Appendix 1 to Letter to the Editor Regarding "A Study of the Routes of Contamination by Lead and Cadmium in Santo Amaro, Brazil" DOI:10.1080/09593330.2013.788071

The Extractive Metallurgy of Lead at Santo Amaro (Brazil)

In the lead roasting-smelting processes the galena concentrate is mixed with limestone, scrap iron, coal and sand. In the roasting process the galena reacts according with the equations [1,2]:

$$2PbS + 3O_2 \xrightarrow[\Delta]{} 2PbO + 2SO_2 \quad (1)$$

$$3PbS + 5O_2 \xrightarrow[\Delta]{} 2PbO + PbSO_4 + 2SO_2 \quad (2)$$

$$PbS + 3PbSO_4 \xrightarrow[\Delta]{} 4PbO + 4SO_2 \quad (3)$$

In the smelting process the lead oxide reacts according to the equations [1,2]:

$$2PbO + C \xrightarrow[\Delta]{} 2Pb + CO_2 \quad (4)$$

$$2PbO + CO \xrightarrow[\Delta]{} Pb + CO_2 \quad (5)$$

The slag generated in the smelting is granulated by quenching the molten silicate phase with water and disposal in the field. Due the fact that the molten lead is an excellent solvent for several elements, a refining process is essential [1,2]. The classical pyrometallurgical lead refining includes: decoppering (removal of Cu), "softening" (removal of Sn, Sb, and As), desilverization (removal of Ag), dezincing (removal of Zn by vacuum distillation), and debismuthizing (removal of Bi) [1,2]. In the sinter-roasting process, in addition to gases (mainly SO_2 and CO_2), a flue dust rich in Pb, Cd and As compounds is produced [1,2].

The Santo Amaro primary lead smelter (Figure 1) used the galena concentrate from the flotation plant of Boquira Mine and the sinter-roasting process (with a Dwight-Lloyd sintering machine for agglomeration) followed by smelting (with water-jackets furnace) and pyrometallurgical refining [1-3].

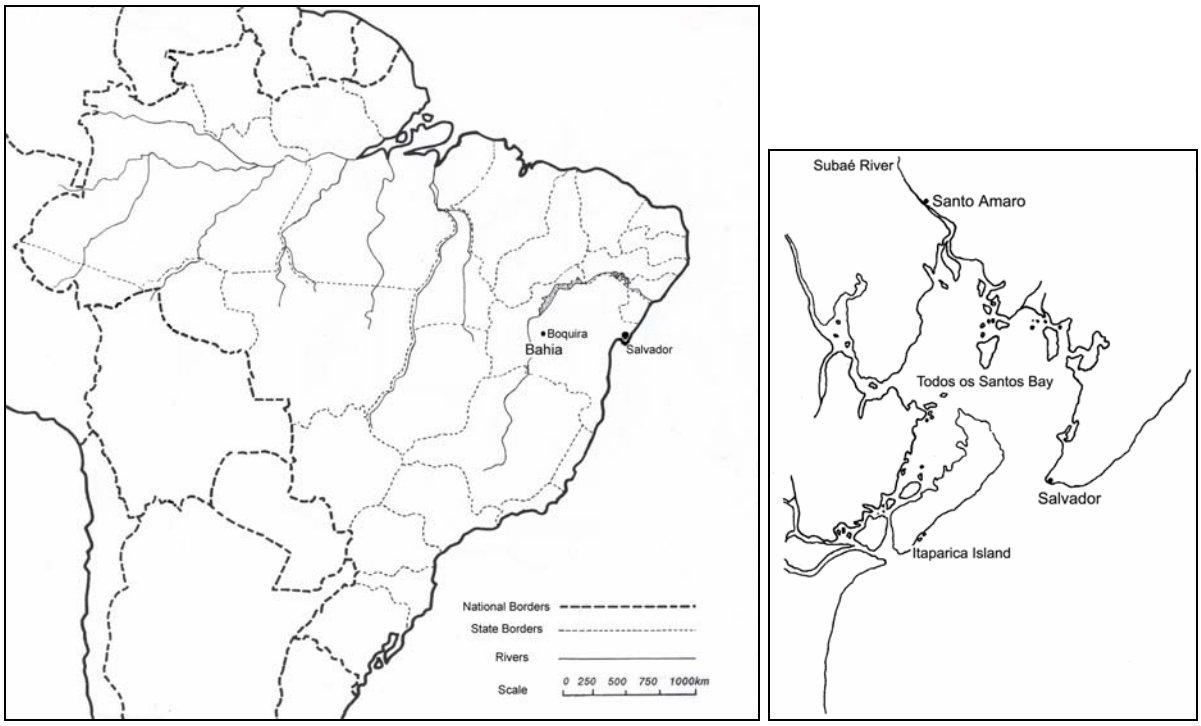

Figure 1: Location of the lead smelter at Santo Amaro city.

