Lead and other toxic metals in playground paints from south west England

Andrew Turner*, Emily R. Kearl & Kevin R. Solman

School of Geography, Earth and Environmental Sciences

Plymouth University

Drake Circus

Plymouth PL4 8AA

UK

*Corresponding author. Tel: +44 1752 584570; Fax: +44 1752 584710; e-mail: aturner@plymouth.ac.uk

Abstract

Paints on surfaces of public playground structures in south west England have been analysed for Pb, Cr, Cd and Sb by field-portable, energy-dispersive XRF. Lead was detected (> 8 $\mu g\ g^{-1}$) in 102 out of 242 cases, with concentrations ranging from 10 to 152,000 $\mu g\ g^{-1}$ (median = 451 $\mu g\ g^{-1}$). Chromium was detected (> 25 $\mu g\ g^{-1}$) in 48 cases, and concentrations ranged from 26 to 24,800 $\mu g\ g^{-1}$ (median = 1,040 $\mu g\ g^{-1}$) and exhibited a significant positive correlation with Pb concentrations. Antimony concentrations ranged from 273 to 16,000 $\mu g\ g^{-1}$ (median = 2,180 $\mu g\ g^{-1}$) in 56 detectable cases, and Cd was detected in eight paints and up to a concentration of 771 $\mu g\ g^{-1}$ (median = 252 $\mu g\ g^{-1}$). The highest concentrations of Pb, Cr and Sb generally occurred in yellow or red paints but were encountered on a variety of structures and equipment (e.g. gates, flooring lines, railings and handles of climbing frames and seesaws, and the interior of a model train) and were observed in both flaking, extant paint and in formulations that appeared to have been recently applied. Maximum bioaccessible concentrations of Pb, Cr and Sb in a range of paints, evaluated in selected samples by ICP analysis following pepsin-dilute HCl extraction, were 2,710, 205 and 23.6 $\mu g\ g^{-1}$, respectively, or 16.6, 2.25 and 0.56% of the respective total concentrations. Total and bioaccessible concentrations of toxic metals in playground paints that exceed various contemporary and historical standards (and in many cases for Pb, by orders of magnitude) is likely to be a more widespread and pervasive issue that needs addressing by the relevant authorities.

Keywords: playgrounds; paint; lead; chromium; health; children

1. Introduction

Many non-essential metals and metalloids (hereafter referred to as toxic metals) are of concern because of their adverse effects on human health coupled with increasing anthropogenic emissions to and dispersion throughout the environment. The toxicity of a metal may be effected by mimicking an essential element or through interference with some metabolic process, and is largely dependent upon concentration (or, strictly, its soluble or accessible concentration). However, chronic exposure to relatively low levels of many metals can also result in bioaccumulation and a variety of diseases, disorders, impairments and organ malfunctions (Ayres and Hellier, 1998).

One important route of exposure of metals and cause of intoxication among humans, and in particular young children, is the inhalation and ingestion of paint dusts (Mielke et al., 2001; Su et al., 2002; Turner and Sogo, 2012). Toxic metals and their compounds have had (and in many cases continue to have) a variety of uses in many paints as, for example, drying agents, preservatives, fire retardants, corrosion inhibitors and pigments for colour or opacity (Abel, 2000). While undisturbed and intact, coatings and their chemical components are relatively safe. However, once the film begins to deteriorate through abrasion or as the binder and pigments degrade via exposure to UV light and moisture, the paint begins to crack, flake and chalk and metal-bearing particulates are mobilised into the environment. The principal metals of concern in this respect, and that have undergone restriction in many paints (including consumer formulations) over the past few decades, are lead, (hexavalent) chromium, arsenic, cadmium, mercury and antimony. The former in particular has been used extensively in paints and is often combined with hexavalent Cr, itself a genotoxic carcinogen, as a series of lead chromate pigments. Lead concentrations in the dry films of various paints have often been reported to be greater than 10% (Gottesfeld et al., 2014; Turner et al., 2014) and in some cases exceed 30% (Martinez, 2000; Mielke and Gonzales, 2008).

