Aim and Scope

The objective of the *Journal of Residuals Science & Technology* is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal and are also welcome.

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Lead-Based Paint Residuals: Culprit or Cop-out?

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ABSTRACT: Adverse health effects from ingestion and/or inhalation of lead-contaminated materials have been recognized for many years, and most frequently associated with lead-based paint in U.S. homes built prior to 1978. There is no question about the hazards of flaking paint or dusts accumulated from paint deterioration or improper paint removal methods. However, there is strong evidence that many lead exposures blamed on lead-based paint are, in fact, due primarily to other sources. This study demonstrates that large areas of heavily lead-contaminated soils cannot reasonably be attributed to lead-based house paint, and that it is possible to use chemical fingerprinting to eliminate paint as a major contributor to interior dust lead levels.

INTRODUCTION

SINCE the early nineteenth century, lead-based paints were used in U.S. housing, with "white lead" [$2PbCO_3 \cdot Pb(OH)_2$] as the principal pigment [1], until paints with high levels of lead were banned in 1978 by the U.S. Congress [2]. Even today, many older homes have residual lead-based paints in deteriorated condition that pose a risk of ingestion and/or inhalation of lead [3,4]. Improper methods of removing old paint may increase exposure risks [5,6,7]. However, the "unique" association of lead poisoning with lead-based paint has become such an established myth that even governmental agencies have perpetuated it [8]. For example, the United States Environmental Protection Agency (USEPA) has made the statement that "Lead contaminated soil is a *lead-based paint hazard* under the Disclosure Rule if the lead is at sufficiently high levels, *regardless of the source of lead contamination*." [9].

In 1924, a new source of widespread lead pollution in the U.S. began with the introduction of leaded gasoline [10]. In spite of numerous studies linking leaded gasoline with increased blood lead levels, especially in children near heavy vehicle traffic areas, the tetraethyl lead additive was not banned in the U.S. until the 1980s, and not in the European Union until 2000. Accordingly, many studies began to associate lead health effects with exposures to both lead-based paint and leaded gasoline [e.g., 11–16].

Many lead compounds, including "white lead" and the residues from leaded gasoline vehicle exhausts, are soluble at pHs < 7, so that topsoils impacted by even slightly acidic rainfall should have dissipated the lead somewhat over the many years since these sources were significant. Even "pure" rainwater saturated with carbon dioxide has a pH below 6. Although paint from older homes may have continued to flake off over the years, and some leaded gasoline is still in limited use (e.g., in some light aircraft), these sources are unlikely to account for much lead in present day topsoils. Recent measurements of soil lead in heavily trafficked areas have shown concentrations averaging less than 150 mg/kg [11,15], and a simple mass balance analysis clearly demonstrates that flaking house paint containing lead cannot account for more than a small amount of present day soil lead.

A MASS BALANCE ANALYSIS

The percentage lead in paints has decreased over the years and is now limited in the U.S. to 0.06%, by weight. Homes that were painted with lead-based paint many years ago will typically have been repainted several times. Therefore multiple coats of varying composition will result in average lead content well below that of the earliest paints. The U.S. government currently

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defines "lead paint" as any paint sample having an average lead content of 0.5% (5,000 mg/kg) or greater, and a "soil lead hazard" as any bare soil in a children's play area exceeding 400 mg/kg, or in the rest of the yard of at least 1,200 mg/kg [8].

If a typical small yard had an area of only 0.3 acre (ca. 1,200 m^2), and the topsoil to a depth of six inches (ca. 0.15 m) had an average lead content of 1,200 mg/kg, how much lead-based paint would have had to flake off and remain mixed with the soil over the years to account for the soil lead content, assuming a soil density of approximately one ton per cubic yard (ca. 1,300 kg/m^3)?

$$\begin{gathered}5{,}000 \text{ mg (Pb)/kg (paint)} \times \text{paint mass} = \\ 1{,}200 \text{ mg/kg (Pb)/kg (soil)} \times 0.3 \text{ acre(soil)} \\ \times 4{,}840 \text{ yd}^2\text{/acre} \times 1/6 \text{ yd.} \times 1.0 \text{ ton/yd}^3 \\ \text{paint mass} = 58 \text{ tons (ca. 53,000 kg)}\end{gathered}$$

Since typical lead-based paints contained less than 10 pounds (4.5 kg) of residual solids per gallon, this would correspond to more than 11,000 gallons (ca. 42,000 L) of paint for a small house, all of which would have had to flake off and be mixed with the soil.

Clearly, even if the paint averaged ten or twenty times as much lead, there is no reasonable expectation that such an extremely large quantity of paint possibly could have flaked off, been mixed into the soil, and avoided dissipation by rain over the years.

ALTERNATE SOURCES OF LEAD

Two sources of large amounts of lead often have been overlooked or minimized: natural occurring lead and "point source" lead (e.g., from industrial operations such as smelters). Fortunately, there are not many areas of high lead deposits in natural soils, although a few are significant, such as the "Missouri Lead Belt" [17]. Point sources, however, are widespread and may be the main sources of soil pollution in many areas. Pollution from improperly designed lead battery production and recycling operations, although relatively rare, has resulted in several cases of severe lead poisoning [18]. Other point sources, for example, include lead mining operations, coal-fired power plants, and galvanizing facilities [19]. Numerous studies have identified very high lead levels in soils near active or abandoned smelter sites [e.g., 20–27]. These are of special interest because so many of these sites have been unrecognized by governmental agencies and the public.

In 2001, William P. Eckel and his colleagues reported that they had located 639 U.S. lead smelter sites, most of which were abandoned and only 186 of which (29%) were known to the U.S. government [28]. Many of these sites were within a few blocks of residential areas in which high soil lead levels were detected. If zinc and other smelter sites emitting lead were to be similarly identified, an even larger number of locations might be recognized as having soil lead content primarily from sources other than lead-based house paint.

It is well established that soil, as blowing dust or "track-in" residue, is a significant contributor to interior household dust [e.g., 29–32]. In fact, the oft-cited argument that higher lead levels in soil around the drip zone from roofs is evidence that flaking exterior paint is the major soil source of lead is equally consistent with the fact that airborne soil [33] accumulated on roofs washes off with rain or melting snow onto drip zones.

Mass balance analysis and evidence of significant point source possibilities cannot be overlooked in assessing probable sources of lead in heavily contaminated areas. A chemical fingerprint may then be able to establish the relative contributions of lead-based paint and alternate sources to interior house dusts.

DATA INTERPRETATION

It is important to realize that samples collected from possibly contaminated sites can provide useful information, but with significant limitations, for example:

Soils

Surface samples (typically taken at 0–3″ depth) can indicate recent deposition of airborne contaminants and, by comparison with indoor samples, the contribution of track-in soil to indoor pollution. Track-in estimates are limited to comparison with soils from typical track-in areas (i.e., areas commonly walked through by persons routinely entering the home).

Surface samples generally do not provide useful information about long-past airborne deposition because of the dissipation of many contaminants by winds, by volatilization (including biological conversion of otherwise nonvolatile species to gases), through uptake by plants, or by dissolution in runoff or percolation water.

Comparison of surface samples with samples at varying depths can help estimate how surface soils have changed over time. However, soil depth comparisons can, at best, offer information limited to surface soil losses by percolation. For contamination that occurred long in the past, the additional losses by runoff, volatilization, and plant uptake will not be indicated by soil depth comparisons.

Comparison with similar type soils from apparently uncontaminated areas ("background") can help estimate the impact of contamination sources.

"Risk Assessment" based on soil sampling will, at the very least, significantly underestimate risk from long term exposures to contaminants deposited years ago. Such assessments may be useful in deciding about remediation needs, but they will be essentially meaningless in estimating anything more than minimal health risks from past long term exposures.

Attic Dusts

Attic dust samples, under ideal conditions, can provide much better information than soil samples about long-term contamination by nonvolatile air pollutants. This is because the attic dust is not dissipated by water, wind, or volatilization to the extent typical of soils—although some substances such as arsenic may be volatilized by household bacteria or fungi.

Only attics having good access to outdoor air through occasionally opened windows or through properly oriented soffit vents will accumulate airborne contaminants. Therefore, individual buildings may vary considerably in attic dust composition depending upon the attic ventilation, and also upon other factors such as distance and direction from contaminant sources, shielding by trees or other buildings. Consequently, a maximum attic dust finding in a particular area probably better reflects historic contamination patterns than would any individual attic dust or area-wide attic dust averages. However, attic dust does become diluted by "clean" dust during times when uncontaminated air is entering the attic. Accordingly, even the highest dust concentration levels will be significantly less than maximum levels that occurred during contamination events.

In interpreting attic dust data, attention must be given to alternative sources of particular contaminants, and especially if the attic is a storage facility for items coming from different locations.

Attic dust is not usually applicable to "risk assessment" unless the specific household has frequent access to the attic. Accordingly, attic dust is rarely used in assessing remediation needs.

"Old" House Dusts

The USEPA has recommended sampling of rarely dusted locations (e.g., tops of ceiling fans or door sills, under furniture, etc.) as useful in assessing "past" contamination. Such samples may reflect both track-in and air-deposited contaminants over a period of months, depending upon the frequency and efficiency of house cleaning activities.

Rarely will such dust samples reflect contamination events several years ago. Thus, risk assessments are limited to cleanup needs or estimates based on the assumption (usually indefensible) that the patterns found will be typical of long term exposures. Risk assessments based on such data are disputable because the areas tested are typically inaccessible for direct contact.

Comparison of such samples with those of track-in soils can help estimate the relative contribution of track-in contaminants to airborne contaminants during the time frame in which the dusts were deposited.

Floor or Doormat Dusts

Comparison of floor and doormat dusts with samples of track-in soils can help estimate the relative contribution of track-in contaminants to airborne contaminants during the time frame since the floor or mat was last cleaned.

Since floors and mats are typically cleaned more frequently than areas of "old" dusts, they are less likely to provide information about long-term exposures.

HVAC Dusts

Dusts collected from HVAC filters, when coupled with information about when the filters were last installed, can provide useful estimates of the average composition of airborne dusts in the home during the time the filter was in place.

Under ideal circumstances, if the total dust on the filter, the filter installation date, the air flow rate, and the periods of HVAC activity are known, then HVAC dusts could theoretically provide information about the average indoor air composition during that time period. This complete set of information is rarely available.

It must be noted that HVAC dusts will consist of both new airborne dusts and resuspended previously deposited dusts. Published studies of dust resuspension can assist in estimating relative contributions.

Dust Loading

The USEPA and other agencies often rely heavily on "dust loading" data—the amount of a contaminant found on a measured area of floor space or other specified location (e.g., window sill). Such data are probably more representative of the frequency and efficiency of house cleaning than of any particular contamination pattern. However, such data may be useful if they show levels above those identified by appropriate agencies as screening levels or action levels.

Unless the total amount of dust AND its composition are known, health risk assessments are essentially meaningless.

Summary

Results from soil and dust sampling provide, at best, a "snapshot" of contamination at the time the samples were collected. To the extent that analyses reveal concentrations of pollutants above recognized "hazard levels", such data can be useful in assessing remediation needs.

It is essential to examine possibilities of alternative sources for any particular contaminants and to carefully estimate appropriate source apportionments in order to establish which, if any, sources are major contributors to contamination.

Except in the case of ongoing contamination reasonably constant over time, current sampling data will not adequately address health risks from past exposures, or from future exposures if they are likely to increase. For contamination resulting primarily from major polluting activities several years in the past, health risk assessments based on current contamination levels will vastly underestimate risk.

A SPECIFIC EXAMPLE: BLACKWELL, OKLAHOMA

From 1916 until 1974, the town of Blackwell in north central Oklahoma was the site of a major zinc smelter which emitted contaminants, including arsenic and lead, into the community during its operation and during parts of its subsequent closure and cleanup [34].

Beginning in 2006, a study was initiated of area soils and house dusts in order to estimate the geographical distribution and magnitude of residual arsenic and lead, and in an attempt to determine the extent to which the lead contamination could be linked to old smelter activities. Since many of the homes in the area are quite old and have deteriorated lead-based paint, as illustrated in Figure 1, it was important to be able to distinguish among possible lead sources.

Figure 1. *A typical 1920s Blackwell, OK home.*

Blackwell has a population of approximately 7,700 and an area of approximately 5 square miles (13 km^2). In order to obtain representative samples, the town was divided into sectors at varying distances and directions from the site of the old smelter, as shown in Figure 2.

Materials and Methods

Sampling was performed by personnel of Aqua-Tech Laboratories, Inc., Bryan, Texas on three occasions: the week of December 3, 2006, the week of July 23, 2007, and the week of September 8, 2008. Sampling personnel wore hooded Ty-Vac suits, gloves, goggles, and dust masks. Suits and other gear were placed in trash bags after leaving each residence to avoid any possibility of cross-contamination. Paint samples were collected from areas believed to have the oldest paint at the home. Topsoil samples were collected from track-in and other areas at homes and, for background comparison, at sites located along roadways five miles from the old smelter. At selected locations soils were also sampled at depths of 0–3″, 0–6″, and 0–12″. House dusts were collected from attics, HVAC filters, measured floor areas, door mats, and rarely dusted locations such as the tops of ceiling fans or beneath large furniture, using Shark™ handheld vacuum cleaners (see www. sharkvac.com). These units are 1,000-watt vacuums with HEPA filter dust cups capable of trapping 99.97% of particles above 0.3 μm aerodynamic mean diameter. Separate vacuum cleaners were used at each location to avoid any possi-

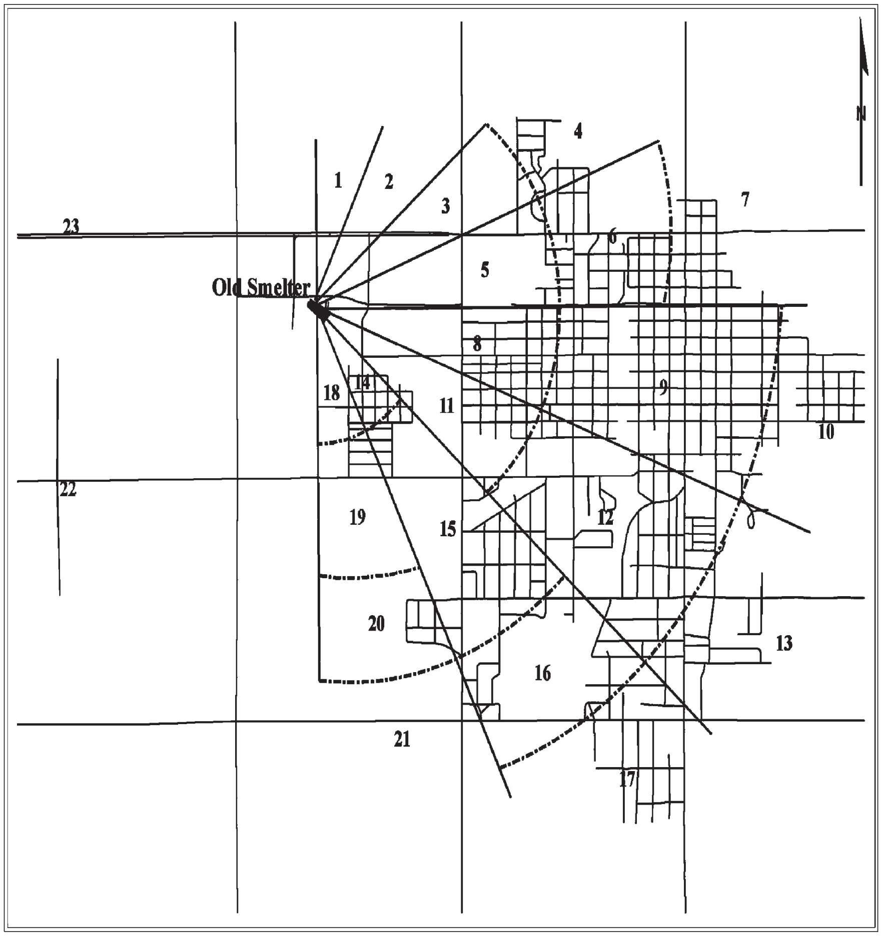

Figure 2. *Sampling sectors in Blackwell, OK. Distance from old smelter to farthest community sample was ca. 2 miles (3.2 km).*

bility of cross-contamination. All sampling and sample preservation was done in conformity with USEPA Standard Operating Procedures, SOP #2012 for soils and SOP #2011 for house dusts.

Samples were prepared and digested according to Method SW846 3050B, then analyzed by ICP (inductively coupled plasma spectrometry) according to SW846 6010B [35]. All parameters followed standard protocol.

Results and Discussion

Most of the homes sampled had lead levels in soils and/or dusts exceeding the recognized hazardous level of lead (150 mg/kg) [36]. Results are summarized in Table 1, with results above 150 mg/kg shown in boldface. Regarding ID numbers in this table, numbers beginning with 6 are from the 2006 sampling; those beginning with 7 are from the 2007 sampling; and those beginning with 8 are from the 2008 sampling. Values indicated by "less than" signs (<) are below laboratory reporting limits, and "NA" entries indicate samples that were unavailable (e.g., no attic access) or not obtained (e.g., paint from newer homes).

Background samples were collected at locations along roadways at varying directions and at five mile distances from the old smelter site, as shown in Table 2. These data show that natural levels of lead in the area are well below the levels found in most Blackwell community topsoils, and that any lead remaining from vehicle traffic in the days of leaded gasoline is negligible.

As a "chemical fingerprint" to distinguish paint from other sources, lead/arsenic ratios were calculated for those fifteen homes (20% of those tested) having paint samples containing at least 5,000 mg/kg lead, and compared with lead/arsenic ratios for soils and dusts (Table 3). Additionally, the soil lead levels around homes built since 1978 show soil lead averaging above 150 mg/kg, and ranging as high as 856 mg/kg, further confirming sources other than lead-based paint residuals. Further comparisons with other soil and dust data (Table 4)

Table 1. Lead and Arsenic in Blackwell, OK (concentrations in mg/kg; decimal values rounded to nearest whole number).