The primary lead smelters produce consistently airborne Pb emissions and slag [1,2,4]. The role of lead smelter emissions on the contamination of the surrounding environment, including soil and people with potentially toxic elements has been well established since the 1970s [4]. It is clear that the maximum Pb accumulation occurs close to the chimney and there is an exponential distance-soil Pb content decline [4]. A 1975 study conducted at El Paso (USA) indicated that the particulate Pb in dust and air accounted for most of the Pb absorption by children, especially within 1.6 km of the smelter [5]. In 1977 a study conducted at Silver Valley (USA) evaluated the relationship between childhood blood Pb levels and environmental exposure [6]. They demonstrated an inverse correlation between soil Pb content and the distance from the smelter. In 1977 a study conducted at Kellogg (USA), near a lead smelter, also demonstrated the inverse correlation between the soil content elements and the distance from the smelter [7].

In the Santo Amaro smelter the airborne emissions from both processes were treated by scrubbing and by filtration and then sent to the chimney [3]. The cleaned gas contained about 1.0 ppm of SO_2, despite the fact that the wastewater, rich in Cd, Pb and A compounds were discharged into the Subaé River without treatment [8,9]. In 1982 the particulate control included baghouse, rotoclone, and a 90 m chimney, which reduced the Pb emissions as particulate material by 78% [9].

In 1989 and 1990, an evaluation of the hair and blood Pb and Cd content in children living within 0.9 km of the Santo Amaro smelter indicated the classical inverse correlation between the Pb content and the chimney distance [9,10].

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Appendix 2 to Letter to the Editor Regarding "A Study of the Routes of Contamination by Lead and Cadmium in Santo Amaro, Brazil" DOI:10.1080/09593330.2013.788071

Primary Lead Production

The major producers of lead in 1968 were: USA (829 kt/year), W. Germany (271 kt/year), United Kingdom (234 kt/year), Australia (203 kt/year), Canada (183 kt/year), Mexico (172 kt/year), Japan (165 kt/year) and France (148 kt/year) [1-4]. At this time and during the 1970s and 1980s the largest lead smelters were Herculaneum (USA), Point Pair (Australia) and Northfleet (United Kingdom) with plant capacities larger than 200 kt/year of refined lead. Other large lead smelters included Mt. Isa (Australia), Trail (Canada), Torreon (Mexico) and Brunswick (Canada), with plant capacities larger than 100 and smaller than 200 kt/year of refined lead [1-4]. In the USA there were 21 primary lead smelters in the 1920s, 7 in 1973, and only 3 in 1999 [4], because nowadays most lead is produced from secondary sources (recycling).

The refined lead production in Brazil was modest and only two smelters were on operation from 1960s to 1990s. In 1971 the total refined lead production was 27.3 kt (21.2 kt from the Santo Amaro smelter and 6.1 from Panelas smelter). In 1972 the refined lead production was 25.1 kt (20.8 kt from the Santo Amaro smelter and 4.3 from Panelas smelter) [5,6].

In 1968 the Santo Amaro smelter capacity was 15 kt/year and in 1977 the plant's capacity grew to 32 kt/year (the partial refined lead production of this plant is summarized in Table 1) [5-7]. In fact, the Santo Amaro smelter processed less than 150 kt of refined lead in the first 13 years (average 11.4 kt/year) and about 80 kt of refined lead in the following 4 years (average 19.4 kt/year). The Santo Amaro Smelter was classified as a small pyrometallurgical plant.

Table 1: Annual primary production of refined lead at Santo Amaro Smelter [5-7]

	Production (kt/year)	Four years production (kt)
1960	5.965	
1961	7.677	
1962	8.668	
1963	11.688	33.998
1964	9.061	
1965	3.627	
1966	9.203	
1967	12.637	34.528
1968	10.783	
1969	11.618	
1970	14.629	
1971	21.254	58.284
1972	20.823	
1973	26.637	
1974	30.502	
1975	26.575	104.537
1980	27.679	
1981	19.810	
1982	14.482	
1983	15.742	77.713

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Appendix 3 to Letter to the Editor Regarding "A Study of the Routes of Contamination by Lead and Cadmium in Santo Amaro, Brazil" DOI:10.1080/09593330.2013.788071