The effects of Pb on human health, including those that impact on the neurological development of children, are well-documented with regard to paint exposure in the urban and domestic settings (Farfel et al., 2005; Schwab et al., 2006; Le Bot et al., 2011; Laidlwa et al., 2014). Very little attention has, however, been paid to the routes and degrees of Pb (and other metal) exposure in children arising from paints in public playgrounds (Taraoka et al., 2006; Mathee et al., 2009). This is, perhaps, surprising, since young children are in regular contact with painted surfaces of playground equipment through climbing, crawling, gripping and swinging. In the present study, therefore, we measure the concentrations of Pb, Cr, Cd and Sb in paints on a wide range of structures and equipment in different public playgrounds in south west England. We use a field-portable x-ray fluorescence (FP-XRF) spectrometer on painted surfaces in situ and on paint flake samples returned to the laboratory, with the latter also being subjected to a physiological extraction and independent analysis in order to evaluate the oral bioaccessibilities of the metals.

2. Materials and methods

2.1. Sampling and sample locations

A total of 47 playgrounds within five administrative regions (County or District Councils) in south west England were visited between September 2014 and June 2015. Specifically, 20 playgrounds were visited in the city of Plymouth (population ~ 250,000), 14 in the South Hams district of Devon, six in the county of Cornwall, five in the Sedgemoor district of Somerset, and two in the New Forest district of Hampshire. In each playground, painted structures (entrance gates, benches, shelters and tarmacked flooring) and play equipment (including swings, slides, roundabouts, ramps, climbing frames, see-saws, rockers and goal posts) were inspected, photographed, colour-coded and categorised. XRF analysis was performed in situ or in the laboratory depending on the condition of the painted surface. Thus, where paint was visibly flaking, samples, with one dimension of at least 3 mm, were taken using a pair of stainless steel tweezers and stored individually in zip-lock specimen bags in a polyethylene box and returned to the laboratory. Paint was either taken from the structure itself, taking care not to disturb the integrity of remaining paint, or from fragments that had accumulated at the base of the installation. Where paint had been newly applied or was not possible to dislodge from its substrate with tweezers, the surface was measured with the XRF on site.

2.2. XRF analysis

The outer surfaces of the paint samples and painted structures were analysed for Pb, Cr, Cd and Sb by energy dispersive FP-XRF using a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+) in 'plastics' mode. Although the XRF has 'lead-in-paint' and 'thin film' modes that are often used to analyse paints, the mode for plastics is capable of handling thin sections through a sample thickness correction algorithm and has the advantage of providing concentrations of Pb and other elements on a dry weight basis rather than on an areal (mg cm^{-2}) basis.

For in situ measurements (n = 102), a smooth area of the painted surface was wiped clean and dry using a medical-grade wipe. The XRF nose, including the measurement window and proximity sensor, was then positioned firmly against an area of 8 mm in diameter and the surface analysed for a period of 200 seconds (100 seconds each for the main and low energy ranges) by depressing the trigger mechanism. Spectra up to 50 keV were quantified by standardless analysis after applying a thickness correction of 50 μm to yield metal concentrations in the dry film in parts per million (μg g^{-1}) and with an error of 2σ (95% confidence). Data were subsequently transferred to a laptop computer in the laboratory using Niton data transfer (NDT) PC software.

For the analysis of paint samples in the laboratory (n = 140), the XRF was secured into a bench top accessory stand and connected to a laptop via USB and a remote trigger. Samples were placed on to a SpectraCertified Mylar polyester 3.6 μm film using a pair of tweezers and with the outer face downwards before the slide was positioned centrally over a 3 mm small-spot collimator above the XRF detector. Measurements were activated through the laptop under conditions identical to those described above and with concurrent transfer of data through the NDT software.