	House		Max Soil			Paint			Attic Dust			HVAC Dust			Max House Dust			Floor Dust	
ID No.	Age	Sector	As	Pb	Pb/As	As	Pb	Pb/As	As	Pb	Pb/As	As	Pb	Pb/As	As	Pb	Pb/As	mg/kg	μg/ft²
601	1950	4	15	**446**	30	1	478	478	6	**327**	54	< 1	23	> 23	8	64	8	37	2
801	1950	4	10	**232**	23	1	214	214	22	**205**	9	19	44	2	3	49	16	49	3
602	1954	5	9	**255**	28	1	23	23	17	**261**	15	1	43	43	4	78	20	34	29
701	1925	5	4	**176**	44	< 2	2,510	> 1,250	11	**548**	50	6	70	12	9	121	13	13	> 1
802	1930	5	50	**373**	7	1	43	43	12	**146**	12	20	126	6	18	**151**	8	**151**	50
603	1920	6	15	**329**	22	3	2,200	733	22	**394**	18	9	**160**	18	9	**192**	21	**192**	17
604	1929	6	8	**394**	49	3	871	290	59	**2,150**	36	56	**189**	3	56	**189**	3	42	< 1
702	1920	6	7	**197**	28	< 2	6,800	>3,400	24	**657**	27	7	72	10	7	94	13	53	1
803	1930	6	5	**290**	58	6	22,100	3,680	7	**775**	111	16	95	6	16	95	6	50	1
804	1929	6	5	141	28	1	413	413	19	**1,920**	10	< 86	< 86	NA	2	**1,890**	940	123	2
605	1930	7	4	**263**	66	1	36	36	NA	NA	NA	3	32	10	11	41	4	7	< 1
606	1920	8	21	**252**	12	5	8,150	1,630	141	**1,650**	12	< 1	90	> 90	8	**310**	39	56	5
703	1920	8	7	**481**	69	< 2	36	> 18	19	**508**	27	7	89	13	8	**159**	20	71	3
704	1980	8	12	**865**	72	NA	NA	NA	NA	NA	NA	19	127	7	19	127	7	41	1
705	1920	8	22	**658**	30	34	37,500	1,100	47	**7,770**	165	NA	NA	NA	7	136	19	61	6
607	1920	9	21	**1,240**	59	19	39,600	2,080	12	**334**	28	9	**485**	54	9	**485**	54	**207**	177
608	1948	9	6	**176**	29	2	355	178	4	92	23	10	95	10	12	**170**	14	80	11
609	1948	9	2	64	32	4	2,960	740	2	64	32	12	66	6	12	**208**	17	42	2
610	1920	9	11	**361**	33	NA	475	NA	3	98	33	11	75	7	15	98	7	83	1
706	1920	9	32	**761**	24	< 2	5	> 2	42	**4,060**	97	4	69	17	11	**180**	16	66	16
707	1920	9	22	**2,650**	120	< 2	1,920	> 960	40	**447**	11	11	**343**	31	9	**636**	71	**636**	54
708	1930	9	13	**451**	35	< 2	5,240	> 2,620	12	**297**	25	8	**242**	30	2	**550**	275	**550**	170
805	1958	9	4	**217**	54	1	589	589	13	**216**	17	6	61	10	7	**608**	87	45	11
806	1925	9	10	**794**	79	8	68,700	8,590	102	**880**	9	8	**203**	25	10	**244**	24	63	3
807	1920	9	16	**1,090**	68	5	10,800	2,160	NA	NA	NA	NA	NA	NA	14	**415**	30	**319**	37
611	1925	10	5	60	12	2	1,790	895	12	**3,180**	265	< 2	37	> 18	4	**332**	83	11	1
612	1920	10	4	138	34	1	126	126	1	106	106	< 1	**154**	> 154	5	**185**	37	142	2
709	1906	10	5	**236**	47	< 2	482	> 2741	17	**548**	32	NA	NA	NA	3	137	46	137	7
710	1920	10	4	**2,330**	582	< 2	9	> 4	9	**211**	23	NA	NA	NA	11	**208**	19	72	4
711	1907	10	5	**175**	35	< 2	285	> 142	< 2	82	> 41	NA	NA	NA	15	107	7	78	8
613	1920	11	9	**228**	25	5	184	37	100	**1,360**	14	5	134	27	7	136	19	82	5
712	1920	11	7	**150**	21	< 2	16,100	> 8,050	31	**475**	15	20	**332**	17	12	**3,280**	273	91	3
713	1920	11	10	**240**	24	< 2	4,380	> 2,190	82	**1,350**	16	7	34	5	10	118	12	65	4
808	1920	11	18	**274**	15	70	141,000	2,010	5	**232**	46	NA	NA	NA	6	**301**	50	**165**	247
809	1924	11	5	**243**	49	120	70,300	586	NA	NA	NA	12	76	6	12	76	6	63	4
614	1920	12	10	**260**	26	9	77,700	8,630	20	**3,700**	185	16	**1,850**	116	16	**1,850**	116	60	2
615	1968	12	8	57	7	1	307	307	20	**368**	18	7	38	5	7	**161**	23	90	21
714	1920	12	4	**174**	43	< 2	50,500	> 25,200	NA	NA	NA	15	129	9	16	**157**	10	49	9
810	1950	12	18	**540**	30	2	941	470	18	**644**	36	14	81	6	13	81	6	25	4

(continued)

Table 1 (continued). Lead and Arsenic in Blackwell, OK (concentrations in mg/kg; decimal values rounded to nearest whole number).

	House		Max Soil			Paint			Attic Dust			HVAC Dust			Max House Dust			Floor Dust	
ID No.	Age	Sector	As	Pb	Pb/As	As	Pb	Pb/As	As	Pb	Pb/As	As	Pb	Pb/As	As	Pb	Pb/As	mg/kg	μg/ft^2
811	1981	12	2	**158**	79	NA	NA	NA	NA	NA	NA	9	81	9	9	81	9	77	2
812	1920	12	2	**212**	106	< 1	687	> 687	NA	NA	NA	18	55	2	74	**250**	33	42	5
616	1945	13	8	114	14	45	72,700	1,620	5	**1,480**	296	16	103	6	16	**499**	31	**499**	5
617	1925	13	7	**371**	53	1	8	8	16	**10,200**	638	4	59	15	6	79	13	45	12
618	1925	13	290	**162**	< 1	21	10,900	519	3	122	41	7	84	12	7	84	12	49	3
619	1940	13	50	**208**	4	6	1,490	248	< 2	**171**	> 86	< 3	**249**	> 83	3	**249**	83	127	57
620	1964	13	6	56	9	3	6	2	7	**230**	33	11	45	4	13	45	3	37	3
621	1996	13	3	20	7	1	218	218	2	80	40	6	53	9	6	53	9	34	< 1
715	1920	13	12	130	11	< 2	20	> 10	6	**284**	47	13	22	2	10	**280**	28	40	1
622	1950	14	6	38	6	2	2	1	32	**473**	15	< 2	16	> 8	17	**170**	10	74	8
623	1920	14	12	**318**	27	5	1,160	232	< 4	**174**	> 43	< 4	127	> 32	13	**225**	17	**225**	72
624	1998	14	15	28	2	NA	NA	NA	NA	NA	NA	2	29	15	7	51	7	51	1
716	1920	14	17	**602**	8	< 2	2	> 1	43	**744**	17	4	35	9	10	94	9	51	2
813	2000	14	5	43	9	NA	NA	NA	6	11	2	10	51	5	10	77	8	25	< 1
625	1968	15	11	**161**	15	1	5	5	15	**1,200**	80	17	74	4	17	74	4	47	3
626	1930	15	5	46	9	5	3,220	644	32	**495**	15	3	42	14	11	63	6	64	30
627	1974	15	9	111	12	1	4	4	1	**387**	387	8	**161**	20	6	**161**	27	78	8
628	1981	15	7	**255**	36	NA	17	NA	4	57	14	< 27	62	> 2	10	**217**	22	105	15
629	1978	15	14	**206**	15	4	25	6	4	126	32	NA	NA	NA	1	43	43	29	2
630	1981	15	5	26	5	NA	NA	NA	4	36	9	< 1	22	> 22	3	51	17	51	2
717	1970	15	11	100	9	< 2	857	> 429	27	**445**	16	5	23	5	8	**127**	16	15	1
718	2004	15	45	**499**	11	NA	NA	NA	< 2	110	> 55	NA	NA	NA	3	40	13	40	< 1
719	1982	15	10	94	9	< 2	5	> 2	< 2	4	> 2	NA	NA	NA	5	67	13	55	2
631	1962	16	7	108	15	2	79,600	39,800	6	**365**	61	NA	NA	NA	3	93	31	93	12
720	1970	16	2	13	7	< 2	9	> 4	11	**151**	14	NA	NA	NA	27	55	2	23	< 1
632	1920	17	8	**532**	67	3	2,300	767	NA	NA	NA	NA	NA	NA	3	94	31	68	7
633	2002	17	5	61	12	NA	NA	NA	NA	NA	NA	27	40	1	61	64	1	59	10
634	1910	17	5	**259**	52	2	243	122	11	**536**	49	NA	NA	NA	4	**6,920**	1,730	59	576
721	1964	17	3	74	25	< 2	1,460	> 730	9	**241**	27	6	134	221	6	134	22	43	1
814	1940	17	4	**257**	64	1	43	43	16	**512**	32	7	65	9	3	**160**	53	46	1
815	1978	18	9	56	6	NA	NA	NA	NA	NA	NA	7	49	7	3	88	29	41	1
722	1975	19	4	62	16	< 2	132	> 61	7	73	10	4	30	8	6	38	6	27	2
723	1978	19	4	73	18	< 2	470	> 235	9	88	10	6	37	6	7	61	9	23	2
816	2000	21	5	27	5	NA	NA	NA	NA	NA	NA	17	43	3	7	51	7	19	< 1
817	1920	23	18	93	5	NA	NA	NA	5	21	4	69	93	1	32	100	3	46	< 1

Table 2. Soil Background Five Miles from Old Smelter.

	Depth								
	0–3″			0–6″			0–12″		
Direction	**As**	**Pb**	**Pb/As**	**As**	**Pb**	**Pb/As**	**As**	**Pb**	**Pb/As**
West	5.43	28.6	5.27	5.52	38.8	7.02	7.86	26.3	3.34
East	2.98	23.0	7.72	3.73	16.3	5.97	1.95	10.3	5.28
North	1.37	49.9	36.4	2.46	57.3	23.3	1.65	55.3	33.5
South	0.496	12.6	25.4	2.29	21.9	9.56	1.47	12.8	8.70
Northeast	3.67	14.1	3.84	4.90	12.6	2.57	4.03	10.8	2.67
Southeast	1.74	14.6	8.39	2.88	9.41	3.26	3.02	9.58	3.17
Average	**2.61**	**23.8**	**14.5**	**3.63**	**26.1**	**8.61**	**3.33**	**20.8**	**9.44**

Table 3. Blackwell, OK Sampling Results for Homes with Paint Lead > 5,000mg/kg. (Concentrations in mg/kg; decimal values rounded to nearest whole number).

ID No.	House Age	Sector	Max Soil			Paint			Attic Dust			HVAC Dust			Max House Dust		
			As	**Pb**	**Pb/As**	**As**	**Pb**	**Pb/As**	**As**	**Pb**	**Pb/As**	**As**	**Pb**	**Pb/As**	**As**	**Pb**	**Pb/As**
702	1920	6	7	**197**	28	< 2	6,800	> 3,400	24	**657**	27	7	72	10	7	94	13
803	1930	6	5	**290**	58	6	22,100	3,680	7	**775**	111	16	95	6	16	95	6
606	1920	8	21	**252**	12	5	8,150	1,630	141	**1,650**	12	< 1	90	> 90	8	**310**	39
705	1920	8	22	**658**	30	34	37,500	1,100	47	**7,770**	165	NA	NA	NA	7	136	19
607	1920	9	21	**1,240**	59	19	39,600	2 080	12	**334**	28	9	**485**	54	9	485	54
708	1930	9	13	**451**	25	< 2	5,240	> 2,620	12	**297**	25	8	**242**	30	2	**550**	275
806	1925	9	10	**794**	79	8	68,700	8,590	102	**880**	9	8	**203**	25	10	**244**	24
807	1920	9	16	**1,090**	68	5	10,800	2,160	NA	NA	NA	NA	NA	NA	14	**415**	30
712	1920	11	7	**150**	21	< 2	16,100	> 8,050	31	**475**	15	20	**332**	17	12	**3,280**	27
808	1920	11	18	**274**	15	70	141,000	2,010	5	**232**	46	NA	NA	NA	6	**301**	50
809	1924	11	5	**243**	49	120	70,300	586	NA	NA	NA	12	76	6	12	76	6
614	1920	12	10	**260**	26	9	77,700	8,630	20	**3,700**	185	16	**1.850**	116	16	**1,850**	116
714	1920	12	4	**174**	43	< 2	50,500	> 25,200	NA	NA	NA	15	129	9	16	**157**	10
616	1945	13	8	114	14	45	72,700	1,620	5	**1,480**	296	16	103	6	16	**499**	31
631	1962	16	7	108	15	2	79,600	39,800	6	**365**	61	NA	NA	NA	3	93	31
				Average	**37**		**Average**	**> 7,410**		**Average**	**82**		**Average**	**34**		**Average**	**49**

Table 4. Lead/Arsenic "Fingerprint" Comparisons (not including outliers, "less thans", or NAs).

Sample Type	**No. Samples**	**Avg. Pb/As**
5-Mile Background Soil	18	11
All Homes Soils	71	31
Post-1978 Homes Soils	11	22
All Attic Dusts	56	50
All HVAC Dusts	51	14
All Max House Dusts	72	30
Lead Paint Homes Soils	15	37
Lead Paint Homes Attics	12	82
Lead Paint Homes HVACs	10	34
Lead Paint Homes Max Dusts	15	49
Lead Paint Homes Paint	**15**	**> 7,410**

clearly demonstrate that, at least in the Blackwell community, lead-based paint is not a significant contributor to soil lead or to most interior house dusts.

Source Apportionment

Having ruled out natural occurring soil lead, lead-based paint, and leaded gasoline residues as major contributors, it was important to consider other well-recognized sources [19,37]. The Blackwell community was not impacted by orchards or potato fields that might have used lead arsenate insecticide. There were no major golf courses using arsenical herbicides. There were no lead battery production or recycling operations. There were no galvanizing plants. A sample of "connie" material, the waste solids from the zinc smelter that was widely distributed in Blackwell as driveway or landfill material, was found to contain 1,340 mg/kg lead.

Accordingly, the only conclusion consistent with the facts is that the widespread lead contamination in Blackwell is primarily residuals from the old smelter operations., from operational emissions, blowing dusts, and distributed waste solids.

CONCLUSIONS

This study clearly demonstrates that neither leaded gasoline residuals, nor the commonly blamed lead-based paint residuals, can possibly account for high levels of lead in large areas of soil. Additionally, the use of "chemical fingerprinting" can help to estimate the relative contribution of lead-based paint and other sources to interior house dusts. Although lead poisoning may sometimes result mainly from inhalation or ingestion of old paint, the widely-held belief that this is the chief source of lead poisoning must be reconsidered.

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Total and Extractable Heavy Metal and Sulfur Concentrations in Fly Ash from a Large-Sized (90 MW) Fluidized Bed Boiler at a Pulp Mill Incinerating Biofuels

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ABSTRACT: In this study, we have assessed the extractability (leachability) of heavy metals (Mn, Fe, Cd, Cu, Pb, Cr, Zn, As, V, Ba, Mo, Al, Ti, Co, Ni) and sulfur in fly ash originated from a large-sized (90 MW) fluidized bed boiler at a Finnish pulp mill incinerating biofuels (i.e. clean bark, wood residues, primary sludge and biosludge). Due to the elevated cadmium concentration (20.1 mg kg^{-1}; d.w.), which exceeded the maximum allowable Finnish heavy metal concentration of Cd (17.5 mg kg^{-1}; d.w.) for forest fertilizers, the fly ash has to be disposed off in a landfill. However, according to a three-stage BCR sequential extraction (exchangeable, easily reduced and oxidizable fraction), a relatively high proportion of cadmium was partitioned in the oxidizable fraction (57.6%), which is not likely to be dissolved under the conditions normally found in nature. Therefore, according to the relatively low total concentration of cadmium (20.1 mg kg^{-1}; d.w.) and due to its extractability behaviour, especially, we conclude that the cadmium in the fly ash investigated in this study does not pose any risk for biota if the ash is disposed off in landfill sites.

INTRODUCTION

THE pulp and paper industry is an energy-intensive industry. Due to the high energy requirements in the pulp and paper mill processes, most of the energy is produced by combustion of all available burnable biofuels, such as black liquor from the pulp-making process, as well as clean bark, woodchips and sawdust, which originate from various wood-handling processes such as wood-handling plant, sawmill and ground-wood mill. Energy generation from those types of industrial residues is a sustainable, environmentally friendly alternative to other energy production processes as it significantly reduces the use of fossil fuel oil. In addition, the use of wood for energy production has a number of advantages over other sources—it is domestic and usually local, creates job and promote silviculture in the forest. The use of wood as fuel allows the utilization of renewable, natural raw material as an energy source without having any marked effects on the carbon balance in ecosystem, and therefore, the use of wood-based biofuels (i.e. bark, woodchips and sawdust) are exempted from electricity tax and CO_2 emissions trading in the European Union [1].

