn	0.42	0.263	0.208	0.176	0.135	0.092	0.067	0.063	0.4
	6.1	*3.972*	*3.527*	*3.093*	*2.604*	*1.898*	*1.416*	*1.219*	
Ni	0.02	0.008	0.005	0.004	0.003	0.002	0.001	1.0E-04	0.02
	0.12	*0.072*	*0.053*	*0.041*	*0.029*	0.018	0.013	0.014	
Pb	0.04	0.006	0.002	0.001	0.001	3.0E-04	2.0E-04	2.0E-04	0.01
	0.17	*0.035*	*0.013*	0.006	0.003	0.002	0.001	0.001	
Zn	1.1	0.197	0.126	0.080	0.047	0.028	0.020	0.019	1.05
	5.4	0.628	0.477	0.346	0.243	0.165	0.116	0.090	
		High rainfall, high evaporation							
Ba	0.76	0.171	0.157	0.102	0.072	0.049	0.030	0.018	0.7
	3.9	*0.830*	*0.723*	0.525	0.370	0.247	0.152	0.089	
Cr(III)	0.1	8.3E-12	3.2E-10	3.8E-10	5.1E-10	2.1E-08	2.0E-08	1.9E-11	0.05
	0.23	2.8E-11	2.0E-09	2.2E-09	2.6E-09	1.3E-07	2.0E-07	1.3E-10	
Hg	0.006	*0.002*	0.001	0.001	8.0E-04	5.0E-04	3.0E-04	2.0E-04	0.001
Mn	0.42	0.070	0.064	0.040	0.026	0.017	0.010	0.006	0.4
	6.1	*1.050*	*0.843*	*0.647*	*0.478*	0.322	0.196	0.112	
Ni	0.02	0	0	0	0	0	0	0	0.02
	0.12	0.010	0.011	0.006	0.004	0.002	0.001	0.001	
Pb	0.04	0	3.4E-12	1.1E-08	1.1E-07	3.1E-07	3.2E-07	2.3E-07	0.01
	0.17	0.001	0.001	4.0E-04	2.0E-04	1.0E-04	7.4E-05	4.2E-05	
Zn	1.1	0.027	0.017	0.008	0.005	0.003	0.002	0.001	1.05
	5.4	0.109	0.074	0.045	0.032	0.020	0.012	0.006	
		Moderate rainfall, moderate evaporation							
Ba	0.76	0.098	0.098	0.072	0.049	0.033	0.020	0.012	0.7
	3.9	0.513	0.546	0.395	0.263	0.173	0.107	0.064	
Cr(III)	0.1	2.2E-15	1.3E-13	8.0E-13	1.8E-12	7.2E-12	1.1E-11	5.7E-12	0.05
	0.23	1.3E-13	3.8E-12	9.5E-12	2.5E-11	6.3E-11	7.7E-11	3.9E-11	
Hg	0.006	9.0E-04	9.0E-04	8.0E-04	6.0E-04	4.0E-04	3.0E-04	2.0E-04	0.001
Mn	0.42	0.036	0.046	0.030	0.018	0.011	0.007	0.004	0.4
	6.1	*0.758*	*0.615*	*0.462*	0.319	0.215	0.132	0.076	
Ni	0.02	0	0	0	0	0	0	0	0.02
	0.12	0.004	0.006	0.004	0.002	0.001	8.0E-04	4.0E-04	
Pb	0.04	0	0	0	0	0	0	0	0.01
	0.17	0.001	0.001	3.0E-04	1.0E-04	7.9E-05	4.6E-05	2.6E-05	
Zn	1.1	0.013	0.010	0.005	0.003	0.002	0.001	0.001	1.05
	5.4	0.070	0.050	0.030	0.019	0.013	0.007	0.004	

0 represents the 90th percentile modeled concentration <1.0E-20 mg L^{-1}

Entries in italics represent modeled values that exceeded the groundwater MCL

[a] Groundwater maximum contaminant level (MCL) under CONAMA (2009)