The Primary Lead Slag Stability and the Contamination Source

The Santo Amaro lead slag was systematically characterized and the Pb content identified as droplets of metallic Pb [1-4]. The Cd content in the slag is low (57.3 mg/kg) [2]. Figure 1 presents a scanning electron microscope image of polished slag particles. This image shows several regions with different gray tonalities in the sample. The white spots are metallic Pb, and the light gray regions are fine-grained dendrites of wüstite ((Fe,Zn)O) or zincite ((Zn,Fe)O), as shown in Figures 2a and 2b. There are gray regions in the slag, around the dendrites and the Pb spheroids, which form the slag matrix, rich in Si and Ca. The dark zones are natural holes and fissures in the slag filled with a polymeric resin during the sample preparation.

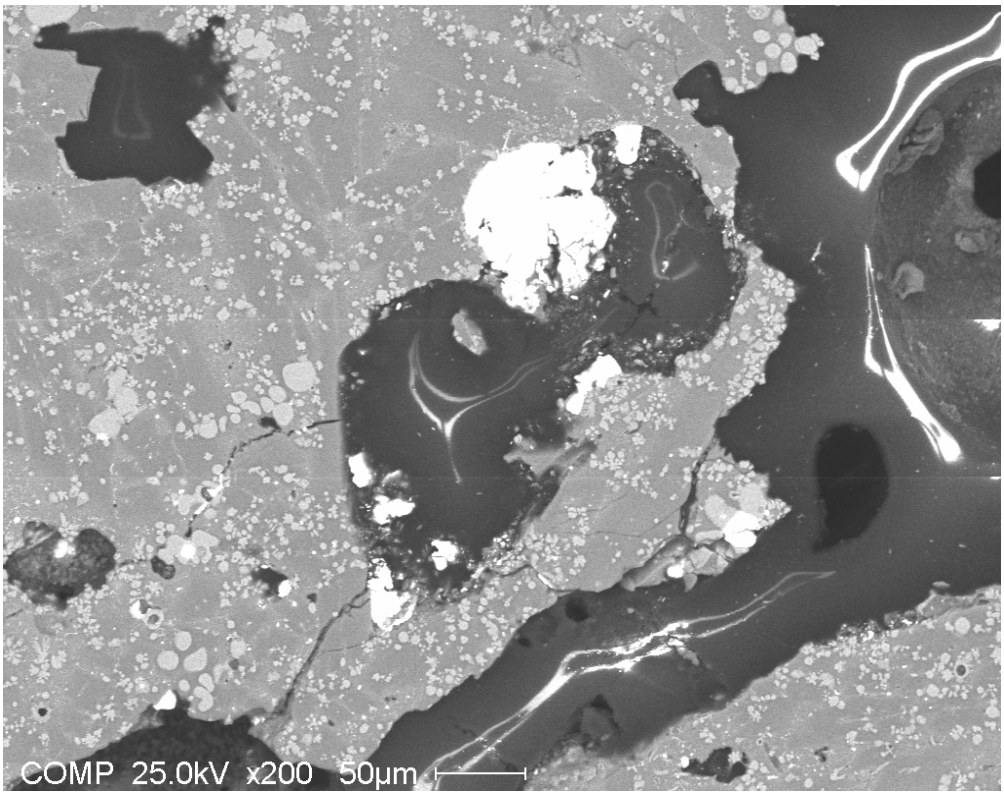
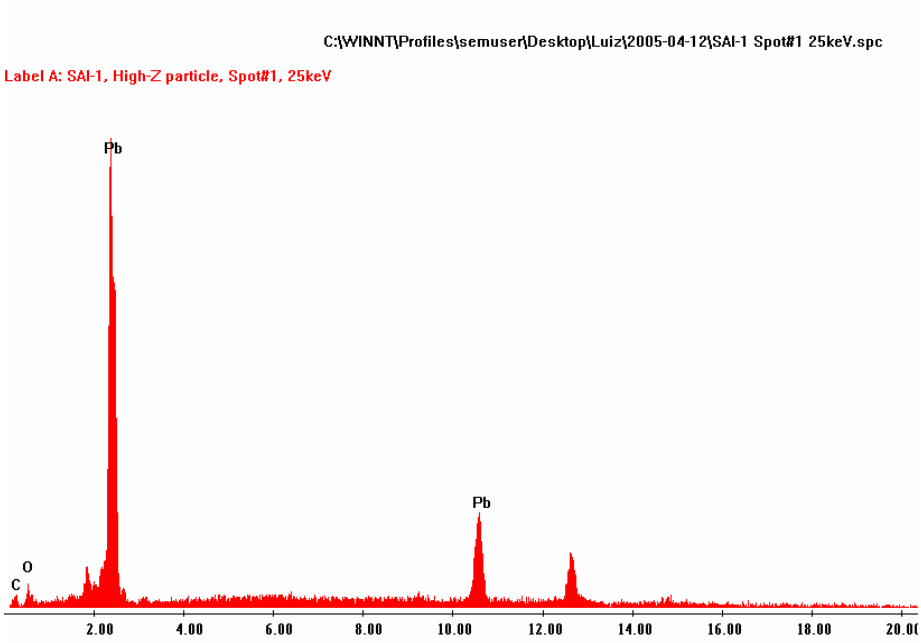
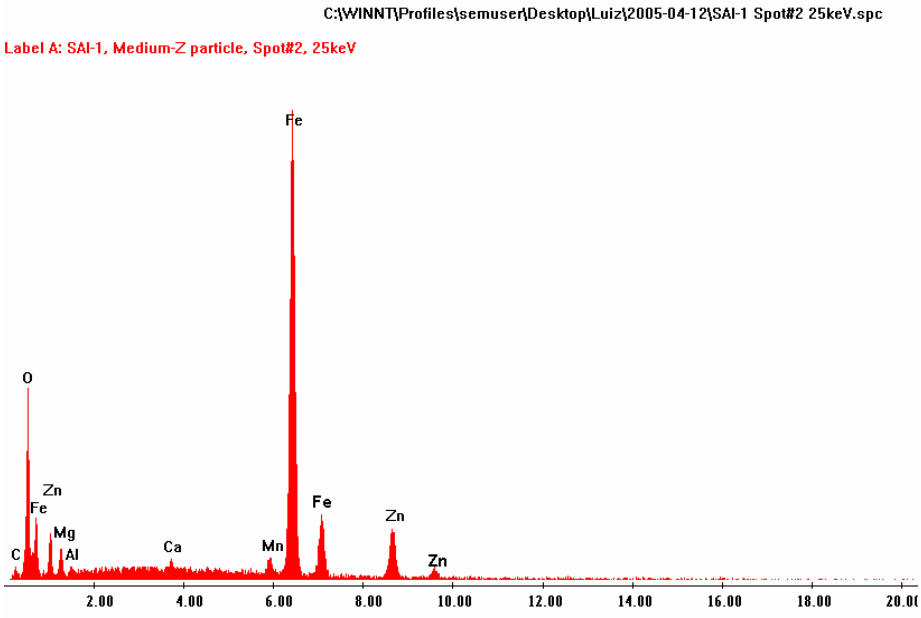