Air contaminants from the energy production plants are emitted into the atmosphere as particulates, aerosols, vapours, or gases. The most common method of eliminating or reducing pollutants to an acceptance level are destroying the pollutant by thermal or catalytic combustion, changing the pollutant to a less toxic form, or collecting the pollutant by use of equipment to prevent its escape into the atmosphere. Fly ash removal from flue gas by using electrostatic precipitators (ESP), cyclones, fabric filters, or wet scrubbings will result in a dry solid particulate material, which is commonly called an air-pollution-control (APC) residue [2]. The disadvantage of incinerating wood-derived biofuels to produce energy in the form of heat, steam and electricity, is that it produces large quantities of ash, in which

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heavy metals are retained. Furthermore, elements with a low volatility will concentrate in the bottom ash, while more volatile elements will concentrate in the air-pollution-control-residues (i.e. fly ash). The consequence of this separation effect in the combustion plants is that the bottom ash and fly ash have a different chemical composition and are therefore variable suited for subsequent utilisations [3].

Extraction is a procedure that puts solids and liquid in contact with each other under defined conditions. Extraction tests are widely used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, for assessing the efficacy of waste treatment process, and after disposal [4]. In the sequential extraction procedure, chemical extractants of various type are applied to the sample each successive treatment being more drastic than the previous one [5]. The goal of this method is to divide the total extractable concentration of metals into separate fractions in order to assess the form in which the metals occur in the waste material. Extraction studies are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile [6].

BACKGROUND

Aims of the Study and Previous Work

The aims of this study was to determine the physical and chemical properties (i.e. plant nutrient concentrations, dry matter content, neutralizing and reactivity values, LOI, TOC, pH and electrical conductivity) in the fly ash originating from the large-sized (90 MW) fluidized bed boiler at a Finnish pulp mill and assess its suitability for a fertilizer used in forestry.

In addition, in order to assess the mobility and potential bioavailability of elements in the fly ash, we used a three-stage BCR sequential extraction (leaching) procedure to determine the distribution of Mn, Fe, Cd, Cu, Pb, Cr, Zn, As, V, Ba, Mo, Al, Ti, Co, Ni and S in fly ash into the following fractions: (1) exchangeable fraction (CH_3COOH), (2) easily reduced fraction (NH_2OH-HCl), (3) oxidizable fraction (H_2O_2 + CH_3COONH_4). This study is a part of a major project in which the sequential extraction procedure is being used for assessing the extractability (leachability) of heavy metals in bottom ash and in fly ash originating from the large-sized industrial power plants, as well as from medium- and small-sized municipal district heating plants [7–9]. In Finland, and elsewhere in the European Union (EU), the total heavy metal concentrations as well as extraction (leaching) characteristics of ash must be known before it can be utilized or disposed of in a landfill.

Sampling

The fly ash investigated in this study was obtained from the electrostatic precipitator of a fluidized bed boiler of a pulp mill located in Finland. The plant has a 90 MW bubbling fluidized bed boiler (BFB), and at the present time, approximately 93.5% of the energy produced by the BFB originates from the incineration of forest residues (i.e. clean bark and wood) and ca. 6.5% from the incineration of the mixture of primary sludge and biosludge. The forest residues are originating from the debarking plant and the primary sludge and biosludge from the biological wastewater treatment plant (i.e. activated sludge treatment plant) of the mill. The primary sludge and biosludge are wood-derived residues, which solid content ranges from 20 to 30%, and consist mainly of wood fibres and biomass. Although this sludge mixture is incinerated in fluidized bed boiler, its energy content is negligible [10].

Fly ash sampling was carried out in June and July in 2008. During this period, a total of 9 individual samples (i.e. one sample per week) were taken and stored in polyethylene bottles in a refrigerator (+4°C). After sampling, all the individual samples were combined to give one composite sample with a weight of 5 kg (wet weight). The sampling period represented normal process conditions for the plant, e.g. O_2 content and temperature. A coning and quartering method [11] was applied repeatedly to reduce the wet ash sample to a size suitable for the laboratory analyses.

EXPERIMENTAL

Determination of the Mineral composition, Physical and Chemical Properties

For the determination of the mineralogical composition of the fly ash, the X-ray diffractogram of the powdered sample was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuKα radiation. The scan was run from 2 to 50° (2-theta-scale), with increments of 0.02° and a counting time of 1.5 seconds per step. Operating conditions were

40 kV and 40 mA. Peak identification was done with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and ICDD PDF-2 Release 2006 package software package (Pennsylvania, USA).

The pH and electrical conductivity (EC) of the fly ash were determined by a combination pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium) and a Phoenix conductivity electrode (Phoenix Electrode Co., Texas, USA) with a cell constant of 1.0. pH and EC were determined according to the European standard SFS-EN 13037 at a solid to liquid (S/L) ratio of 1:5. Determination of the dry matter content of the fly ash was carried out according to the European standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105°C. The organic matter content, as measured by the loss-on-ignition (LOI), was determined according to the European standard SFS-EN 12879, in which an oven-dried (105°C) sample is heated overnight in a muffle furnace (Box Furnace, Lindberg, Blue M, Asheville, USA) at 550°C. The total organic carbon (TOC) content was determined according to the European standard SFS-EN 13137 using a Leco CHN-600 analyser (Leco Inc., USA), in which a sample is combusted and the evolved carbon dioxide is measured by infrared spectrometry. The neutralizing (liming effect) value and reactivity value were determined according to the European standards SFS-EN 12945 and the SFS-EN 13971, respectively. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous study [7].

Determination of the Total Element Concentrations

For the determination of total element concentrations in the fly ash, the dried sample was digested with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM corp., Matthews, USA) using USEPA method 3051A [12]. The cooled solutions were transferred to 100 mL volumetric flasks and the solutions were diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system (Elga, Ltd; Bucks, England). All reagents and acids were suprapure or pro analysis quality.

Except for Hg, the total element concentrations in the ash were determined with a Thermo Elemental IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer (Franklin, USA). The concentration of Hg in the ash was determined with a Perkin Elmer Aanalyst 700 cold-vapour atomic absorption spectrometry (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90plus autosampler.

Sequential Extraction Procedure and Determination of Extractable Concentrations in Extractants

For the partitioning of heavy metals and sulfur in the fly ash between the exchangeable (CH_3COOH), easily reduced (NH_2OH-HCl) and oxidizable (H_2O_2 + CH_3COONH_4) fractions, the three-stage sequential extraction procedure given in Table 1 was used. This procedure is so called BCR procedure has been widely applied for metal fractionation in various matrices, e.g. ash, soil, sediment and sludge [13].

Extraction was carried out by shaking 4 g of the fly ash. The extraction was carried out in polypropylene bottles. In order to minimize possible chemical and/or microbiological changes in the ash, the extraction was carried out using the ash sample as such, instead of a dried sample since, according to Kosson et al. [14], it is preferable to avoid sample drying before extraction. After each extraction step the extracts were separated from the solid residue by filtration through a 0.45 μm membrane filter (47 mm diameter; Schleicher & Schuell, Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering ash particles from the previous extraction stage were also

Table 1. The Three-stage BCR Sequential Extraction Procedure for Element Partitioning in the Fly Ash.

Stage	Fraction	Reagent/1 g Sample	Shaking Time and Temperature
1	Exchangeable	40 mL CH_3COOH (0.1 M; pH 2.9)	16 h at 25°C
2	Easily reduced	40 mL NH_2OH—HCl (0.1 M; pH 2.0)	16 h at 25°C
3	Oxidizable	10 mL H_2O_2 (30%); evaporation + 10 mL H_2O_2 (30%); evaporation + 50 mL CH_3COONH_4 (1.0 M; pH = 2.0)	1 h at 85°C 1 h at 85°C 16 h at 25°C

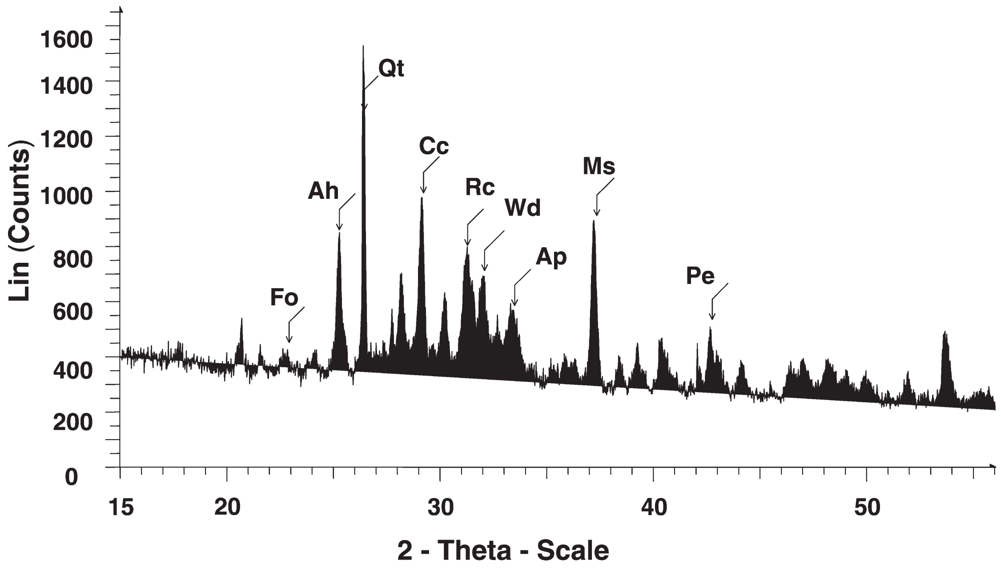

Figure 1. XRD pattern of the fly ash. Mineral abbreviations and their abundance (%): Ah = Anhydrite [$CaSO_4$; 10.9%]; Ap = Apophyllite [$(K,Na)Ca_4Si_8O_{20}(F,OH)–8H_2O$]; 6.6%]; Cc = Calcite [$CaCO_3$; 14.0%]; Fo = Fosterite [$(Mg,Fe)_2SiO_4$; 7.9%]; Ms = Magnesite [$MgCO_3$; 15.1%]; Pe = Periclase [MgO; 3.8%]; Rc = Rhodochrosite [$MmCO_3$; 8.5%]; Qt = Quartz [SiO_2; 27.2%]; Wd = Weddellite [$Ca(C_2O_4)–2H_2O$; 6.1%].

included in the next stage. After addition of 200 µL of 65% HNO_3 in the supernatant phase, it was stored in a refrigerator (+4°C) until the element determinations. The element concentrations in the extracts (i.e. extraction stages 1–3) were determined with a Thermo Elemental IRIS Intrepid II XDL inductively coupled plasma optical emission spectrometer (Franklin, USA).

RESULTS AND DISCUSSION

Mineral Composition, Physical and Chemical properties

The XRD pattern shown in Figure 1 indicates that several distinct peaks were observed and the following mineral classes and minerals were identified in the fly ash: carbonates (i.e. calcite, magnesite and rhodochrosite), oxides (i.e. periclase, quartz), sulfates (i.e. anhydrite), silicates (i.e. apophyllite, fosterite) and organics/oxalates (i.e. weddellite). Although the mineral composition of fly ash depends significantly e.g. on the combustion temperature and the type of boiler, the fly ash capturing mechanism, as well as the fuels burnt [15], our results agree with the findings of Martins et al. [16], that calcite ($CaCO_3$) and quartz (SiO_2), especially, are typically observed in wood ash.

In this context it is worth noting that, although XRD analysis can be useful to identify chemical species of crystalline particles in ash, in our case only a few minerals could be identified. An XRD spectrometer is unable to identify the amorphous (glass) phase (i.e. non-crystallised matter), and its detection limit is normally 1–2% (w/w). This is probably the reason why crystalline compounds containing the elements listed in Table 2 were not mostly identified by XRD, despite the fact that the concentrations of these heavy metals could be measured quantitatively by ICP-OES.

The most important physical and chemical properties of the fly ash are given in Table 2. The results are means of triplicate samples and are expressed on a dry weight (d.w.) basis. However, the standard deviations are not given to all elements, because the triplicate samples had exactly the same element concentrations. As seen in Table 2, the pH of the fly ash was strongly alkaline (pH 13.1). According to Van Herck and Vandecasteele [17], an alkaline pH indicates that part of the dissolved metals in the ash occur as basic metal salts, oxides, hydroxides and/or carbonates, and the XRD spectra in Figure 1 support this assumption. Therefore, the proportion of

Table 2. The Physical and Chemical Properties of the Fly Ash (results are means of triplicate samples (n = 3) and expressed on a dry weight basis (d.w.).

Parameter	Unit	Fly Ash
TOC	mg kg^{-1}; (d.w.)	14
LOI (550°C)	% (d.w.)	< 0.5
Dry matter content (105°C)	%	99.8 ± 0.2
Neutralizing value (NV)	% (Ca; d.w.)	24.9 ± 0.2
Reactivity value (r_{ac})	% (Ca; d.w.)	23.1 ± 0.2
pH	—	13.1 ± 0.1
Electrical conductivity (EC)	mS cm^{-1}	34.7 ± 0.5

soluble basic metal salts, oxides, hydroxides and carbonates in the fly ash outweighs the proportion of soluble acidic components, and the fly ash subsequently generates an alkaline pH. According to the electrical conductivity value (34.7 mS cm^{-1}), which in an index of the total dissolved electrolyte concentrations, the extraction solution of the fly ash has a relatively high ionic strength, which also indicates that part of the dissolved metals occur in the ash as dissolved basic metal salts. However, in this context it is worth noting that, it is not self-evident that the water fraction of ash is alkaline. The pH of coal fly ash can vary from 4.5 to 12.5 depending largely on the S content of the parent coal [18].

The low total organic carbon (TOC) value (14 mg kg^{-1}; d.w.) indicates that the fly ash contains almost no unburned organic material. The low loss-on-ignition (LOI) value (< 0.5%; d.w.) supports this, although it does not necessarily represent well the amount of unburned carbon in ash, but rather the volatile fraction. According to Heiri et al. [19], other reactions than the burning can take place at 550°C, e.g. dehydration of metal oxides and loss of volatile salts. Thus, LOI is an indirect measure of the organic matter content of ash. The almost complete combustion of organic matter in the fluidized bed boiler is reasonable due to the fact that the incineration temperature in the bed sand varies between 810 and 830°C and in the upper zone of the boiler between 1100 and 1200°C. According to our previous studies [8,20], it is not uncommon if the TOC and LOI values are elevated in the fly ash. This phenomenon is due to the fact that the fly ash particles rise with the flue gas into the electrostatic precipitators remaining for a shorter time in the combustion chamber than those particles which are associated with the bottom ash fraction. The very high dry matter content (99.8%) of the fly ash is disadvantage, since it can cause dust problems during handling.

The neutralizing value (NV) of 24.9% expressed as Ca equivalents (d.w.) indicates that 1.5 tonnes of fly ash would be required to replace 1 tonne of a commercial ground limestone produced by SMA Saxo Mineral Ltd., the neutralizing value of which is 38% (Ca equivalents; d.w.). The reactivity value (r_{ac}) was determined in order to assess the speed and effectiveness of the neutralizing potential of the ash. The r_{ac}/NV ratio indicates that the so-called "fast acting" capacity of the ash is ca. 93%. This means that fly ash is therefore a potential soil conditioner agent.

Total and Extractable Heavy Metal and Sulfur Concentrations in the Fly Ash

The total heavy metal and sulfur concentrations in the fly ash as well as the current Finnish limit values for the maximal allowable heavy metal concentrations for fertilizers used in forestry are given in Table 3. These limit values came into force in March 2007 [21], and are based on the European Union (EU) directives and regulations. According to Table 3, the total element concentrations of Cu, Pb, Cr, Zn, As, Ni and Hg in the fly ash

Table 3. Total Element Concentrations (USEPA 3051A; n = 3) in the Fly Ash, the Sum of Element Concentrations in Extraction Stages 1–3 (n = 1), Recoveries (%), and the Current Finnish Limit Values for Maximal Allowable Heavy Metal Concentrations for Wood-, Peat- and Biomass-derived Ashes used as Forest Fertilizer.

Element	Total Concentration in the Fly Ash (mg kg^{-1}; d.w.)	Sum of Extraction Stages 1–3 in the Fly Ash (mg kg^{-1}; d.w.)	Recovery (%)	Limit Value for Forest Fertilizers (mg kg^{-1}; d.w.)
Cd	20.1 ± 0.1	18.8	93.5	17.5
Cu	111 ± 1.0	73.6	66.3	700
Pb	47.8 ± 0.3	2.6	5.4	150
Cr	58.6 ± 0.5	6.0	10.2	300
Zn	3650 ± 23	3034	83.0	4500
As	3.6 ± 0.1	3.4	94.4	30
V	35.4 ± 0.5	10.7	30.2	—
Ni	53.4 ± 0.3	28.5	53.4	150
Ba	2680 ± 25	175.7	6.6	—
Mo	4.6 ± 0.3	1.6	34.8	—
Hg	0.2 ± 0.1	n.d.	n.d.	1.0
Mn	16200 ± 173	10752	66.4	—
Fe	12900 ± 58	15.9	0.1	—
Al	14600 ± 58	1357	9.3	—
Co	14.1 ± 0.1	9.3	65.9	—
Ti	472 ± 8.7	3.2	0.7	—
S	37000 ± 551	37000	100	—

were significantly lower than the current Finnish limit values for forest fertilizers. Only the total concentration of Cd (20.1 mg kg^{-1}; d.w.) in the fly ash exceeded slightly its limit value (17.5 mg mg^{-1}; d.w) for a fertilizer used in forestry and therefore the fly ash has to be disposed off in landfill site.

However, in this context we would like to point out that although the Cd concentration was slightly elevated in the fly ash investigated in this study, its concentration in biomass derived ashes in Finland is usually low and biomass derived ashes can be used as forest fertilizer. In addition, it is worth noting that the utilization as well as landfill disposal of ash and other industrial residues always need approval by the competent authority.