Table 7 Maximum possible leachate concentrations for use in IWEM without exceeding the groundwater maximum contaminant levels at a hypothetical well 1 m downgradient from land applied waste foundry sands (mg L^{-1})

Element	90th Percentile		90th Percentile		90th Percentile		MCL[a]
	Max. leachate conc.	High rainfall, low evaporation	Max. leachate conc.	High rainfall, high evaporation	Max. leachate conc.	Moderate rainfall and evaporation	
Ba	1.1	0.694	3.4	0.696	5.5	0.696	0.70
Cr(III)	95.7	0.032	1,000[b]	0.014	1,000[b]	0.005	0.05
Hg	0.001	5.1E-04	0.003	7.8E-04	0.006	9.2E-04	0.001
Mn	0.62	0.394	1.6	0.386	2.6	0.389	0.40
Ni	0.04	0.019	0.17	0.018	0.30	0.019	0.02
Pb	0.05	0.008	0.57	0.0099	0.97	0.0099	0.01
Zn	9.2	1.045	200	1.034	401	1.045	1.05

[a] Groundwater maximum contaminant level (MCL) under CONAMA (2009)

[b] Maximum permissible value in IWEM

three climate regimes at a well distance of 1 m (Table 7). These results indicate that the transport of metals from land applied WFSs to groundwater generally decreases when there is less rainfall and water for infiltration. Considering the high rainfall totals in southern and southeastern Brazil (~125–200 cm y^{-1}), maximum leaching of WFS constituents can be expected. It is important to note that soil chemistry is complicated, as metals can form insoluble precipitates or sorb to organic matter and Al, Fe, and Mn oxides, thus affecting their partitioning between solid and liquid phases. Even at high concentrations, many elements are so insoluble in aerobic soils between pH 5.5 and 8 that they do not present a risk (Basta et al. 2005). Although IWEM does consider physical phenomena (i.e., transport, diffusion), the model also takes into account chemical reactions as affected by pH, groundwater composition (carbonate and non-carbonate), and concentration of sorbents (ferric oxide, particulate organic matter, dissolved organic matter), anthropogenic organic acids, and metals. Assuming the high rainfall, high evaporation scenario is most representative of our regions of interest, then the results in Table 7 (when compared to Table 4 values) indicate that only Ba and Mn would potentially exceed the groundwater MCLs. Only three sands (nos. 5 and 6 and 10, respectively) had TCLP leachate concentrations that exceeded 3.4 mg Ba L^{-1} and 1.6 mg Mn L^{-1}. Our results for Hg were inconclusive because the MDL of 0.006 mg L^{-1} was greater than the modeled maximum leachate concentration of 0.003 mg L^{-1}.

4 Conclusions

The results from this study revealed that ferrous WFSs from Brazil contained total metal concentrations that fell within ranges as reported in the literature. While metal concentrations in TCLP leachates were also within reported ranges, some of the concentrations were found to exceed drinking water and groundwater MCLs. This outcome was expected because of the low pH conditions associated with the TCLP test. Through probabilistic modeling, it was predicted that the land application of some WFSs could potentially cause the downgradient groundwater concentrations of Ba, Hg, Mn, Ni, and Pb to exceed health-based MCLs, especially under high rainfall, low evaporation conditions. Under high rainfall, high evaporation and moderate rainfall, and moderate evaporation scenarios, only 3 of 16 WFSs were predicted to cause metal levels to exceed the MCLs for Ba and Mn. Because conservative leachate concentrations were utilized in the modeling scenarios, the results likely represent an overestimation of groundwater metal concentrations that would occur under actual conditions. Considering all information, our results suggest that unconsolidated applications of ferrous WFSs in most of southern and southeastern Brazil will be protective of groundwater quality and human health. However, land application of sands with a high metal leaching potential should be evaluated under realistic conditions if they are to be used in high rainfall, low evaporation areas.

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