Figure 1: SEM image of the Santo Amaro slag particle



(a)



(b)

Figure 2: a) EDS of the larger white spot, and b) EDS of the larger dendrite.

By performing the classical leaching protocols (TCLP, SWEP, and SPLP) at an accredited laboratory (Activation Laboratories Ltd., Canada) it was shown that the Santo Amaro lead slag does not have potentially toxic element solubilization above the acceptable limits [1-4].

In a study to evaluate the stability of the Santo Amaro slag over a wide pH range [2,4], samples of the slag of sizes smaller than 2.0 mm were placed in a 250 mL Teflon® beaker for about 24 hours in solutions of hydrochloric, acetic and nitric acids and sodium hydroxide at room temperature. The solid/liquid ratio was 10, and after filtration, the Pb content of the liquid phase was analyzed using the induced coupled plasma (ICP-OES). The results of the slag leaching behavior are presented at Figure 3 [4]. It is interesting to note that Pb solubilization is significant only below pH 3.5, which is explained by the fact that the Pb in the primary lead slag occurs as metallic droplets [2].

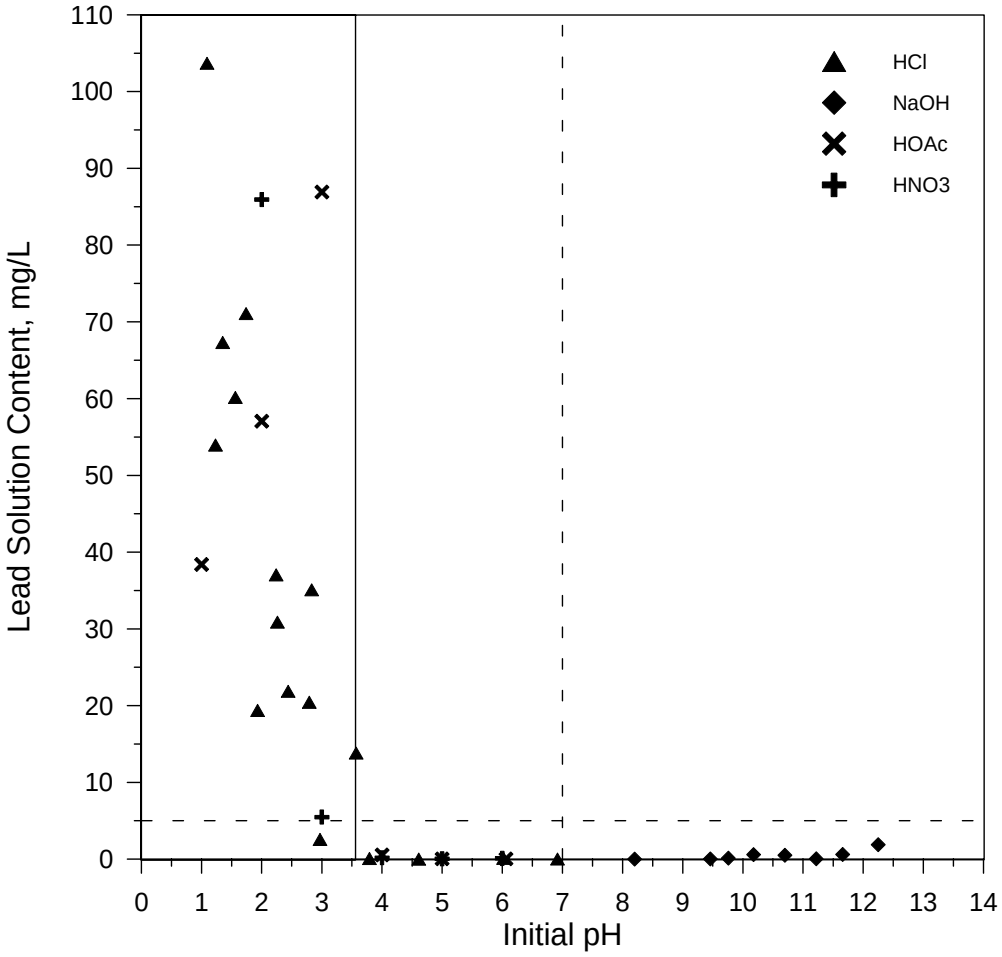


Figure 3: Lead solution content after the Santo Amaro slag leaching tests with hydrochloric, nitric and acetic acids and sodium hydroxide.

The Santo Amaro slag, the flue dust and the top soil collected close to the smelter were analyzed using induced coupled plasma with mass spectrometry (ICP-MS) and instrumental neutron activation analyses (INAA) [1-4]. A summary of these results is presented in Table 1. It can be seen that the soil has a larger amount of Pb and Cd and significant As, Ag, Zn and Cu contents as well as the flue dust is rich in Pb, Cd, and Ag.

Table 1**:** Trace elements in the Santo Amaro slag, flue dust and soil

	[a]Slag	[b]Flue Dust	[c]Soil
Pb	37000	3660	7510
Zn	76000	2470	650
As	541	528	43
Cu	358	143	166
Cd	57.3	> 2000	49.7
Ag	3.48	32.2	5.8

[a]Actlabs Job A05-1209 and IGN Job Luizb; [b]Actlabs Job A10-4967; [c]Actlabs Job A10-0041

By performing a cluster analysis [5] of the composition results for the Santo Amaro slag, flue dust and soil presented at Table 1, the correlation between the soil and the emissions is evident (see Figure 4). These results confirm the well established effect of the primary lead smelter emissions on the soil contamination around the smelter [6-8].

Despite the fact that the lead slag landfilled can undergo changes as a result of the environment over several years, the role of the slag on the levels of contamination with potentially toxic elements in the region of the primary lead smelter seems to be negligible in contrast to levels of airborne emissions [7,8].