If inorganic materials and by-products, e.g. ash, are disposed off in landfills, the concentrations of harmful compounds must be low and the harmful components must be tightly bound to the matrix [22]. During transport, disposal and storage, it is possible that the ash is subjected to leaching effects of rain and to other substances, e.g. chloride, sulfate, and organic matter, which may form complexes with heavy metals. The change of pH in a landfill environment may also occur, e.g. sulfide oxidation, buffering capacity of natural waters, acid rain, and atmospheric CO_2. Measurement of the total concentration of metals provides relatively misleading information for assessing the possible bioavailability and mobility of metals. The total elemental concentration represents a source term only for the unrealistic environmental scenario in which the entire mineral structure of the solid material is dissolved. Therefore, extraction tests, e.g. single and sequential, have been applied in order to determine the potential bioavailability and environmental mobility of elements in waste materials [5,17,22].

The distribution of heavy metals and sulphur in the fly ash after a three-stage BCR extraction (leaching) procedure between exchangeable fraction (CH_3COOH), easily reduced fraction (NH_2OH-HCl) and oxidizable fraction (H_2O_2 + CH_3COONH_4) are shown in Figure 2. However, Hg is not fractionated due to its low total concentration (see Table 2).

When the sequential extraction procedure is applied for the partitioning of heavy metals in environmental samples (e.g. ash, sludge, sediment, soil etc.), the ability of different extraction agents to release metal ions depends on their association with specific fractions in the sample. Extractants like electrolytes, weak acids and chelating agents release metals from the coordination sites, while strong acids and redox agents are capable of releasing additional quantities of metals as a result of the decomposition of the solid matrix. Thus, consecutive extraction techniques allow us to obtain information about the mobility of major and trace elements under different environmental conditions, such as acidic or alkaline, oxidizing or reducing behaviour, the action of chelating agent etc [23].

The exchangeable fraction (F1), extractable with CH_3COOH, gives an indication of the amount of metals bound on the surface of the particles, as well as metals that are released as acid-soluble salts such as carbonates. This fraction is potentially bioavailable and corresponds to the form of metals that are most available for plant uptake, and can be released by merely changing the ionic strength of the medium. The use of acetic acid as leachant emulates the organic acids produced from decomposing waste in anaerobic environments such as landfill since, in the acetogenesis phase during the anaerobic degradation of organic matter, carboxylic acids (e.g. acetic acid), volatile fatty acids and ethanol are produced and transformed into acetate, carbon dioxide and hydrogen by acidogeneous bacteria [13, 24]. The proportion of Cr (35%), Ba (21.7%), Mo (66.3%), Ti (31.3%) and S (59.8%) showed a clear partitioning in this fraction, whereas the proportion of Pb (15.4%), V (14.9%) and As (11.8%) were slight.

The use of hydroxylamine hydrochloride (NH_2OH-HCl), which is a strong reducing agent, as extractant in the easily reduced fraction (F2) simulates anoxic conditions that are likely to occur in a natural medium. The use of NH_2OH-HCl as extractant in this fraction influences the complexation of metals with chloride. The elements in this fraction are thermodynamically unstable in anoxic conditions [13,25]. The metals in this fraction can be mobilised with increasing reducing or oxidising conditions in the environment. The proportion of Mn (64.8%), Cd (42.3%), Cu (29.6%), As (29.4%), V (32.7%), Ba (28.8%), Ti (31.3%), Co (55.9%), Ni (39.4%) and S (28.8%) showed a clear partitioning in this fraction, whereas the proportion of Fe (8.8%), Pb (15.4%), Cr (13.3%) and Mo (15.7%) showed a slight partitioning. The proportion of Pb and Ti in this fraction was equal to their proportions in the previous fraction. Only Cr and S showed a lower partitioning in this fraction than in the previous one.

The oxidizable fraction (F3), in which the combination of H_2O_2/NH_4OAc is used, corresponds to metals that are organically bound or occur as oxidizable minerals, e.g. sulphides [13]. As metals bound to this fraction can be released under oxidising conditions, an oxidation process is usually applied to extract out metals associated with the above-mentioned phase. The hydrogen peroxide (H_2O_2), which is used as an oxidising reagent in this fraction, is a strong oxidant. In general, hydrogen peroxide applied to a heated medium (i.e. 85°C) is the reagent preferred for dissolving organic matter as a compromise between the complete degradation of organic matter and the minimum alteration of silicates; heating promotes the oxidation process. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions [26]. However, according to the total organic carbon (TOC) value of 14 mg kg^{-1} (d.w.), the amount of organic matter in the fly ash is very low (Table 2), and it is therefore not very likely that the degradation of organic matter under oxidizing conditions can lead to significant release of the metals bound to these organic components. According to Smichowski et al. [27], the organic fraction released in the oxidizable step is not considered to be very mobile and available. From utilization point of view, the low organic matter in the fly ash is a favourable phenomenon since, if present, the organic matter may form complexes with toxic heavy metals [28]. Except of Mn, Mo, Co and S, the proportion of Fe (84.9%), Cd (57.6%), Cu (69.8%), Pb (69.2%), Cr (51.7%), Zn (93.4%), As (58.8%), V (52.4%), Ba (49.5%), Al (99.6%), Ti (37.4%) and Ni (57.6%) was highest in this fraction.

When the results of the total element concentrations (i.e. concentrations after microwave oven digestion with a mixture of HNO_3 and HCl) and of the sum of three-stage sequential extraction analysis are compared (Table 3), it can be seen that the recovery values (i.e. solubility) of elements varied between 0.1 and 100%. The lowest R-value (0.1%) was observed for Fe, and the highest (100%) for S. However, the R-values in Table 3 indicates that most of the elements do not occur in ash as readily soluble compounds. The extractability of Cd (i.e. the R-value) was high (93.5%). However, according to Figure 1, the proportion of Cd in the exchangeable fraction (F1), which is the form of metal that is most available for plant uptake, was only ca. 0.3%, whereas its proportion in the easily reduced fraction (F2) was ca. 42%, and in the oxidizable fraction (F3) it was ca. 57%. This indicates that although Cd was

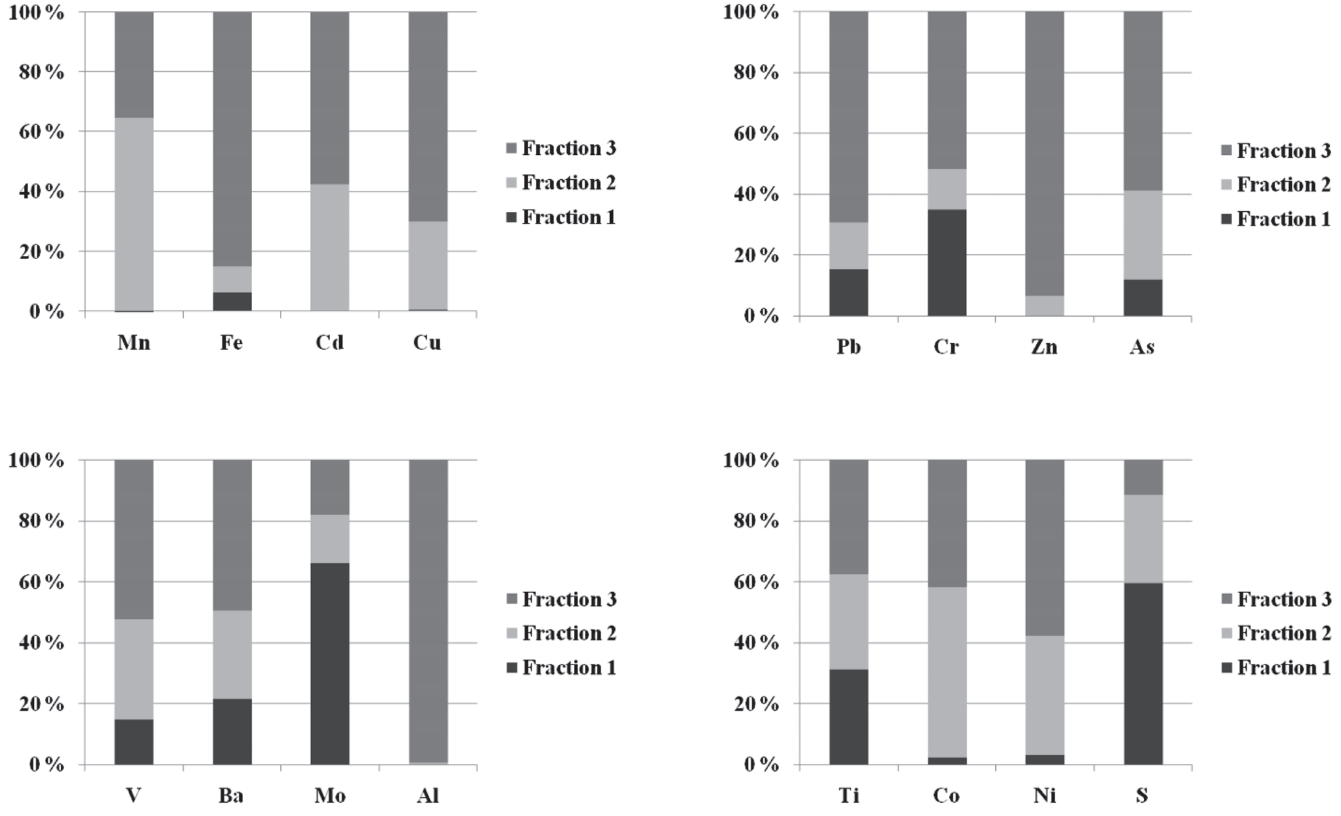

Figure 2. Partitioning of heavy metals and sulfur in the fly ash between exchangeable fraction (F2), easily reduced fraction (F2) and oxidizable fraction (F3).

extractable in all the fractions, a relatively high proportion of cadmium was partitioned in the oxidizable fraction (F3), which is not likely to be dissolved under the conditions normally found in nature. Although cadmium is one of the heavy metals considered to be the major priority concern due to its toxicity, its toxicity is mainly related to its bioavailability, not to its total concentration [29]. Therefore, we conclude, that cadmium will not pose any threat to the environment if the ash is disposed of in landfill site.

It is worth noting the very high (37000 mg kg^{-1}, d.w.) sulfur concentration in the fly ash as well as its distribution in extraction fractions (see Figure 2). During combustion, sulfur sublimates or reacts by forming gaseous compounds such as SO_2 and SO_3. As a result, most of the S passes to the vapour phase, and reacts with inorganic components to form sulfates. During combustion, the solid organic matter in fuel is decomposed and elements that form ash such as alkali metals and alkaline earth metals are released. In the part of the boiler where the flue gas is rapidly cooled, the sulfates condense on the particles of fly ash or on the tube surfaces. In wood ash, alkaline and alkaline earth elements are primarily present as oxides, hydroxides or carbonates, but also as chlorides [30]. According to Obernberger [31], the efficiency of S-fixation in the ash depends on the concentration of alkaline earth elements, and especially of Ca in the ash, as well as of the efficiency and technology used for dust precipitation. However, this is beneficial from the environmental point of view, because SO_2 is removed from the flue gases, thus decreasing the SO_2 emissions from the plant. Obernberger [31] reported that 40 to 90% of the total S in biofuel remains in the ash and the rest is emitted as SO_2 and SO_3 in the flue gas. In the fly ash, sulfur showed considerable partitioning in the exchangeable fraction (59.8%) and in the easily reduced fraction (28.8%). However, sulfur is not a chemical substance considered to be a major priority concern [32], and therefore we conclude that its extractability (leachability) will not pose a threat to the environment if the ash is disposed of in landfill site.

CONCLUSIONS

In Finland, the new limit values for maximal allowable concentrations of Cd, Cu, Pb, Cr, Zn, As, Ni and Hg in forest fertilizers came into force in March 2007. Except of Cd, the concentrations of Cu, Pb, Cr, Zn, As, Ni and Hg in the fly ash originating from a large-sized (90 MW) fluidized bed boiler at a Finnish pulp mill incinerating biofuels (i.e. clean bark, wood residues, primary sludge and biosludge) were significantly lower than their limit values. Due to the elevated cadmium concentration (20.1 mg kg^{-1}; d.w.) in the fly ash, the ash has to dispose off in landfills. However, according to a three-stage BCR sequential extraction (exchangeable, easily reduced and oxidizable fraction), a relatively high proportion of cadmium was partitioned in the oxidizable fraction (57.6%), which is not likely to be dissolved under the conditions normally found in nature. Therefore, according to the relatively low total concentration of cadmium (20.1 mg kg^{-1}; d.w.) and due to its extractability behaviour, especially, we conclude that the cadmium in the fly ash investigated in this study does not pose any risk for biota if the ash is disposed off in landfill sites.

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The Impact of Centrifugal Force and Cake Properties on Methanogenesis from Dewatered Sludge Cakes

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ABSTRACT: This study investigated the impact of centrifugal dewatering on the methanogenic population of dewatered anaerobically digested sludge solids. The two parameters investigated were shear intensity and cake solids concentration, as they have been reported in the literature to have positive correlation with the VOSC emissions from biosolids. The data from this preliminary experiment show that not only does increasing shear and cake dryness increase odors but also result in a greater inhibition of the methanogenic population of the biosolids. The increase in inhibition was noted by low headspace methane concentrations and extended time to methanogenic recovery as measured by the ratio of methane to VOSC in the headspace.

INTRODUCTION

THE relationship between centrifugation and the generation of nuisance odors in the form of volatile organic sulfur compounds have been well documented (Adams *et al.* (2003) and Novak *et al.* (2006)). Muller *et al.* (2004) further developed relationships between different centrifugal forces, sludge cake characteristics and the generation of VOSC odors. The study by Muller et al (2004) demonstrated that VOSC generation from dewatered biosolids increased with the intensity of shearing associated within the centrifugation process and as cake dryness. These changes in VOSC emissions were attributed to the release and recollection of degradable substrate into the caked due to shear and polymer interactions and the inhibition of methanogenesis, with the latter being the most poorly understood.

Higgins *et al.* (2006), through the addition of bromoethane sulfonic acid, demonstrated that VOSCs under a static headspace were persistent when the methanogenic activity was inhibited. Methanogens, specifically methylotrophic methanogens, are critical to the reduction of VOSC emmisions from anaerobically digested sludge cake. A typical VOSC generation and consumption profile is shown in Figure 1. After an initial lag period, typically 24–48 hours following centrifugation, there is a net release of VOSCs from the cake product to the surrounding atmosphere. The release, under static headspace conditions, reaches a peak value and then decreases with time. During this decrease there is a measured increase in headspace methane due to the activity of the methylotrophic methanogens.

The rate and extent of the production VOSC is a function of shear intensity and cake dryness as previously mentioned but the health of the methanogenic population will also be impacted these parameters. During anaerobic digestion many factors can impact the health or robustness of the methanogenic population including; the presence of toxins, interspecies competition, population composition and digester perturbations. Digester perturbations could be extended to the dewatering processes as they introduce significant amounts of shear energy and oxygen.

Oxygen is known to be toxic to methanogens because they are strict anaerobes so when solids are removed from the digester, as in dewatering, the exposure to oxygen will result in an added stress. Another factor to consider is the impact of shearing. The shear forces with in a centrifuge, as quantified by velocity gradient estimates (Gt), range from 30,000 to 120,000 depending on the centrifuge type (Higgins *et al.* (2006b)). Shear may impact the methanogens in several ways, first by potentially damaging the cell, second by disrupting of the

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flocs which can result in oxygen exposure during and following the centrifugation process, and finally by the separation of the organisms themselves. Methanogens, specifically those involved in digestion, depend upon a syntrophic relationship with fermenting organisms within the digester to obtain sufficient substrate and maintain the process balance (McCarty and Smith (1986)). Stroot et al. (2001) demonstrated that over mixing, or shearing, can result in process destabilization through the loss of these syntrophic relationships. Thus the shear of a centrifuge may have the same effect, though more short term.

This preliminary study was undertaken to determine if there is evidence that shear forces and cake solids concentrations, which effect odor production, effect the methanogenic population.

MATERIALS AND METHODS

Sludge Sample: Samples were collected from the Los Angeles County Sanitation District Joint Water Pollution Control Facility and sent overnight under refrigerated conditions. Once the sample arrived at the facility they were place in a constant temperature room at 4°C until use. While these conditions are not ideal for methanogenic populations the impact would be systematic. The objective of refrigeration was to ensure that the maximum amount of endogenous odor generating substrate was preserved to ensure that there was sufficient material to detect changes between the samples.

Dewatered Cake Characteristics: The total and volatile solids content of the sludge and dewatered cake were measured according to Standard Methods (APHA, 1998).

Centrifuge Simulation: Rather than operate a full scale centrifuge at varying torques and solids concentrations, a laboratory simulation was employed to provide a greater degree of control over the experiment. The method utilized was developed by Muller *et al.* (2004).

The sludge cake incubation vessels for static headspace analysis were ICHEM brand borosilicate glass serum bottles, 250 mL in total volume. The bottle was capped using a Teflontm lined silicone septa. All bottles were acid washed in nitric acid and triple rinsed with distilled water to remove any potential absorption or reaction sites on the bottle for sulfur compounds prior to use.

VOSC Headspace Analysis: VOSCs in the headspace were assessed using a modification of the method described by Novak *et al.* (2002). The polyethylene terephthalate bottle was replaced to with a 250 mL borosilicate glass serum bottle with a polytetrafluoroethylene (Teflon™) lined septa. The VOSCs measured in this study include methanethiol, dimethylsulfide, dimethyld disulfide and dimethyl trisulfide. Hydrogen sulfide was not measured as it is a metabolic end product and also chemically reactive with iron making its measurement less reliable.