The detection limits of the XRF are dependent on a number of factors, including the element, mode of application, measurement time, composition and thickness of material, effective diameter of the detector and presence and nature of a substrate. Furl et al. (2012) suggest that a measurement detection limit of the Niton XL3t can be approximated by multiplying the counting error by 1.5, and on this basis, and for the lowest three values of 2σ reported for samples that were detectable, we estimate detection limits for paint samples and painted surfaces (in μg g^{-1}) of around 8, 25, 40 and 70 for Pb, Cr, Cd and Sb, respectively. It is worth noting that Hg was not detected in the samples and that while As often returned a result, inspection of the spectra usually revealed significant overlap of its principal peak ($K_{\alpha 1}$ at 10.544 KeV) with one of the main Pb peaks ($L_{\alpha 1}$ at 10.551 KeV).

As a calibration-accuracy check, two Niton reference polyethylene discs, 31 mm in diameter and 13 mm thick and that had been impregnated with various elements, were analysed in quintuplicate without thickness correction. Thus, measured concentrations (in μg g^{-1}) of Pb, Cr and Cd in PN 180-554 (batch SN PE-071-N) were 944±12, 1090±12 and 139±5, compared with respective reference values of 1002±40, 995±40 and 150±6, while measured concentrations (in μg g^{-1}) of Pb, Cr, Cd and Sb in PN 180-619 (LOT#T-18) were 143±6, 124±3, 262±7 and 88±11, compared with respective reference values of 155±12, 106±10, 292±20 and 94±10.

Since metals were measured both on painted surfaces in situ and on samples returned to the laboratory, a comparison between the two approaches was made on a number of surfaces where intact areas were adjacent to visibly flaking areas. Despite possible differences between adjacent regions in terms of thickness of paint application, exposure of underlying paint layers and degree of corrosion, coupled with any potential confounding effects associated with the underlying substrate itself, good agreement was observed between concentrations across a range of surfaces and concentrations. Thus, for Pb, Cr, Cd and Sb data combined: [ex situ] = 1.19* [in situ] (r = 0.925, n = 18). Note that where painted surfaces were measured both in situ and in the laboratory, averaged concentrations are reported in the results.

2.3. Physiological extraction of paint samples

Where sufficient material was collected, selected samples (n = 11) were extracted in a physiological solution in order to evaluate the oral bioaccessibilities of the metals. Thus, between 50 and 150 mg of samples that had been ground to < 2 mm in an agate pestle and mortar were accurately weighed into individual 15 ml screw-capped polyethylene centrifuge tubes to which 10 ml aliquots of a solution of 2 g pepsin (from porcine gastric mucosa; Sigma Aldrich) in 0.075 M HCl (Fisher Scientific TraceMetal grade) were added. The tubes were capped and secured in a lateral shaker that was set at 100 rpm while immersed in a water bath at a temperature of 37 ^{o}C. After 2 h, paint particles were allowed to settle out of suspension for a few minutes before 5 ml aliquots of the extracts were transferred to new centrifuge tubes pending analysis. Controls were performed in triplicate under the same conditions but in the absence of paint.

2.4. Extract analysis

Lead, Cr, Cd and Sb were analysed in the pepsin-HCl extracts by ICP-optical emission spectrometry (ICP-OES) using a Varian 725-ES (Mulgrave, Australia). The power was set at 1.4 KW, and plasma, auxiliary and nebuliser flows (in L min^{-1}) were 15, 1.5 and 0.68, respectively. Samples were introduced via a Sturman-Masters spray chamber and V-groove nebuliser and measurements were made with a replicate read time of 2 s and at a viewing height of 8 mm above the load coil at resonance lines of 220.353 nm for Pb, 283.563 nm for Cr, 228.802 nm for Cd and 217.581 nm for Sb. Calibration was achieved using five mixed standards (and a blank) prepared by serial dilution of SPEX CertiPrep plasma emission solutions in 0.1 M HCl. Detection limits, in μg L^{-1} and based on 3σ of multiple analyses of the controls, were about 20 for Pb, 5 for Cr, 10 for Cd and 35 for Sb.