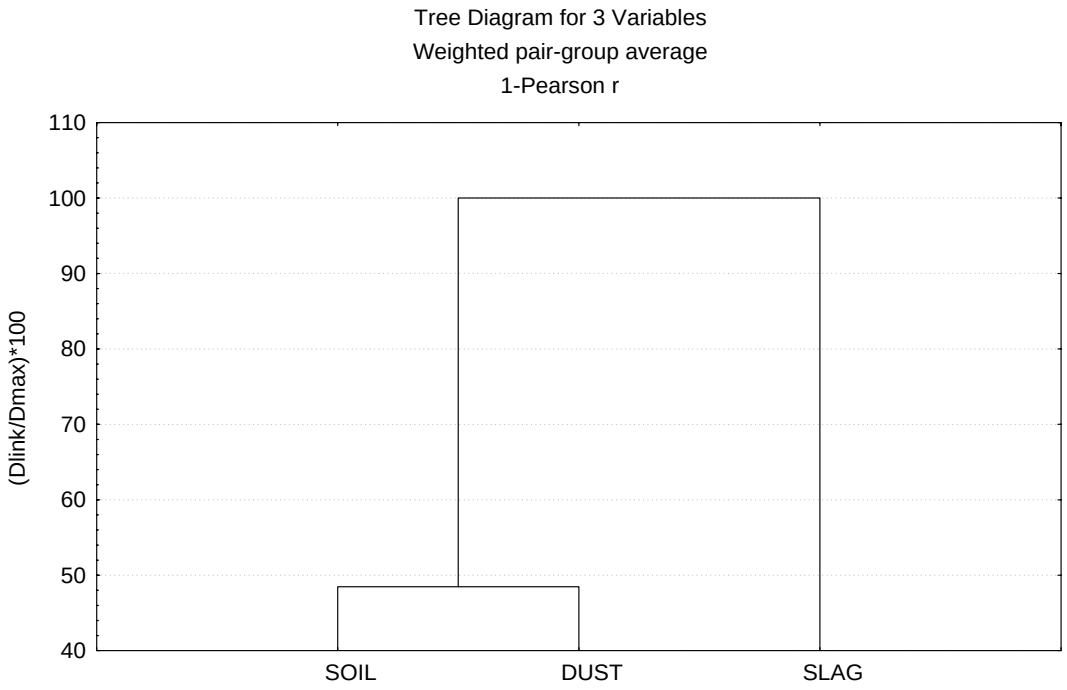


Figure 3: Dendrograme showing the similarity between the soil, the flue dust and the slag collected at the Santo Amaro smelter region.

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Appendix 4 to Letter to the Editor Regarding "A Study of the Routes of Contamination by Lead and Cadmium in Santo Amaro, Brazil" DOI:10.1080/09593330.2013.788071

Atmospheric Dispersion Simulation

The Gaussian plume model is widely used to simulate the air pollutant dispersion [1]. Assuming a constant diffusivity (K), the ground-level (z=0) pollutant concentration of a point source is given by [1]:

$$C(x,y,0)=\frac{Q}{2\pi Kx}\exp\left(-\frac{u\left(y^2+H^2\right)}{4Kx}\right) \quad (1)$$

where, x and y are the horizontal distances from the source (x is the horizontal distance at the wind direction), Q is the emission rate, u is the wind speed, and H is the source height. At the plume center line (y=0) Equation 1 can be simplified to provide the ground-level concentration as:

$$C(x,0,0)=\frac{A}{x}\exp\left(-\frac{B}{x}\right) \quad (2)$$

$$A=\frac{Q}{2\pi K} \quad (3)$$

$$B=\frac{uH^2}{4K} \quad (4)$$

where A and B are constants.

The simulated ground-level concentration along the plume center-line using Equation 1 is presented in Figure 1, for different values of A and B. It can be seen at this plot the classic concentration peak that moves toward the source with the reduction of B (see curves 4, 2 and 5). The plot also shows effect of the reduction of A on the concentration peak, which move down (see curves 3, 2 and 1).