Headspace Methane: The concentration of methane was measured along with the VOSC for each day of the analysis. A 100 μL sample was taken from each bottle and injected on to a Shimadzu GC-14 A/B with a thermal conductivity detector. Methane separation was achieved using a 1/4″ × 6′ (I.D. × L) copper column packed with Haysep D. Quantification was achieved by mixing a 99% methane standard with varying volumes of 99% carbon dioxide to achieve a dose response curve for methane on a percent volume basis.

Variation of Shearing Intensity: To investigate how shearing intensity impacts the methanogenic population of centrifugally dewatered sludges the method described in Muller *et al.* (2004) was modified. The modification used was to vary the time of exposure to shear in the Waring Blender to produce three distinct shear intensities, Gt = 0; 82,500 and 165,000. These Gt values were obtained by holding the shear intensity (G) constant and varying the shearing time. In each case the optimum polymer dose was determined to be the polymer dose that resulted in the lowest capillary suction time at the shear of interest (Muller *et al.* (2004)). Approximately, equivalent masses of each sample were added to each incubation bottle. To account for changes in methane and VOSC production each reported value is normalized to the mass of volatile solids in the incubation bottle at the start of the experiment.

Variation in Cake Solids Concentration: In order to determine effect that the cake solids concentration has on methanogenic activity the previously described centrifuge simulation method by Muller *et al.* (2004) was used. In order to generate cake with a range of solids concentrations the amount of cake placed in the piston press, the final step in the simulation process, was varied. By varying the solids volume over a fixed filtration area the dewatering efficiency, for a fixed period of time, varied and thus the cake concentration varied. Other than varying the cake volume, all sample were handled in the same manner.

Methane to VOSC Ratio: The ratio of methane to VOSCS was used in this study, is defined as a means of investigating the recovery of the methanogenic population. Typically in a stable anaerobic environment the concentration of methane is at least several orders of magnitude greater than that of VOSCs. Thus the higher the ratio of methane to VOSC the more in balance the system is and greater the methanogenic activity and health. A lower ratio would indicate some retardation of the methanogenic activity. This analysis will be used through out this study to provide qualitative analysis the overall health of the methanogenic population under different experimental conditions.

Definition of Peak VOSC: Through out this paper data will be reported in one of two ways. Either a time profile will be used in which the change in VOSC concentration with incubation time will be provided, producing the curve shown in Figure 1 or the peak VOSC for a particular profile. The peak VOSC value is defined as the maximum concentration achieved during the incubation period of the sample. Essentially the peak value represents the inflection point between the generation and consumption phases of VOSC.

RESULTS AND DISCUSSION

The Relationship between VOSC and Methane Production from Cake Solids

Methylotrophic methanogenesis utilizes VOSCs for cellular growth and energy production resulting in the release of methane and hydrogen sulfide. In anaerobic digesters these populations are in balance but following a perturbation, such as centrifugal dewatering, this balance is disrupted. Figure 1 shows the methane and VOSC profiles of the cake solids run through the centrifuge simulation described by Muller *et al.* (2004). The profile indicates is that following centrifugation there is an immediate cessation of methanogenic activity and a sharp increase in protein degradation as indicated by the rapid increase in VOSCs in the headspace, amino acids serve as VOSC precursors (Higgins *et al.*, 2006).

Only after the methanogenic population recovers does the headspace VOSC decrease, bringing the two metabolisms back into balance. The production and consumption patterns observed in this study are reminiscent to those of volatile acids and methanogenesis during digester upset, suggesting that as with those populations the VOSC producers and methylotrophic methanogens are normally in balance in an undisturbed system. Similar profiles VOSC have been reported by Adams *et al.* (2003) and Higgins *et al.* (2006).

While these two metabolic activities are interdependent in the sludge cake environment, the data to date has primarily focus on the generation of VOSCs and how centrifugation impacts the generation profile. The following sections present data which will verify the trends previously reported in the literature for VOSC

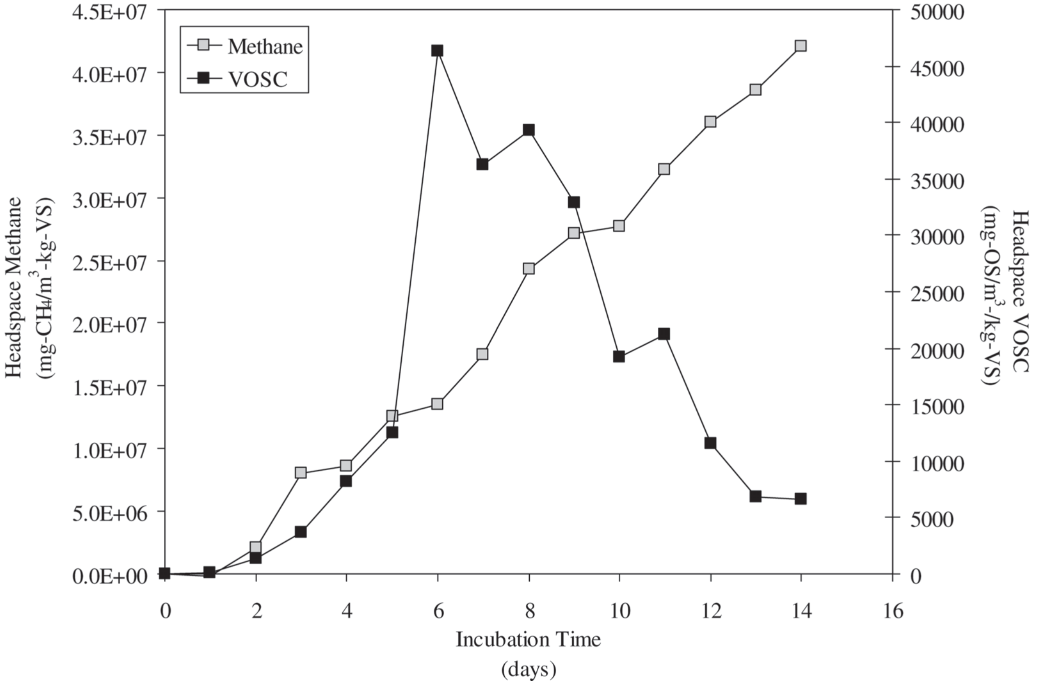

Figure 1. *VOSC and Methane Generation Profile of Centrifugally Dewatered Cake Solids Under a Static Headspace.*

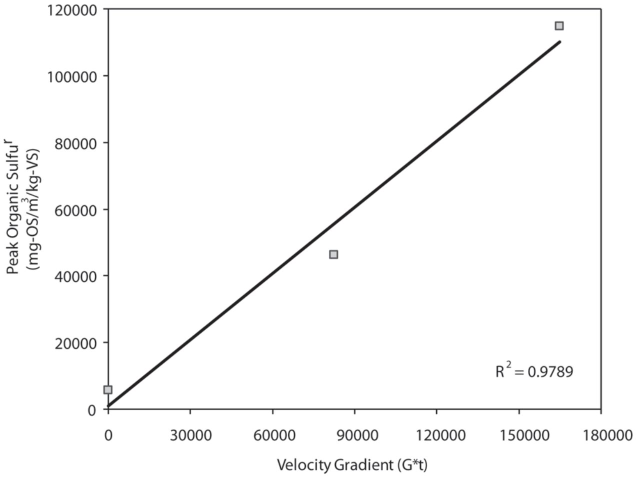

Figure 2. The Impact of Increasing Shear Intensity on Peak VOSC Values.

generation, shear and cake solids concentration, and extend the investigation to look at the impacts on the methanogenic population.

The Impact of Shear Intensity on VOSC production and Methanogenesis

Muller *et al.* (2004) reported that increasing the shear intensity to sludge during dewatering will increase the total emission of VOSCs from the cake as a result of the rendering of organic material bioavailable. When the peak VOSC value for each of the shear intensities tested is plotted as a function of Gt there is a strong linear correlation, $R^2 = 0.98$, as shown in Figure 2. These results are inline with the literature reported values.

However, when the concentration of methane in the headspace is plotted as a function of velocity gradient at the peak VOSC concentration there is no obvious trend (Figure 3). This result is counter to the prevailing theories in the literature which indicate that a strong inhibition of methanogenesis allows for the evolution of VOSCs from cake solids.

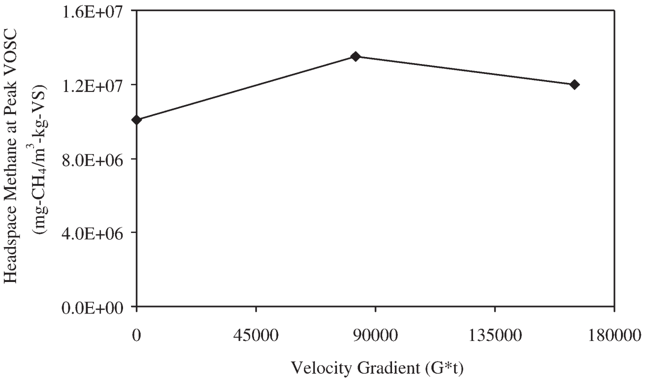

Figure 3. Headspace Concentration of Methane at Peak VOSC Concentration at Different Shearing Intensities.

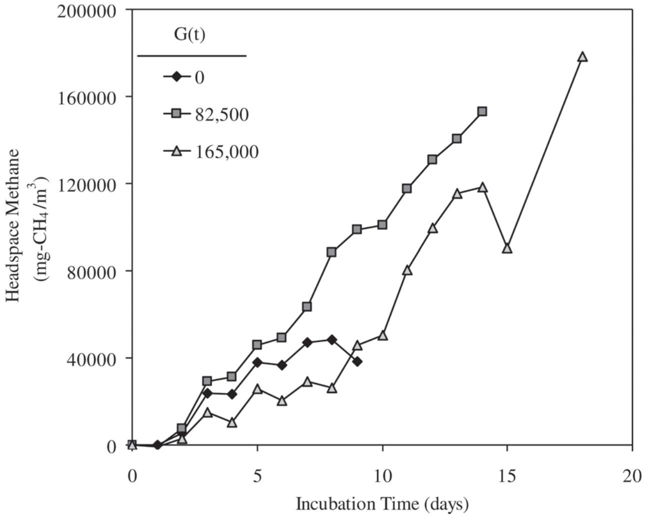

Figure 4. Methane Production Profile of Dewatered Cake Solids Exposed to Varying Levels of Shear During Dewatering.

If increasing shearing intensity has minimal effect on the methanogenic population of a dewatered sludge cake then one would expect to see a rapid on set of methanogenesis once the incubation period has started for each sample. The data in Figure 4 is contrary to this assertion as in even under the no shear condition there was a retardation of methanogenic activity noted by a delay in the accumulation of methane in the headspace.

The data in Figure 4 indicates that dewatering temporarily inhibits methanogenic activity. The data also shows that increasing shear intensity can exacerbate the inhibition. In Figure 4, the initial methane production rates at the 82,500 and 0 shear intensities are greater than that at a shear intensity of 165,000. What this initial rate increase suggests is that under the no shear and 82,500 shear conditions the methanogenic population can recover more rapidly from the stress(es) associated centrifugation than under the high shear condition, 165,000.

To further investigate the negative effect of shear energy on the methanogenic populations associated with dewatered cake the ratio of headspace methane to VOSC was plotted as a function of incubation time. Data in Figure 5 shows that the lower the shear intensity, the more rapid the methanogenic recovery, as indicated by the rapid increase in the CH_4/VOSC ratio; 7 days at Gt = 0, 12 days at Gt = 82,500 and 18 days at Gt = 165,000.

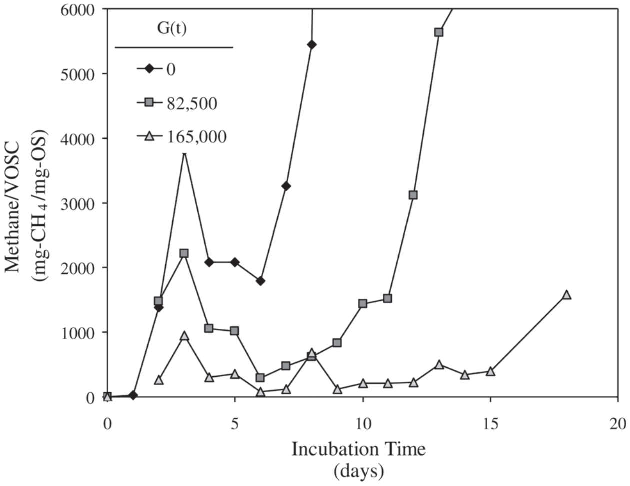

Figure 5. *The Change in the Methane to VOSC Ratio with Incubation Time.*

What the data indicates is the ratio of methane to VOSC is a better predictor of methanogenic activity than methane concentration alone. Figure 6, plots the ratio of CH_4/VOSC at the peak VOSC concentration as a function of Gt or shearing intensity. The data in Figure 6 shows that methanogenic activity decreases drastically with increasing shearing intensity.

Based on the data in Figures 2, 3, 4, 5 and 6 it appears that the interaction of shear and the methanogenic population is more complicated than that reported for VOSC forming organisms.

To assume that the concentration of methane alone dictates overall health of the methanogenic population appears to over simplify the complex interactions between the VOSC producing organisms and the methanogens. The ratio of the amount of methane to VOSC under a static headspace appears to be more indicative of methanogenic health and its progress toward recovery.

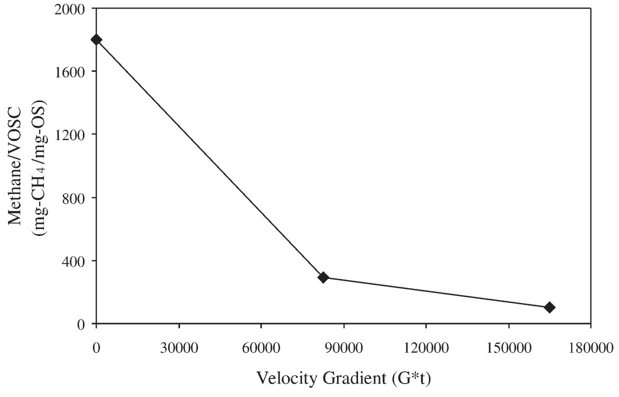

Figure 6. *The Effect of Shearing Intensity on the Methanogenic Health of Dewatered Biosolids.*

Based on the ratio of methane to VOSC is it quite evident that the shearing of anaerobic sludge has a negative impact on the methanogenic population which in turn results in the persistence of VOSC emission from the sludge. This is due primarily to the increase in time for recovery of the methanogens following shearing by a centrifuge.

The Impact of Cake Solids Concentration and Methanogenesis

Increasing cake solids concentrations have been shown to positively correlated with increasing release of VOSCs from centrifugally dewatered sludge (Muller *et al.*, 2004). The impact of cake solids, or cake dryness, on the health of the methanogenic population in dewatered cake has yet to be determined. In this study, changes in cake solids concentration under 3 different shearing intensities were evaluated. These shear variations were meant to mimic different dewatering pieces of equipment were evaluated.

The data in Figure 7, verifies that increasing cake solids concentration, regardless of shearing intensity, results in an increase in the emission of VOSCs from dewatered cake. However the data also shows that as cake solids concentration increases above approximately 27% there is a net reduction in the total VOSC emissions, suggesting an inflection point where overly dry cakes may become less biologically active. While there is a reduction in VOSC emissions at the highest cake concentrations, for each increase in shear intensity tested ever higher peak VOSC emission resulted at an equivalent cake solids.

The data in Figure 8, shows how the concentration of headspace methane changes with cake solids at the peak VOSC concentration. As was shown in the previous

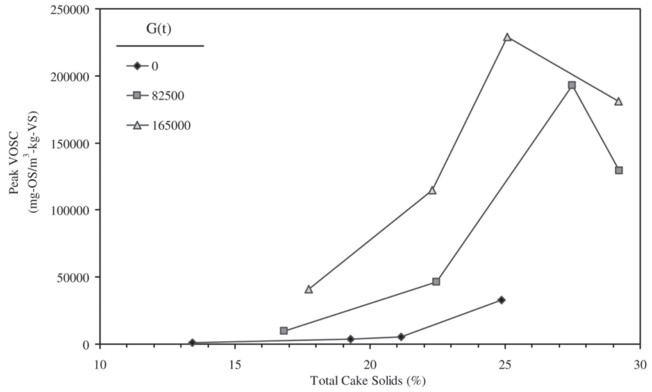

Figure 7. *The Impact of Increasing Cake Solids Concentration on Peak VOSC Concentrations.*

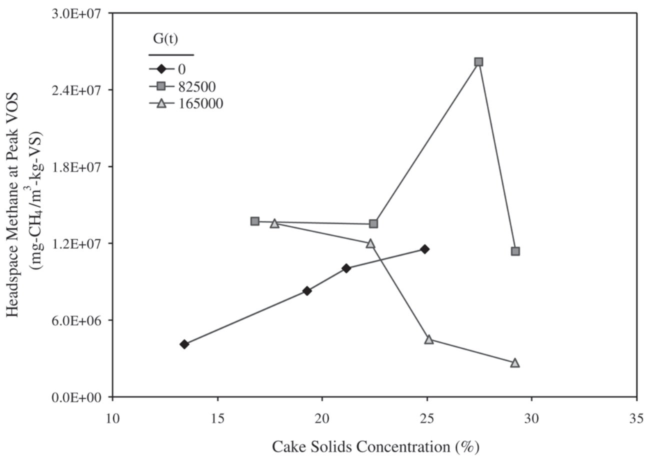

Figure 8. *The Concentration of Headspace Methane at Peak VOSC Concentration.*

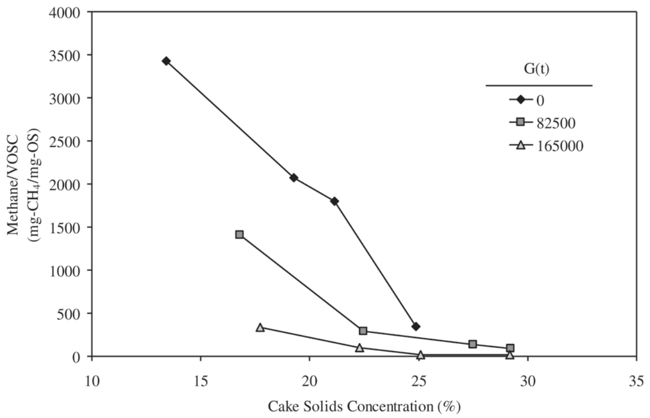

Figure 10. *The Change in the Methane to VOSC Ratio at the Peak VOSC as a Function of Cake Solids Concentration.*

section with shear intensity, headspace methane alone does not provide sufficient information to the overall condition of the methanogenic population.