Table 1: Classification of the playground structures (and components thereof) and distribution of paint colours. Note that blue includes purple, green includes turquoise, grey includes silver and yellow includes orange.

	black	blue	brown	green	grey	red	white	yellow	no. analyses
support	6	22	3	17	2	35	1	10	**96**
railing		15		20	2	19	1	16	**73**
handle		4		3		4	1	5	**17**
seat	1	1	1	5	1	5	1	3	**18**
interior				2		2		2	**6**
gate	1			1	1	9		8	**20**
games				3	1	2	5	1	**12**
total	**8**	**42**	**4**	**51**	**7**	**76**	**9**	**45**	**242**

3. Results and Discussion

3.1. Structure description and classification

In total, 242 analyses were performed on paint samples from, or painted surfaces of, 140 different structures. With the exception of seven wooden components of two frame-slide constructions and two lines painted on tarmacked flooring, all substrates were metallic.

Table 1 shows the colour distribution of paints among seven different categories of structure-equipment (or components thereof) that are based on the likelihood and nature of contact with a child. Regarding colours, red, green, yellow and blue were most abundant, with all but the latter being encountered in every structural category. With respect to structure, 'support' refers to any supporting element (frame, panel, flooring, roofing, steps) of a construction like a swing, slide, ramp, climbing frame, see-saw or roundabout that, while not designed for direct contact with children, is likely to result in occasional encounters. 'Railing' denotes a component that is used by a child to aid their support, balance or ascent-decent of a structure and that is likely to be in common but intermittent contact with a child's hands. 'Handle' refers to a component that is designed for a child to hold on to or grip and that necessitates contact that is either prolonged (e.g. see-saw handle, monkey bars) or abrasive (e.g. fireman's pole). 'Seat' represents a structure or component of play equipment that is designed for a child to sit or rest on, thereby engaging contact with both hands and clothing, and includes purpose-built benches and the seats of see-saws and spring rockers. 'Interior' refers to a component of equipment that is designed for a child to crawl through, such as a model train or the tubing of a frame-slide construction, with contact likely on both hands and clothing but in a more abrasive manner than that effected by seating. By entering or leaving a playground, a child has occasional hand contact with a ‘gate’, and through ‘games’, a child may have occasional contact with basketball posts, skateboard ramps, football goals and painted lines.

3.2. Concentrations and distributions of Pb, Cr, Cd and Sb

Tables 2, 3 and 4 provide overall and category-specific summaries of the concentrations of Pb, Cr and Sb, respectively, in paints on the playground structures and equipment. Overall, Pb was detected (> 8 μg g^{-1}) in the most cases (102 out of 242 analyses) and in all structural categories, and the data exhibited positive skewness (+3.28) and excess kurtosis (12.1), with median and grand mean concentrations of 451 and 11,600 μg g^{-1}, respectively, and a range that spanned four orders of magnitude. Concentrations exceeded 10,000 μg g^{-1} (or 1 % by weight) in paints from all categories and exceeded 100,000 μg g^{-1} (or 10% by weight) in one railing paint and one gate paint. Based on category-specific medians, concentrations of Pb were greatest in interiors and lowest on supporting components. Lead was encountered in all colours but paints with concentrations of Pb in excess of 10,000 μg g^{-1} were mainly yellow (n = 7) or red (n = 9).