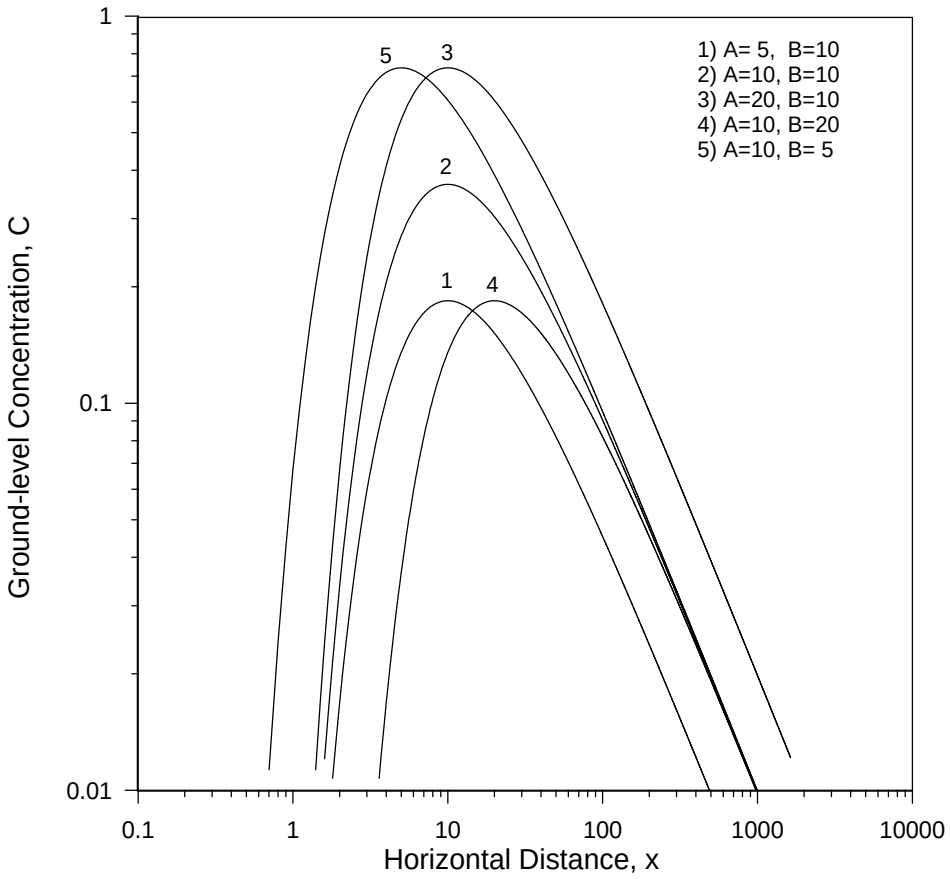

Figure 1: Simulated ground-level concentration along the plume center-line versus the downwind distance.

For particulate emissions, Equation 1 has to be modified to take into account the settling velocity and the particle deposition and absorption that tends to move the plume toward the soil surface. It will modify the curves presented in Figure 1. Evidently, these effects depend on the particle size, shape and density [1,2].

Taking into account these factors, the simulation of the particle dispersion from the 90 m chimney at the Santo Amaro smelter performed in the 1980s indicated that most of the particles emitted were at ground level for a distance between 400 and 900 m from the chimney [3].

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Appendix 5 to Letter to the Editor Regarding "A Study of the Routes of Contamination by Lead and Cadmium in Santo Amaro, Brazil" DOI:10.1080/09593330.2013.788071

Slag Leaching Tests

The Pb, Cd, and As results for the Santo Amaro slag leaching tests developed at the authors facilities are summarized in Table 1 [1,2]. One remarks that no basic statistical treatment was presented and ambiguous results are shown. For instance, the Pb solution content in both cases (acetic acid and water leaching) oscillates between high and low values.

Table 1: Leaching tests performed with the Santo Amaro slag by the authors [2]

Leaching Agent	Samples	Pb (mg/L)	Cd (mg/L)	As (mg/L)
Acetic Acid	borehole 33 : 1.0 to 1.99m	13.00*	0.18	<0.3
	borehole 33 : 3.0 to 3.99m	2.02	0.29	<0.3
	borehole 33 : 6.0 to 6.9m	8.68*	0.072	0.35
	borehole 34: 1.0 to 1.99m	9.94*	0.11	<0.3
	borehole 34: 3.0 to 3.99m	2.84	0.13	<0.3
	borehole 34: 6.0 to 6.9m	13.60*	0.50	<0.3
	Brazilian Limit [3,4]	5.0	0.5	5.0
Water	borehole 33 : 1.0 to 1.99m	<0.05	<0.005	0.0130
	borehole 33 : 3.0 to 3.99m	0.061*	<0.005	0.0190
	borehole 33 : 6.0 to 6.9m	<0.05	<0.005	0.0220
	borehole 34: 1.0 to 1.99m	0.140*	0.0094*	0.0076
	borehole 34: 3.0 to 3.99m	0.072*	<0.005	0.0320
	borehole 34: 6.0 to 6.9m	<0.05	<0.005	0.0100
	Brazilian Limit [3,4]	0.05	0.005	0.05

* Exceeds the NBR limits

Another leaching test study performed with the Santo Amaro slag and cited by the authors is summarized at Table 2 [6]. In this case also obscure leaching results can be seen.

For instance, for leaching using acetic acid the Pb solution contents oscillate between 1.8 and 159 mg/L. In addition, for samples ESC/05 and ESC/06 the Cd solution contents for leaching with water is higher that the case of leaching using acetic acid. This is not expected because the process variables and raw materials for the plant remained almost the same throughout the plant operation [2]. Therefore, likely, there are quality control issues in these tests.