Once again analyzing the change in the ratio of methane to VOSC in the headspace provided significant insight into the overall health of the system. Figure 9, shows a plot of the change in the CH$_4$/VOSC ratio as a function of incubation time. The data in Figure 9 indicates that at a fixed shear intensity, the time to recovery of the methanogenic population increases with increased cake dryness. As the cake solids concentration increase from approximately 17% to 29% the time to recovery increases from 8 days to 18 days.

Therefore replotting the data in Figure 8, as shown in Figure 10, as the change in the CH$_4$/VOSC ratio with cake solids at the peak VOSC concentration shows that increasing cake dryness has a negative effect on methanogens. The no-shear condition can be considered to reflect cake dryness alone while the 82,500 and 165,000 Gt values would represent a low and high solids centrifuge, respectively. For each shear condition tested, an increase in the cake solids concentration reduced the overall methanogenic health.

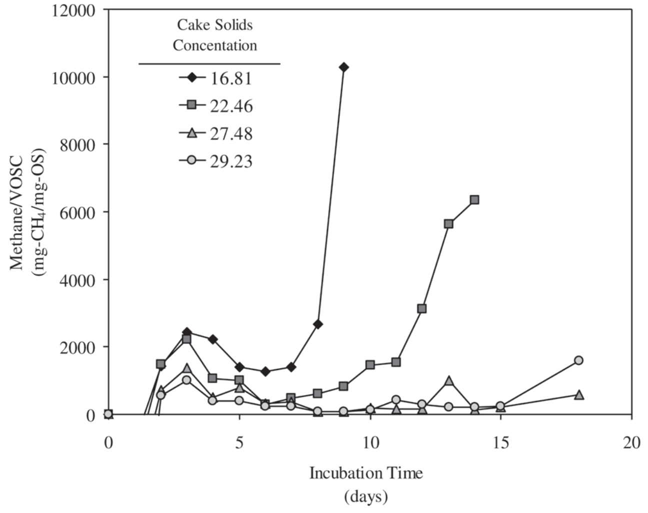

Figure 9. *The Change in the Methane to VOSC Ratio Over Time at Different Cake Solids Concentrations (Gt = 82,500).*

As with increased shear intensity an increase in cake solids concentration has a negative impact on the methanogenic health of the dewatered biosolids. As a result of this increased inhibition on the methanogenic population there are increased odors associated with dryer biosolids, up to the limits tested.

Implications

This study provides several important observations. First, dewatering devices that incorporate high intensity shear will cause increased odor generation from the dewatered cake. This is already known for centrifuges. Second, odors can be expected to increase as cakes become drier, even for low shear devices. It is expected that new generations of belt presses will generate higher cake solids. While the odor generation will not likely be as great as for high solids centrifuges, it will increase over conventional belt presses. Finally, although preliminary, it appears that if the cakes solids can be increased above 30%, the odors may decrease. This could be an important consideration for newer devices and for digestion processes that generate higher cake solids sludges.

CONCLUSIONS

Based on the data presented increasing cake solids and shear intensity with in a dewatering device will result in greater odor production in terms of VOSC emissions. The magnitude of the odor generation is a function of several additive effects. First increased shear renders a greater amount of undegraded organic material bioavailable, which is likely protein as it has been reported that amino acids serve as the precursors for VOSC compounds in sludge. Second, the shear energy provides sufficient stress upon the methanogens that their overall activity is reduced. Finally increasing the cake dryness will result in further inhibition of methanogens exacerbating the odor problem. Overall high shear and dry cake products (<~30%) result in solids with a higher potential for odor generation, in terms of VOSC release.

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Soil Treatment with Lignin Sulphide Chemical Stabilizer: Environmental and Structural Assessment

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ABSTRACT: This laboratory study was undertaken to evaluate the utilization of lignin sulphide for soil treatment and stabilization. We evaluated the change in soil properties, and the safety of lignin based stabilizer as a soil amendment. The environmental tests results of the treated samples and leaching characteristics test were determined. These tests includes: COD, BOD, P-PO_4^{3-}, N-TKN, Sulfide, pH, Solubility, and Bio-assay test. The compaction and California Bearing Ratio (CBR) characteristics of the resulting mixes were evaluated. Soil samples were stabilized with various percentages of stabilizer concentrations. As a result, the application of the soil stabilizer enhances the hydro-physical properties of the soil as indicated by CBR tests and facilitates the immobilization of pollutants according to environmental tests. It was found that this stabilizer is effective, environmentally friendly and relatively cheap to be used for a variety of purposes. The results of the effects and the suitability of the soil stabilizer are discussed in this paper.

1. INTRODUCTION

1.1. General Overview

SOIL stabilization implies the modification of the properties of soil-water-air system in order to obtain lasting properties which are compatible with a particular application. Stabilization is necessary for soil that used for different interests. The amount and type of applied stabilizer should be determined by experiment (Alferd B. N. 1997).

Many types of soil stabilizers are introduced by workers (Telysheva G. 1995, Mulligan, C. N., 2001). These includes, Chloride based products ($CaCl_2$, $MaCl_2$, etc.), Lignin based products (Lignosulfonates), PAM (polyacrylamides), petroleum emulsions, resin emulsions, organic oils, cement clin, fly ash and enzymes (Shulga G., 2001, Telysheva G. 1995, Alferd B. N. 1997, Randy S., 1994 and Gerald A. M. 2000, Wang Y. M., 2001, Nalbantoglu Z., 2004).

Soil stabilizer discussed in this work is a material composed mainly from lignin. Lignin is a naturally occurring substance, which refers to a group of phenolic polymers that confer strength and rigidity to the woody cell wall of plants. This is one of the reasons, why lignin-based conditioners are characterized by pronounced adhesive properties. Owing to the latter, these are capable of adsorbing at the surface of soil particles, converting the unstructured soil into the macrostructural one, thereby regulating the hydro-physical properties of the soil (Shulga, G., 2001). These compounds make up the second most abundant class of chemicals found in wood. Lignin and lignin derivatives are non-toxic natural by-product of the manufacture of pulp and paper, and so their use has the two-fold benefit of eliminating a disposal problem whilst improving manufacturing performance in other industries. Commercial lignin is produced as a co-product of the paper industry, separated from trees by a chemical pulping process. Lignosulphonates are the soluble derivatives of lignin, a major constituent of wood. As a binder, the lignosulphonate increases the strength and durability of the agglomerate (Shulga, G., 2001, Lignin and the Environment , 1991). The lignin-based conditioners are obtained from pulp industry wastes. Hence, they are offered as a cheaper product in comparison with synthetic water-soluble polymer structures (Shulga G., 2001).

1.2. Lignin Applications and Uses

Lignin sulphonate has the ability to bind dust particles together to form very hard durable mass. It could be

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used as a dispersant in manufacturing concrete admixtures, use on roads to reduce dust, in oil well drilling mud, as a binder for use in animal feed pelleting, as a dispersant in leather tanning, as a dispersant in manufacturing ceramics, as a dispersant in manufacturing dyestuffs, as a dispersant in manufacturing insecticide sprays, as a dispersant in pipeline transport (Lignin and the Environment, 1991). Other uses includes, soil stabilization, toxic metal immobilization, soil drift, ground water contamination, solid waste leachate remediation, erosion control (Bill Wong, 2002).

The structural analysis is important due to its effectiveness to the strength of the soil. As the strength of the soil increases by using the soil stabilizer, it will be a very powerful tool for the geotechnical engineers to solve the geotechnical problems in respect to soft and weak ground. Furthermore, soil stabilizer improves the stress-strain properties of soil at any site, it would be possible to use the existing soil for any kind of constructions, which will bring a great ease and economical solutions to the projects. On the other hand, by improved stability, embankments would be prevented from collapse and erosion. It is a fact that, all these improvements are for the human being safety and economy. For that reason, the environmental impact of any kind of material that will be added to the soil and consequently to the aquifer, should not be beyond of the research.

In Turkey, 428000 tons of different paper types are produced every year which produce large amounts of lignin related byproduct (DIE, 2004). When this substance is applied to any kind of soil it enhances its strength and improves its usability for construction and soil erosion purposes (Bryan Tisch, 2003).

The aim of this work is to evaluate the effect of lignin sulphide for soil treatment and stabilization. Furthermore, the possible environmental effects of this soil stabilizer will be investigated.

2. METHODS AND EXPERIMENTS

Soil samples obtained from house building project site in Istanbul city were used as the experimental specimen. The major constituents of the soil samples are mainly clay and gravel. The soil samples were brought to the laboratory in polyethylene bags. The required weight of the sample was determined after eliminating the large stones from the sample and mixing the soil to homogenize the sample. The leachate samples and the dilution of the original soil stabilizer were done using de-ionized water (Millipore). The soil sample was divided into two: first portion (specimen A) was treated with the chemical stabilizer and second portion (specimen B) untreated sample that is used for control purposes and blank determination.

2.1. Soil Physical Properties

Grain size distribution of the soil samples was performed by the help of sieve analysis test which is an effective test in determining the amount of material present in the smaller particle sizes. This test was performed using; 2-1/2, 1-1/4, 1/2 inch and No: 10, 18, 40, 100, 200 sieves according to ASTM method number ASTM C92-95, 1999.

In addition to that, a standard CBR test was performed according to method number ASTM-D1883-99, to identify the relation between load and penetration. Furthermore, natural water content in samples was also determined.

2.2. Soil Stabilizer Environmental Assessment

In order to assess the potential environmental impacts that could be encountered from usage, transportation and application of this soil stabilizer, a series of laboratory environmental experiments has been performed. These experiments include, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Phosphorus (P-PO_4^{3-}), Nitrogen (N-TKN), Sulfide, pH, Solubility, Bio Assay. These experiments were performed according to Standard Methods for Analysis (APHA, 1995; Franson M. A. H., 1998).

The conducted tests results to evaluate the possible environmental impacts of soil stabilizer are listed in Table 1.

The leachate experiment was performed according to the Standard Test Method for Leachate Solid Material in a Column Apparatus, designation: ASTM

Table 1. Environmental Impact Evaluation Parameters.

Test Abbreviation	Test Name
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
P-PO_4^{3-}	Phosphate as Phosphorus
TKN	Total Kjeldahl Nitrogen
S^{2-}	Sulfide
pH	Hydrogen ion strength
Solubility	Total Solids
Bio assay	Toxicity dilution factor (Fish Test)

Table 2. Grain Size Distribution of Soil Stabilizer Unapplied Material.

Sieve ID	Sieve Size (mm)	Material Passed (gr)	Material Retained (gr)	% of Retaining Material	% of Passing Material
2-1/2	63.500	2112.00	0.00	0.00	100
1-1/4	31.750	2053.00	59.00	2.79	97.21
1/2	12.700	1408.00	645.00	30.54	66.67
No. 4	4.750	1033.00	375.00	17.76	48.91
No. 10	2.000	805.00	228.00	10.80	38.12
No. 18	1.000	649.00	126.00	7.39	30.73
No. 40	0.425	391.00	258.00	12.22	18.51
No. 100	0.144	265.00	126.00	5.97	12.55
No. 200	0.074	249.00	16.00	0.76	11.79
PAN		**0.00**	**249.00**	**11.79**	**0.00**
TOTAL			**2112.00**	**100.00**	

D4874-95. This method was chosen because it provides the advantage of preparing the soil in a manner that simulates the state of the soil as it undergoes leaching in the field. There are 3 methods for aqueous leachate production. In addition to that, this method provides leachate suitable for organic and inorganic environmental analysis. Furthermore, this method mimics the conditions of leachate formation at the field. All the environmental analysis was carried out on the samples of soil stabilizer and leachate without pre filtration.

3. RESULTS AND DISCUSSION

3.1. Soil Analysis

A filling material should have a liquid limit less than 70, and plasticity index less than 40 as required by the "Technical Specifications for Roads" that issued by the General Directorate of Highways, the Ministry of Public Works, Turkey. These values are also required by the standards TS 1900, AASHTO T-89 and 90. According to the technical guide, the plasticity index should be 6 or greater, less than 36 preferably between 6 and 20.

The results of the soil tests performed on the treated soil with the lignin stabilizer meet the above-mentioned requirements. The application of the stabilizer increases the liquidity of the soil, which means the advantage of keeping more water safely. Furthermore, the soil type used in this experiment is suitable for construction purposes, especially platform constructions and unpaved roads. The stabilizer will treat a wide spectrum of materials ranging from fine particles (clay and silt) to coarse particles (gravel) soil which should have some cohesive properties.

Table 2, shows the grain size distribution properties of the soil. The percentage of the fine particles (size = 0.074 mm) in the sample is 11.79 %. According to Unified Soil Classification System (USCS) (ASTM 2487-90, 1999) the specimen is well-graded clayey soil (SW-SC). Table 3 shows the grain size distribution of soil stabilizer applied soil specimen. After the application of soil stabilizer, the percentage of fine materials increased to 17.72 %, which is clayey sand (SC) with high clay ratio that allows higher rigidity and shear

Table 3. Grain Size Distribution of Soil Stabilizer Applied Material.

Sieve ID	Sieve Size (mm)	Material Passed (gr)	Material Retained (gr)	% of Retaining Material	% of Passing Material
2-1/2	63.500	2336.00	0.00	0.00	100
1-1/4	31.750	2162.00	174.00	7.45	92.55
1/2	12.700	1215.00	947.00	40.54	52.01
No. 4	4.750	844.00	371.00	15.88	36.13
No. 10	2.000	679.00	165.00	7.06	29.07
No. 18	1.000	604.00	75.00	3.21	25.86
No. 40	0.425	538.00	66.00	2.83	23.03
No. 100	0.144	436.00	102.00	4.37	18.66
No. 200	0.074	414.00	22.00	0.94	17.72
PAN		**0.000**	**414.00**	**17.72**	**0.00**
TOTAL			**2336.0**	**100.0**	

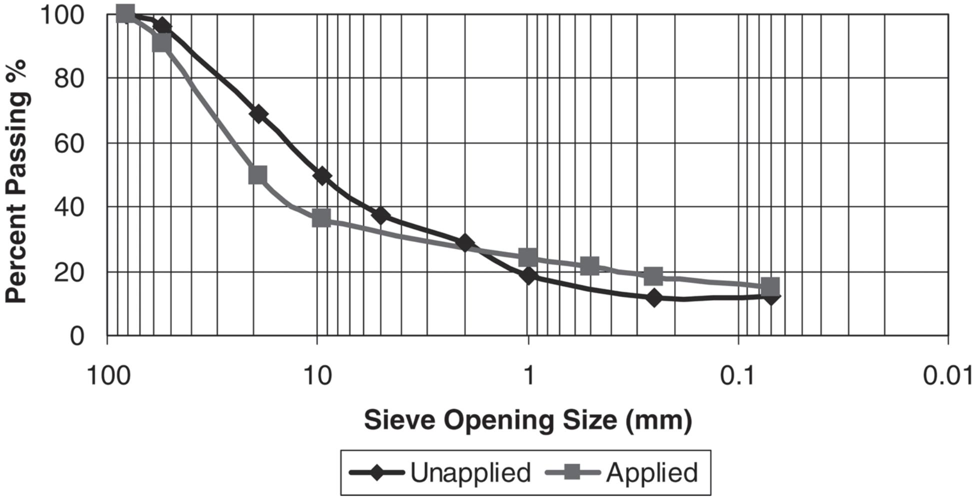

Figure 1. *Grain Size Analysis of Unapplied and Applied Soil Specimen.*

strength for the embankment and pavement due to better compaction and stabilization.

The grain size analysis is plotted (Figure 1) in order to determine the uniformity coefficient (Uc) and coefficient of curvature (Uc′) of applied and unapplied soil specimen.

The empirical tests, that measures the water contents at which certain changes in the physical behavior of the soil, has been carry out according to ASTM 2487-90, 1999. These tests are the liquid limit (LL), plastic limit (PL), and plasticity index (PI), from which it is possible to estimate the engineering properties of the soil. However, further mechanical tests should be conducted on the treated samples in order to find out the increasing ratio of the strength that could be used in designing a structure. The results of the conducted tests are summarized at Table 4. The results indicate that the performed test has been changed in the favor of improving the soil sample properties for the treated sample compared to the untreated one.

Table 4. General Properties of Soil.

Parameter	Value of Unapplied Soil Specimen	Value of Applied Soil Specimen
Uc–Coefficient of Uniformity	190	533.33
Uc′–Coefficient of Curvature	1.90	9.19
PL-–Plastic Limit	15.38%	18.94%
LL–Liquid Limit	22.61%	23.97%
PI–Plasticity Index	7.23%	5.03%
Clay + silt	11.79%	17.72%
Well Graded Gravel	48.91%	36.13%
Optimum Water Content	5.6%	11.5%
Max Dry Density	2.29 gr/cm^3	1.99 gr/cm^3

In addition to the mentioned tests, CBR tests were also performed on both treated and untreated soil samples, to understand the change in the strength of the soil. For that reason, two different samples were prepared. The first specimen (sample A) is treated with the lignin based soil stabilizer and the other (sample B) is prepared from the same type soil used in sample A, but kept without treatment to be used for control purposes. Both samples have 9% of natural water content. The prepared samples are placed into the CBR-mold according to the standards of ASTM-D1883-99, 1999, to identify the relation between load and penetration. The CBR test results are shown in Table 5.