Chromium was detected (> 25 μg g^{-1}) in 48 cases and in all categories, with median and grand mean concentrations of 1,040 and 2,800 μg g^{-1}, respectively, and skewness (+3.36) and excess kurtosis (12.4) that were similar to respective values for Pb. The range in Cr concentrations spanned three orders of magnitude, with maximum concentrations in excess of 10,000 μg g^{-1} encountered in the same railing and gate paints that contained the greatest Pb concentrations. Category-specific medians were greatest for gates and lowest for railings, despite the highest measured concentration overall in the latter category. As with Pb, the highest concentrations of Cr were generally associated with red or yellow paints; specifically, when ranked according to Cr concentration, the top 16 paints were either red (n = 8) or yellow (n = 8), with blue, green, black and white paints making increasing representations with decreasing rank order.

Antimony was detected (> 70 μg g^{-1}) in 56 cases and in all categories, but concentrations spanned less than two orders of magnitude and skewness (+2.46) and excess kurtosis (6.71) were considerably lower than the respective values for Pb and Cr. Consequently, overall median and grand mean concentrations (2,180 and 2,950 μg g^{-1}, respectively) were relatively close and category-specific median concentrations were rather similar across the different structures. Although Sb concentrations above 10,000 μg g^{-1} were associated with red or yellow paints, they were not the same paints that had the highest concentrations of Pb or Cr; rather, three of these paints had no detectable Cr and Pb was only above 1,000 μg g^{-1} in one case. Overall, Sb was largely distributed among red (n = 23), yellow (n = 17) and green (n = 12) paints, and was never detected in black, brown, white or grey formulations.

Cadmium was only detected (> 40 μg g^{-1}) in eight paints and its distribution among the different categories is not tabulated. Concentrations ranged from 140 to 771 μg g^{-1}, with a median and grand mean of 252 and 314 μg g^{-1}, respectively. Detectable Cd was not associated with particularly high concentrations of Pb, Cr or Sb, but was limited to yellow, red and green paints on supporting structures, railings and handles.

Table 2: Distribution and summary statistics for Pb concentrations ($\mu g\ g^{-1}$) in paints among the different structural categories measured.

	no. detected	$< 10^2$	10^2-10^3	10^3-10^4	10^4-10^5	$>10^5$	min.	max.	median
support	34	8	18	3	5		30	46,500	278
railing	29	8	14	3	3	1	34	129,000	258
handle	10		5	2	3		137	89,300	932
seat	5	1		3	1		72	13,500	2,880
interior	6		2		4		244	50,000	26,200
gate	14	1	6	3	3	1	27	152,000	2,040
games	4	1		1	2		10	99,800	8,970
total	**102**	**19**	**45**	**15**	**21**	**2**	**10**	**152,000**	**451**