Table 2: Leaching tests performed with the Santo Amaro slag and cited by the authors [2,5]

Leaching Agent	Samples	Pb (mg/L)	Cd (mg/L)
Acetic Acid	ESC/01	115.8*	0.22
	ESC/02	159.0*	0.30
	ESC/03	73.2*	0.13
	ESC/04	72.5*	0.12
	ESC/05	14.6*	0.05
	ESC/06	119.1*	0.04
	ESC/07	138.2*	0.19
	ESC/08	30.6*	0.12
	ESC/09	1.8	0.05
	ESC/10	47.2*	0.05
	Brazilian Limit [3,4]	5.0	0.5
Water	ESC/01	2.98*	0.16*
	ESC/02	0.96*	0.26*
	ESC/03	0.38*	0.07*
	ESC/04	4.95*	0.10*
	ESC/05	0.52*	0.28*
	ESC/06	0.50*	0.28*
	ESC/07	0.12*	0.01*
	ESC/08	0.29*	0.03*
	ESC/09	0.09*	0.005
	ESC/10	0.73*	0.03*
	Brazilian Limit [3,4]	0.05	0.005

* Exceeds the NBR limits

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Appendix 6 to Letter to the Editor Regarding "A Study of the Routes of Contamination by Lead and Cadmium in Santo Amaro, Brazil" DOI:10.1080/09593330.2013.788071

Atmospheric Dispersion Fit Using Empiric Model

The experimental data of the Pb and Cd soil content spatial distribution was fitted using the equation [1]:

$$\hat{C}(x) = \hat{A}\exp\left(-\hat{B}x\right) \quad (1)$$

where $\hat{A}$ and $\hat{B}$ are constants and x is the horizontal distances from the source. The ground-level concentration calculated using Equation 1 is presented in Figure 1 for different values of $\hat{A}$ and $\hat{B}$.

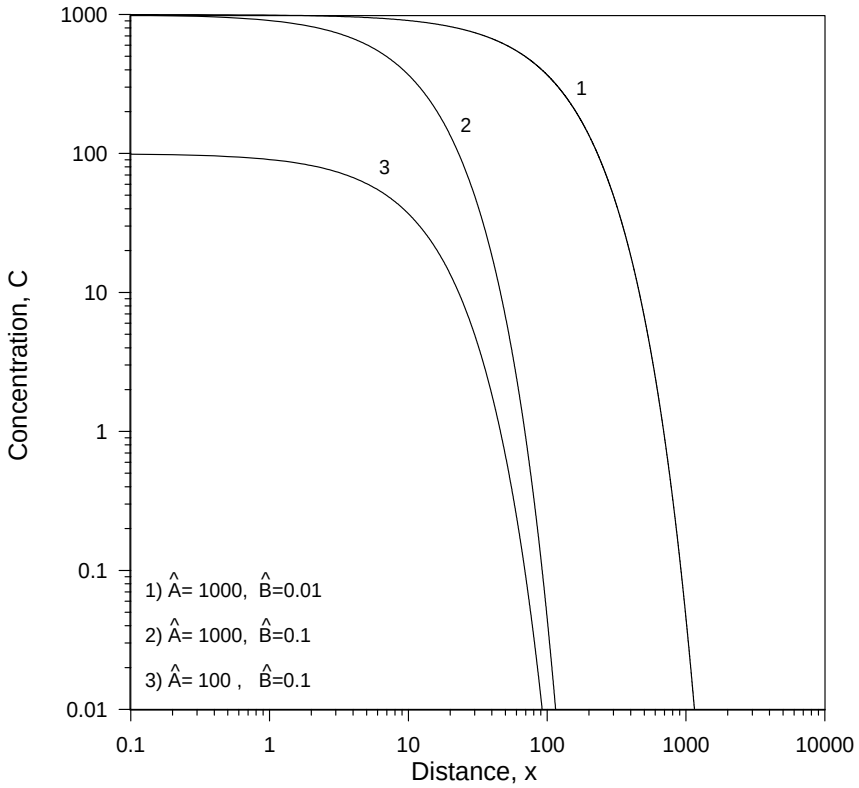

Figure 1: Simulated ground-level concentration.

The plots exhibit a very different behavior to the classical Gaussian model [2]. In this case there would be no concentration peak in the soil and there would be already deposition of pollutants inside the chimney, which has no physical meaning.

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