Soil samples were compacted in a standard CBR mold for 4 days, and then the CBR tests were performed in the laboratory. The results are shown in Fig ure 2. It is obvious from the results of CBR tests shown in Table 5 that, the ionic stabilizer treated soil sample shows almost 56% increase in strength after 4 days test period. There is an increase in bearing capacity with depth and treated sections are stable with water content up to 25%. As this stabilization is ongoing process, and will continue to increase.

3.2. Environmental Impact

The results of the performed environmental impact

Table 5. The CBR Test Results.

Sample	CBR on 2.5 mm	CBR on 5 mm
Sample A (Treated)	23%	533.29%33
Sample B (Untreated)	11%	14%

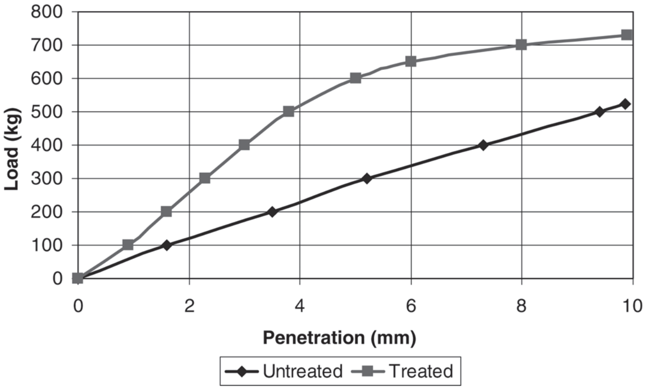

Figure 2. *Load-penetration Curve of Untreated and Treated Material.*

assessment of the lignin soil stabilizer tests are summarized in Table 6. The soil stabilizer is found to be a highly soluble material (lignin sulphonate) with a typical solubility of 95%. The pH of the diluted soil stabilizer sample is approximately 4.0. This pH should be in the range of 3.5 to 6.5 when tested in accordance with ASTM D-1293 method to get the sought results from the lignin soil stabilizer. The pH of the treated soil was found 7.34 which is the average pH of unpolluted soil or water bodies.

Nitrogen and phosphorus are important nutrients for biota if present in appropriate ratio and concentration. They are present as a natural component in the lignin which is being found in appreciable amounts in the soil stabilizer solution. The concentrations of nitrogen and phosphorus in the treated soil leachate are found to be 1.67 mg/L and 0.73 mg/L respectively. The possible dilution of these concentration by run-off water make it difficult initiate algal growth when it washed by runoff water to the receiving water bodies. This is also applied for Sulphide (0.69 mg/L) which comes from the derivative lignin sulphide in the lignin stabilizer.

The bioassay of the soil stabilizer aimed to estimate the biohazourds from direct contact of the 2% soil stabilizer solution with the aquatic environment. The results showed that it should be diluted with dilution factor of 8 in order to reduce any potential damage. The leachate test provides information about the effect of natural processes as runoff water by the action of rain and the soil stabilizer leachate after application on to the filed soil. The average rain in Istanbul is about 780 mm/year. The amount of distilled water applied for leachate production was calculated to be in the same range of the annual rainfall.

Table 6. Soil Stabilizer Environmental Analysis Results.

Parameter	2% Soil Stabilizer	Soil Stabilizer Leachate	% Retention
COD (mg/L)	13760	63.1	99.5
BOD (mg/L)	1400	2.61	99.8
TKN-N (mg/L)	65.32	1.67	97.4
Total P (mg/L)	117.7	0.73	98.8
Sulfide (mg/L)	40	0.69	98.2
pH	3.95	7.34	86.7
Solubility %	95	—	—
Bio-toxicity	8	0.3	96.2

This ration can be achieved for even for shallow lakes and small streams. This means that, if soil stabilizer come in direct contact to a water body accidentally, the dilution ratio of 8 should be established to avoid the risk of harming the aquatic life in that water body.

The leachate test suggest that there is a significant reduction of the investigated pollution parameters concentration when the stabilizer applied to the soil due to the high binding efficiency of soil stabilizer to the soil particles. The resulted lechate pH is about 7.3, which is the pH of unpolluted soil. The results of the environmental pollution impact tests are given in Table 6. As seen from the table, more than 97% of all the measured pollution parameters is retained and bind to the soil and the leached fraction is insignificant to cause any harm environment.

Generally, the main component of the soil stabilizer, which is lignin sulphonate, is being accepted by many countries around the world as a dust stabilizer (e.g Saskatchewan Highway and Transportation in Canada) is not harmful to the environment after its application to the soil. Furthermore, the soil stabilizer itself needs to be diluted 8 times if it spilled accidentally in any water body.

4. CONCLUSION

The application of the soil stabilizer enhanced the hydro-physical properties of the soil, consequently, the formation of water resistant macro structure. The performed environmental assessment tests suggest that, the application of this stabilizer will enhance the soil properties without causing any damage to the environment. From the eco-environmental point of view, the used stabilizer is a cheap, safe and effective for soil remediation purposes since it is natural and ultimately, biodegradable product.

In order to improve the engineering properties of soil, ionic stabilizer material can be used with optimum dosage which depends on the type of soil used. The engineering properties, such as compressive strength, stiffness, durability, etc, increase substantially after the application of ionic stabilizer. The applied soil layer provided adequate support for the base ground that will lead to stabilized, safe and economic embankments and foundations.

The results of soil stabilizer analysis suggest that this substance should be diluted to 8 times if it comes in direct contact with any water body (accidentally) to reduce the risk of harming the aquatic life environment. This ratio can be attained easily if the spillage happens in a medium water body like lakes or rivers.

The leachate analysis results show a significant decrease of all the measured parameters (less than 97%) compared to soil stabilizer itself to a degree that does not cause harm to the environment. These levels are to be diluted more when come in contact with any water body, which makes them less harmful.

This stabilizer could be used to stabilize contaminated soils with heavy metals or any other hazardous pollutants since its application is easy, rapid and inexpensive.

5. AKNOWLEDGEMENT

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Pb and Cd Contamination in Agricultural Crops of Corlu: The Effects of Transportation and Industry

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ABSTRACT: Tissue cadmium (Cd) and lead (Pb) concentrations of agricultural crops grown in and around Çorlu district in the vicinity of an industrial zone and main highway leading from Istanbul to Europe were investigated. Plant samples were taken from 11 locations and were analysed by ICP (Inductively Coupled Plasma Spectrometry). The concentrations of lead were between 0.221–0.383 mg kg^{-1} in wheat, 0.526–0.754 mg kg^{-1} in sunflower, 5.865–0.223 mg kg^{-1} in corn, 1.469–3.517 mg kg^{-1} in lettuce, 2.013–2.323 mg kg^{-1} in parsley, 0.587 mg kg^{-1} in peppers, 2.672 mg kg^{-1} in potatoes and 1.367–4.586 mg kg^{-1} in onions. The samples contained cadmium concentrations between 0.026-0.048 ppm in wheat, 0.072–0.093 ppm in sunflower, 0.452–0.025 ppm in corn, 0.501–0.621 ppm in lettuce, 0.209–0.396 ppm in parsley, 0.014 ppm in pepper, 0.462 ppm in potato and 0.213–0.513 in onion.

Accordingly, heavy metal pollution was detected in the plants growing in and in the surroundings of Çorlu according to the Turkish Food Codex requiring measures against the pollutant sources.

INTRODUCTION

METALS which cause environmental pollution and which are not essential for the human body reach the general population through mainly food, air and drinking water. Consequently an "overcarry of body metal" is formed. Some of these metals for instance Al, V, Ti, Cr, Sr, Sn, Cd and Pb are continuously accumulated in human tissue by age one [1].

The best method to monitor the most accurate risk estimation for people who have been exposed to heavy metals environmentally should include details such as; sources of heavy metal concentrations, the route they follow in the environment, minimum concentrations measured, and the characteristics of the population exposed to these metals [2].

While many metals can be a normal component of nutrients, they can also be found as a source of pollution. The reasons behind the metal pollution in nutrients are the residues of fertilizer and pesticides containing metals and metal salts; contact of containers and packaging made of metals; and introduction of metals that exist in soil and water (due to environmental pollution) into the food chain following biological accumulation in plants and animals [3].

Metals are known to be resistant to biodegradation. However, the metals existing in rivers and soils in "composite" or "metallic" forms can easily be introduced into the food chain by gaining "lipofy1" characteristic with the help of plants and anaerobic bacteria [4].

Heavy metal intake through nutrients, water and air may lead to some irregularities and damages in the body, depending on their concentrations. Such irregularities are characterized by symptoms such as sleep disorder, central nervous system disorders, dizziness, anorexia, difficulty in breathing and memory difficulties [5,6]. In addition, they can play a role in the development of cardiovascular diseases and damages in blood producing systems. Heavy metals are also known to cause cancer, anemia, poisoning and early death [3,7].

Some metals are considered as toxic metals (that can be harmful for human health when a specific dosage is exceeded) such as lead, cadmium, chromium, arsenic and mercury.

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The Çorlu District, selected as the study area, is 38 km from the Tekirdag Province and is located between 41° 07′ 30″ East longitude and 27° 45′ 00″ North latitude. Çorlu is 20 km north of the Marmara Sea and is located on the Ergene Basin which is nearly in the center of Thrace. It is surrounded by Kırklareli, Saray and Çerkezköy on the North, the Silivri District of Istanbul on the East, Tekirdağ and Muratli on the West and Marmara Ereğlisi and the Marmara Sea on the South. It has a surface area of nearly 951 square km [10].

A continental climate prevails in the vicinity of the research area. The Çorlu District is located in the part of Thrace that has the least rainfall due to being inland. Annual rainfall is 550 mm in Çorlu district. The distribution of this rainfall occurs as follows: 20% in spring, 10% in summer, 30% autumn and 40% in winter. According to long term averages, the highest maximum temperature average is 29°C, the highest minimum temperature average is 16.8°C and the highest average temperature value is 22.5°C and is observed in July. The lowest maximum temperature average is observed in January with 6.9°C, the lowest minimum temperature average with 0.4°C in February and the lowest average temperature with 3.6°C in January and February. The prevalent wind direction is north-northeast with speeds of up to 3.4 m/sec. The winds that bring damp air masses and cause rainfall are from the south-southwesterly direction winds called lodos and kıble. Karayel, which is a wind prevalent in the winter, causes snowfall by bringing cold air waves [12,13,14].

The Çorlu District of Tekirdağ Province is under the threat of environmental pollution due to its rapidly increasing population and industrial development. Soil, water resources and plants are contaminated by the lead, chromium and cadmium resulting from excessive use of fertilizers and pesticides during intensive farming practices, industrial wastes and residues, and emission of exhaust gases by vehicles. Consequently, people consuming plant products are exposed to these pollutants. It is of great importance for protecting public health and informing people about the amounts of these pollutants in the nutrients, an important indicator of environmental lead, cadmium and chromium pollution. In the scope of this study, the goal is the detection of lead, cadmium and chromium concentrations in the plants growing in Çorlu, a district combining agriculture and industry and having a heavy traffic flow. The purpose is to reveal the contribution of these pollutant sources in contamination; to examine this pollution within the scope of the "Communiqué on Detecting Maximum Levels of Specific Contaminants in Nutrients" under the Turkish Food Codex; and to define the possible effects of these pollutants in human health [15].

Codex Alimentarius defines a contaminant as follows: "Any substance not intentionally added to food, which is present in such food as a result of the production (including operations carried out in crop husbandry, animal husbandry and veterinary medicine), manufacture, processing, preparation, treatment, packing, packaging, transport or holding of such food or as a result of environmental contamination. The term does not include insect fragments, rodent hairs and other extraneous matter".

Foods and feeds can become contaminated by various sources and processes. Contamination generally has a negative impact on the quality of the food or feed and may imply a risk to human or animal health. Contaminant levels in foods shall be as low as reasonably achievable. The following actions may serve to prevent or to reduce contamination of foods and feeds:

- preventing food contamination at the source, e.g. by reducing environmental pollution.
- applying appropriate technology in food production, handling, storage, processing and packaging.
- applying measures aimed at decontamination of contaminated food or feed and measures to prevent contaminated food or feed to be marketed for consumption.

The effects of long-term exposure to chemical hazards in food are of particular concern. Symptoms related to prolonged low-level exposure may not be apparent until later in life and, when they do occur, they may be chronic and irreversible. Serious illness due to long-term exposure to various toxic chemicals may include damage to the immune and nervous systems, impairment of reproductive function and development, congenital anomalies in offspring, cancer and organ-specific damage.

Cadmium is a relatively rare element, released to the air, land, and water by human activities. In general, the two major sources of contamination are the production and utilization of cadmium and the disposal of wastes containing cadmium. Increases in soil cadmium content will result in an increase in the uptake of cadmium by plants; the pathway of human exposure from agricultural crops is thus susceptible to increases in soil cadmium. The cadmium uptake by plants from soil is greater at low soil pH. Edible free-living food organisms such as shellfish, crustaceans, and fungi are natural accumulators of cadmium. Similar to humans, there are increased levels of cadmium in the liver and kidney of horses and some feral terrestrial animals. Regular consumption of these items can result in increased exposure. Tobacco is an important source of cadmium uptake in smokers.

Lead

Lead is one of the most dangerous chemicals to children. Aside from its acute toxicity, the most important effect of exposure is chronic neurotoxicity, which is particularly severe during the first two to three years of life when early development of the central nervous system occurs. Exposure to lead during this time increases the risk of mild mental retardation, attention deficit hyperactivity disorder and other developmental disabilities [5–7]. There are many different ways in which children can be exposed to lead, including through contaminated food and drinking-water, the use of lead-glazed ceramics in cooking and ingestion of paint-chips (especially connected with pica-syndrome typical of poor nutrition) [4]. Cumulative exposure from all of these sources should not exceed the provisional tolerable weekly intake (PTWI) of 25 µg/kg body weight/week [1].

Plants exposed to high levels of lead from ambient air and soils can accumulate the metal and manifest toxicity. The toxicity and presence of other trace metals vary greatly among plant species. Based on *in vitro* studies, toxicity sequences have been determined for several species. Barley plants were shown to be more sensitive to Pb than to Cr, Cd, Ni, or Zn, and exposure to relatively high levels of Pb was shown to inhibit seed germination. The effect of lead on germination, however, was found to be less severe compared to several other metals such as Cd, As, and Hg. It is important to note that, following plant uptake, lead moves into the food chain and thus can affect animals and humans.

Cadmium

Cadmium is present at very low levels in a wide variety of food, and food products and account for more than 90% of human exposure to cadmium, except in the vicinity of cadmium-emitting industries.

Nevertheless, poisoning due to cadmium in food is rare. The main food sources are the kidneys of animals, which are generally higher in cadmium than are other foods, as well as contamination of rice, soy beans and seafood with cadmium by local industrial and mining operations.

The packaging materials for pre-prepared and fresh foods may contain considerable levels of cadmium that may migrate into food. Intake of highly cadmium-contaminated food causes acute gastrointestinal effects, such as vomiting and diarrhea [8]. The main problem for patients chronically exposed to cadmium is kidney damage [9] with a perturbance of phosphorus and calcium metabolism and a possible higher risk of kidney stones. The amount of cadmium in the kidney tubular cells increases during a person's lifespan and makes up the major part of the cadmium body burden. Maternal exposure to cadmium is associated with low birth weight and an increase of spontaneous abortion [10,11]. The International Agency for Research on Cancer (IARC) classifies cadmium as a human carcinogen group I.

Cadmium is accumulated by all plants. The extent of Cd accumulation, however, varies markedly with species and variety. Soil pH is the most important factor controlling Cd uptake by plants, with lower pH favoring its uptake. Tobacco plants have been shown to absorb high levels of Cd from the soil. Phytotoxicity of Cd is manifested by stunting, chlorosis, reduction in photosynthesis, wilting, and necrosis. Like Pb, Cd inhibits seed germination under laboratory conditions. Seedlings exposed to solutions of Cd salts exhibit decreased root elongation and development.

MATERIALS AND METHODS

Plant samples were collected from E-5 highway with heavy industry and busy transportation; D-100 Edirne Highway; the area between Çerkezköy-Çorlu, particularly the section with TEM connection; between Velimeşe and Karamehmet Villages; Türkgücü Village road; and the surrounding's of Tekirdağ-Çorlu Highway. Sampling periods were June 2006, September 2006, January 2007 and April 2007 based on harvest periods of crops (Figure 1). A total of 44 plant samples have been taken in 4 periods from 11 sampling areas from sunflower (*Helianthus annuus* L.), wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), pepper (*Capsicum annuum* L.), potato (*Solanum tuberosum* L.), onion (*Allium cepa* L.), lettuce (*Lactuca sativa* L.) and parsley (*Petrosellinum crispum* L.) (Table 1).