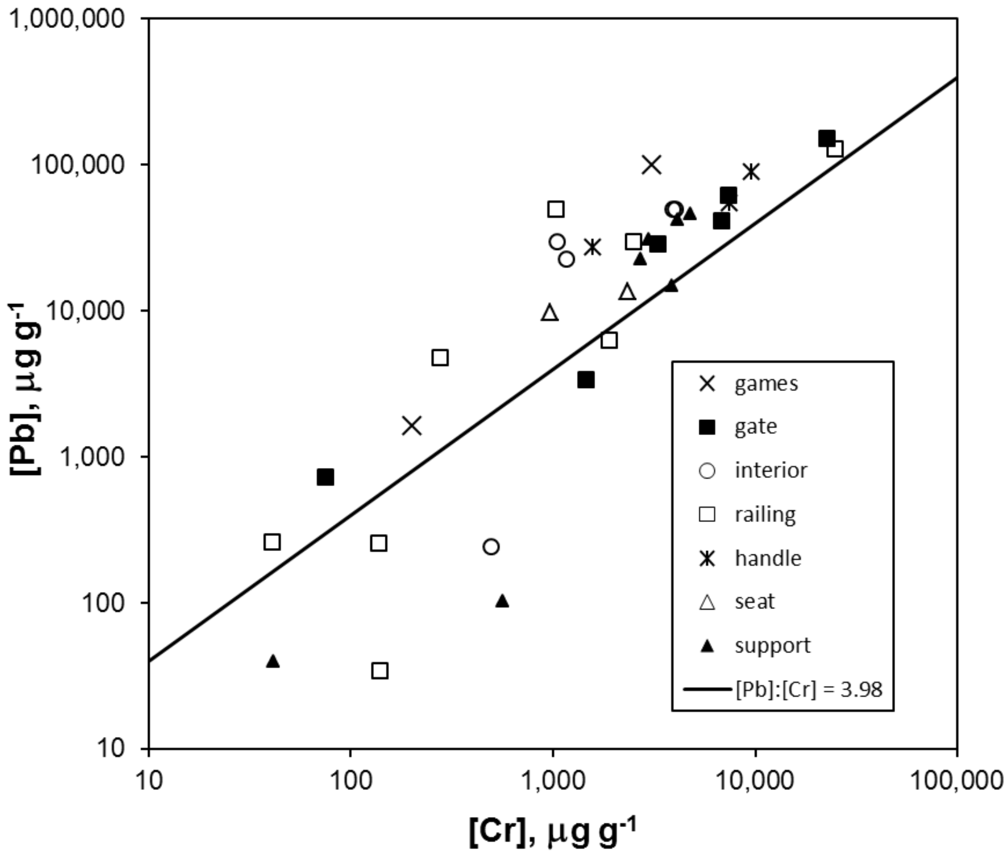
Table 3: Distribution and summary statistics for Cr concentrations ($\mu g\ g^{-1}$) in paints among the different structural categories measured.

	no. detected	$< 10^2$	10^2-10^3	10^3-10^4	10^4-10^5	$>10^5$	min.	max.	median
support	10	3	1	6			37	4,810	2,270
railing	15	5	6	3	1		26	24,800	139
handle	4			4			1,580	9,590	5,400
seat	3		2	1			410	2,330	964
interior	5		1	4			412	4,020	1,170
gate	8	2	1	4	1		42	22,700	2,380
games	3	1	1	1			70	3,080	202
total	**48**	**11**	**12**	**23**	**2**		**26**	**24,800**	**1,040**

Table 4: Distribution and summary statistics for Sb concentrations ($\mu g\ g^{-1}$) in paints among the different structural categories measured.

	no. detected	< 10^2	10^2-10^3	10^3-10^4	10^4-10^5	>10^5	min.	max.	median
support	12		3	8	1		767	10,200	2,760
railing	20		8	11	1		273	12,000	1,460
handle	5		1	4			313	4,620	2,260
seat	3		2	1			590	2,220	979
interior	6		1	5			460	4,230	2,450
gate	9		2	5	2		478	16,000	2,660
games	1			1			1,260	1,260	1,260
total	**56**		**17**	**35**	**4**		**273**	**16,000**	**2,180**

Figure 1: Concentrations of Pb versus concentrations of Cr in the paints on the different structures (and as categorised). Note, the line represents the mass ratio of Pb to Cr in lead chromate.



3.3. Relationship between Pb and Cr

Given the similarities in the distributions of Pb and Cr concentrations among the paints noted above, the relationship between these two metals was investigated further. Figure 1 shows a scatter plot of Pb concentration versus Cr concentration for all cases in which both metals were detected, and distinguishes the data according to structural category type. Overall, there was a significant ($p < 0.05$) correlation between the metals (Pearson's $r = 0.842$; $n = 32$), with a slope (m) defining the best fit line forced through the origin of 6.78; among the different categories, the strongest correlation between Pb and Cr was for the gates ($r = 0.992$; $n = 6$; $m = 6.83$). Also shown in Figure 1 is the mass ratio of Pb to Cr in lead chromate ($PbCrO_4$ = 3.98), a colour pigment that was commonly employed in paint formulations, by itself or as a mixed phase, to effect a range of yellows, red and greens (Abel, 2000). Since the data lie reasonably close to the line of slope 3.98 and most of the points define paints that are red, yellow or green, we may infer that lead chromate is a significant source of Pb and Cr in many playground paints analysed. On this basis, points lying below the line and the general dispersion among the data may be attributed to the heterogeneous but preferential weathering and dissolution of Pb over Cr from $PbCrO_4$-based pigments (White et al., 2014). Points lying above the line, and paints in which Pb was detected but Cr was not (and vice versa), require the presence of additional (or alternative) pigments, including those used for opacity or corrosion inhibition, with different Pb to Cr ratios or which contain just one of the two metals.