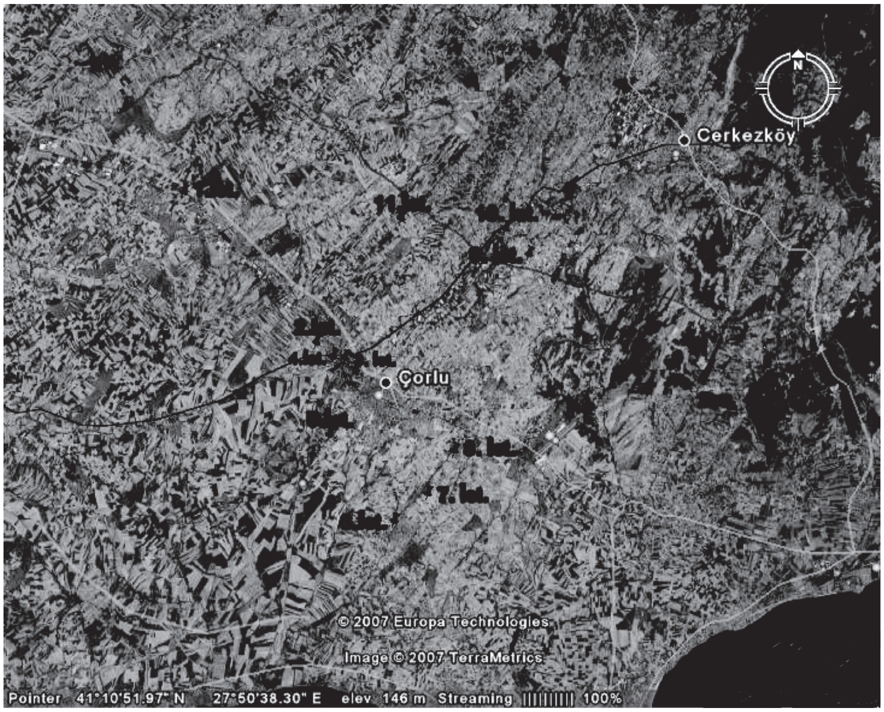

Figure 1. *Sampling Stations.*

There are 11 sampling stations. Samples were taken four times from each station with 3 month intervals.

Plant samples (Table 1) were brought to the laboratory in plastic bags. After washing and cleaning; root, leaves and fruit sections were separated before being dried in the oven for 1 hr at 60°C followed by 24 hr at 105°C. Dried plant materials were ground in a porcelain garlic press. Plant extraction was performed via the "Microwave Digestion Method" with an ETHO TC model microwave oven (Milestone brand). The average weight of plant samples has been detected as 0,2500 ± 0,0020 g; extraction procedure has been performed in pressurized Teflon tubes by adding 8 ml HNO_3 and 1 ml H_2O_2. At the end of the extraction procedure, samples were left for cooling. Solutions were then filtered with No. 41 Whatman filter paper, poured into balloon jojes to make up the final volume to 50 ml with distilled water. Samples were kept in a refrigerator at +4°C until analysis. Heavy metal analysis were made by using MPX Simultaneous model ICP device of VARIAN brand at the Soil Laboratory of Edirne Board of Trade, Turkey.

Table 1. Information on the Plant Species Collected from the Stations PTWI .

Station	June 2006	September 2006	January 2007	April 2007
Station 1	wheat	sunflower	lettuce	wheat
Station 2	pepper	pepper	lettuce	onion
Station 3	wheat	sunflower	potato	onion
Station 4	wheat	sunflower	onion	onion
Station 5	corn	corn	parsley	lettuce
Station 6	wheat	sunflower	wheat	wheat
Station 7	wheat	sunflower	wheat	wheat
Station 8	wheat	parsley	wheat	wheat
Station 9	wheat	sunflower	wheat	wheat
Station 10	wheat	sunflower	wheat	wheat
Station 11	wheat	sunflower	wheat	wheat

RESULTS

Comparisons of Pb and Cd concentrations, detected in the edible parts of the plant species collected from the stations, are given in Figures 2–9 and compared to the Turkish Food Codex. The amount of lead has been found to be 0.221–0.383 ppm in wheat, 0.526–0.754 ppm in sunflower, 0.223 ppm in corn, 1.469-3.517 ppm in lettuce, 2.013–2.323 ppm in parsley, 0.587 ppm in pepper, 2.672 ppm in potato and 1.367–4.586 ppm in onion; the amount of cadmium has been found to be 0.026–0.048 ppm in wheat, 0.072–0.093 ppm in sunflower, 0.025 ppm in corn, 0.501–0.621 ppm in lettuce, 0.209–0.396 ppm in parsley, 0.014 ppm in pepper, 0.462 ppm in potato and 0.213–0.513 ppm in onion.

More heavy metal accumulation was observed in the edible parts of tuberous crops such as onion and potato

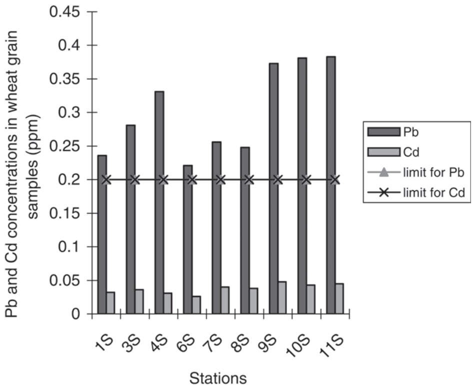

Figure 2. *Comparisons of Pb and Cd Concentrations in Wheat Grain Samples on the basis of Turkish Food Codex Limits.*

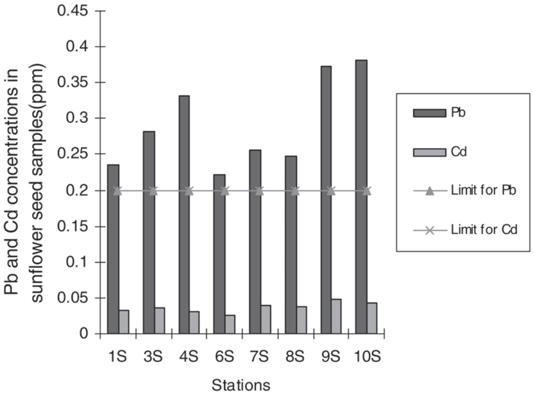

Figure 3. *Comparisons of Pb and Cd Concentrations in Sunflower Seed Samples on the basis of Turkish Food Codex Limits.*

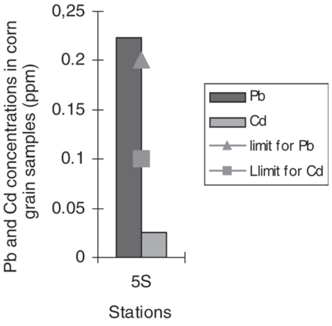

Figure 4. *Comparisons of Pb and Cd Concentrations in Corn Grain Samples on the basis of Turkish Food Codex Limits.*

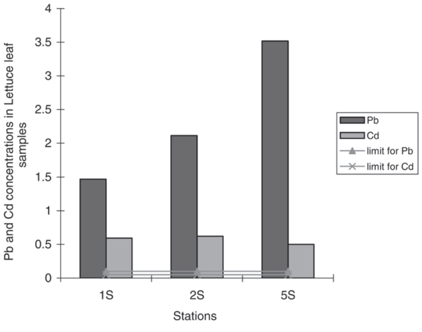

Figure 5. *Comparisons of Pb and Cd Concentrations in Lettuce Leaf Samples on the basis of Turkish Food Codex Limits.*

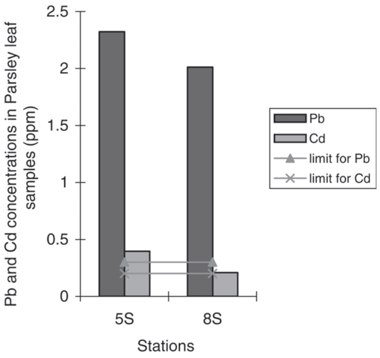

Figure 6. *Comparisons of Pb and Cd Concentrations in Parsley Leaf Samples on the basis of Turkish Food Codex Limits.*

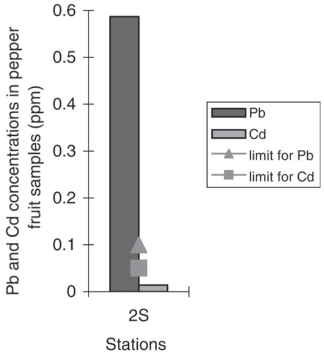

Figure 7. *Comparisons of Pb and Cd Concentrations in Pepper Fruit Samples on the basis of Turkish Food Codex Limits.*

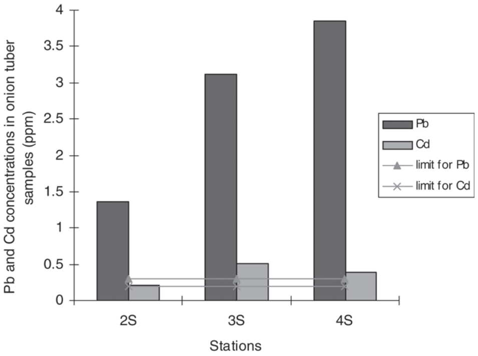

Figure 8. *Comparisons of Pb and Cd Concentrations in Onion Tuber Samples on the basis of Turkish Food Codex Limits.*

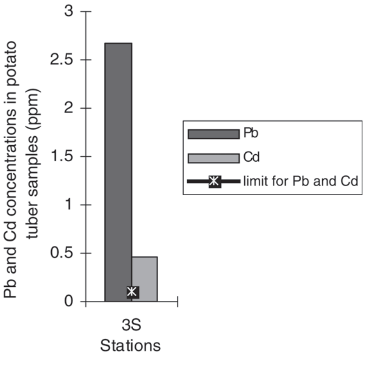

Figure 9. *Comparisons of Pb and Cd Concentrations in Potato Tuber Samples on the basis of Turkish Food Codex Limits.*

Table 2. Heavy Metal Contamination of Plants taken from Station 1.

	June 2006			September 2006			January 2007		April 2007	
	Wheat			Sunflower			Lettuce		Wheat	
ppm in Dry Matter	Root	Leaf	Fruit	Root	Leaf	Fruit	Root	Leaf	Root	Leaf
Pb	4.613	2.349	0.236	6.121	2.961	0.605	7.261		6.124	3.487
Cd	0.255	0.053	0.032	0.673	0.152	0.083	0.982	0.593	0.286	0.062

Table 3. Heavy Metal Contamination of Plants taken from Station 2.

	June 2006		September 2006			January 2007		April 2007		
	Pepper		Pepper			Lettuce		Onion		
ppm in Dry Matter	Root	Leaf	Root	Leaf	Fruit	Root	Leaf	Root	Stem	Bulb
Pb	6.421	2.013	5.811	1.431	0.587	7.861	2.113	6.126	3.887	1.367
Cd	1.030	0.087	0.097	0.063	0.014	0.912	0.621	0.419	0.336	0.213

Table 4. Heavy Metal Contamination of Plants taken from Station 3.

	June 2006			September 2006			January 2007	April 2007		
	Wheat			Sunflower			Potato	Onion		
ppm in Dry Matter	Root	Leaf	Fruit	Root	Leaf	Fruit	Bulb	Root	Stem	Bulb
Pb	5.138	2.677	0.281	9.313	3.215	0.712	2.672	12.321	5.971	3.121
Cd	0.328	0.047	0.036	0.992	0.175	0.078	0.462	0.843	0.689	0.513

Table 5. Heavy Metal Contamination of Plants taken from Station 4.

	June 2006			September 2006			January 2007			April 2007		
	Wheat			Sunflower			Onion			Onion		
ppm in Dry Matter	Root	Leaf	Fruit	Root	Leaf	Fruit	Root	Stem	Bulb	Root	Stem	Bulb
Pb	6.892	2.976	0.331	7.846	3.231	0.748	15.372	7.336	4.586	11.762	6.871	3.112
Cd	0.302	0.053	0.031	0.473	0.093	0.072	0.936	0.627	0.471	0.641	0.327	0.299

Table 6. Heavy Metal Contamination of Plants taken from Station 5.

	June 2006		September 2006			January 2007		April 2007	
	Corn		Corn			Parsley		Lettuce	
ppm in Dry Matter	Root	Leaf	Root	Leaf	Fruit	Root	Leaf	Root	Leaf
Pb	5.865	2.799	3.013	1.168	0.223	3.293	2.323	8.074	3.517
Cd	0.452	0.072	0.407	0.068	0.025	0.412	0.396	0.791	0.501

Table 7. Heavy Metal Contamination of Plants taken from Station 6.

	June 2006			September 2006			January 2007		April 2007	
	Wheat			Sunflower			Wheat		Wheat	
ppm in Dry Matter	Root	Leaf	Fruit	Root	Leaf	Fruit	Root	Leaf	Root	Leaf
Pb	3.671	1.925	0.221	3.453	2.180	0.526	4.815	2.943	4.285	2.174
Cd	0.326	0.056	0.026	0.508	0.271	0.093	0.926	0.028	0.068	0.030

Table 8. Heavy Metal Contamination of Plants taken from Station 7.

	June 2006			September 2006			January 2007		April 2007	
	Wheat			Sunflower			Wheat		Wheat	
ppm in Dry Matter	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Root**	**Leaf**
Pb	5.823	2.647	0.256	6.185	2.751	0.652	6.472	3.875	6.180	3.094
Cd	0.437	0.061	0.040	1.230	0.112	0.087	0.851	0.159	0.735	0.130

Table 9. Heavy Metal Contamination of Plants taken from Station 8.

	June 2006			September 2006		January 2007		April 2007	
	Wheat			Parsley		Wheat		Wheat	
ppm in Dry Matter	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Root**	**Leaf**	**Root**	**Leaf**
Pb	5.021	2.235	0.248	6.732	2.013	5.932	3.276	5.674	2.736
Cd	0.367	0.071	0.038	0.347	0.209	0.831	0.083	0.746	0.077

Table 10. Heavy Metal Contamination of Plants taken from Station 9.

	June 2006			September 2006			January 2007		April 2007	
	Wheat			Sunflower			Wheat		Wheat	
ppm in Dry Matter	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Root**	**Leaf**
Pb	10.231	2.847	0.373	12.331	4.027	0.692	14.247	4.129	12.762	3.320
Cd	0.623	0.091	0.048	0.934	0.106	0.081	0.734	0.099	0.672	0.096

Table 11. Heavy Metal Contamination of Plants taken from Station 10.

	June 2006			September 2006			January 2007		April 2007	
	Wheat			Sunflower			Wheat		Wheat	
ppm in Dry Matter	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Root**	**Leaf**
Pb	12.457	3.124	0.381	16.754	4.745	0.736	16.448	4.537	13.894	3.485
Cd	0.446	0.071	0.043	0.847	0.092	0.079	0.863	0.083	0.579	0.055

Table 12. Heavy Metal Contamination of Plants taken from Station11.

	June 2006			September 2006			January 2007		April 2007	
	Wheat			Sunflower			Wheat		Wheat	
ppm in Dry Matter	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Fruit**	**Root**	**Leaf**	**Root**	**Leaf**
Pb	12.652	3.427	0.383	17.834	5.019	0.754	14.892	3.942	13.847	3.573
Cd	0.459	0.068	0.045	0.638	0.116	0.088	0.674	0.087	0.612	0.059
Mean of stations 1										
Pb	7.388	2.689	0.301	9.979	3.516	0.678	10.467	3.783	8.966	3.124
Cd	0.393	0.063	0.037	0.786	0.139	0.082	0.813	0.089	0.528	0.072
Standart Deviation 1										
Pb	3.471	0.468	0.067	5.21	0.992	0.08	5.256	0.581	4.304	0.51
Cd	0.112	0.014	0.008	0.261	0.061	0.007	0.093	0.042	0.256	0.033

and in leaves of lettuce and parsley compared to the grains of cereals (wheat and corn) and seeds of sunflower. Pb accumulation order was onion > potato > lettuce > parsley > sunflower > pepper > wheat corn; and Cd accumulation order as lettuce > potato > onion > parsley > sunflower > wheat > corn > pepper.

DISCUSSION AND CONCLUSIONS

In recent years serious environmental pollution has been experienced in Çorlu due to the rapid increase of population, unplanned industrialization and poorly-planned urbanization. Metal contamination of agricultural products can be affected by the geographical characteristics (soil structure and existence of surface waters such as lakes, ponds and rivers), climate conditions of the region and other activities performed in the areas where the plants are grown.

Within this framework, heavy metal contamination was detected in the plants grown in and in the surrounding's of Çorlu. Lead amounts exceeding the Turkish Food Codex limits have been detected in tuberous crops, leafy plants and in all cereals. The highest lead pollution has been recorded in onion while the lowest pollution has been observed in pepper. The major accumulation in cereals is observed in sunflower. Lead pollution is considered to result from the burning of fuels with Pb-alkyl additive used by vehicles; use of coals with high Pb content in industry for energy generation purposes; unconscious use of pesticides and fertilizers with Pb additive in agricultural lands; and irrigation with waste water. When we compare the cadmium concentrations in lettuce, potato, onion, parsley, sunflower, wheat, corn, pepper in fruit and vegetables with the limit of codex allimentarus, our results sometimes exceed the standards.

When we compare the lead concentrations in lettuce, potato, onion, parsley, sunflower, wheat, corn, pepper in fruit and vegetables with the limit codex allimentarus, our results sometimes exceed the standards.

- Cadmium amounts exceeding the Turkish Food Codex limits have been detected in all tuberous crops and leafy plants. The highest cadmium pollution has been recorded in lettuce while no cadmium pollution has been detected in wheat, sunflower, corn and pepper. The major accumulation in cereals is observed in sunflower. Cadmium pollution is considered as a result of the use of fertilizers with high Cd content; burning of solid and liquid fuels; and irrigation with waste water.
- While no considerable concentration differences have been observed in general during the winter, fall and summer months in terms of heavy metal amounts in plants, heavy metal concentration in plants has been recorded to follow root > leaf > fruit order.

In conclusion, lead and cadmium levels of the plant samples growing in plantation lands close to industrial facilities and heavy traffic of Çorlu have been found to be quite high. The rate of the samples exceeding the limits of the Turkish Food Codex is too immense to ignore. For this reason, heavy metal levels recorded in some edible plant samples have the potential to pose risks for public health.

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Table 5. Comparison of state-of-the-art matrix resins with VPSP/BMI copolymers.

Resin System	**Core Temp. (DSC peak)**	**T_E**	**Char Yield, %**
Epoxy (MY720)	235	250	30
Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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