3.4. Bioaccessibilities of Pb, Cr and Sb

Table 5 shows the results of the extractions of various paints samples by the physiological solution (pepsin in dilute HCl). Here, the concentrations of extractable

Pb, Cr and Sb are shown on a dry weight basis (μg g^{-1}) along with total concentrations determined by XRF analysis, and results are ordered according to total Pb concentration. Note that cells have been left blank where the trace metal was not detected by XRF or in the physiological extract, and that no paint samples contained Cd that was detectable by XRF. Also shown in the table are the oral bioaccessibilities of Pb, Cr and Sb, defined as extractable concentrations relative to corresponding total concentrations and on a percentage basis. Regarding Pb, extractable concentrations ranged from less than 1 μg g^{-1} in red and green paints from different components of separate climbing frames, to about 2,700 μg g^{-1} for white paint on a small (1 m high) goal post. Extractable concentrations of Pb were not, however, correlated with corresponding total concentrations, with the result that oral bioaccessibility varied among the samples; specifically, accessibility spanned two orders of magnitude from less than 0.1% in blue and red paints from the handle and support of separate climbing frames to 16.6 % for the white paint on the aforementioned goal post. Although total Cr and Pb concentrations were significantly correlated ($p < 0.05$) among the samples, extractable Cr was not correlated with extractable Pb, with bioaccessible Cr ranging from less than 0.1 % on green interior paint from a frame-slide complex to 2.25 % for yellow paint from the same structural component. These observations suggest that while Pb and Cr in brightly coloured paints containing both elements (e.g. as lead chromate) have variable, but limited, oral bioaccessibilities, Pb in paints without Cr (for example, as white lead, $2PbCO_3 \cdot Pb(OH)_2$), is considerably more accessible. With respect to Sb, the metalloid was detected by XRF in the six samples with the highest Pb and Cr concentrations but extractable Sb was only detected in three cases, with bioaccessibilities that were between about 0.3 and 0.5 % and that was greatest for the sample displaying the highest Cr accessibility.

3.5. Comparison of concentrations and accessibilities with relevant regulations and guidelines

A 1977 EC Directive required that all paints containing more than 5,000 $\mu g\ g^{-1}$ Pb should be labelled with a warning that they must not be applied to surfaces likely to be chewed or sucked by children, a concentration that was subsequently regarded as an international ‘safety level’ in both the domestic setting and urban environment (Horner, 2004). Regarding guidance specific to playgrounds, European Standards BS EN 1176 and BS EN 1177, harmonising earlier guidelines from Britain (BS 5696), France and Germany, recommend that new paint is lead-free or contains less than 2,500 $\mu g\ g^{-1}$ in the dry film; for older, lead-based paints in poor condition, it is recommended that the surface is stabilised, coated with a non-lead-based paint and monitored for subsequent deterioration (RoSPA, 2004). In the US, the Consumer Product Safety Commission (1996), while banning the sale of paint containing in excess of 600 $\mu g\ g^{-1}$ Pb at the time, adopted a 5,000 $\mu g\ g^{-1}$ limit for playground coatings according to the Residential Lead-Based Paint Hazard Reduction Act (enacted in 1992). For coatings exceeding this threshold, the Commission recommended interim measures that included covering the paint with unleaded paint, and permanent measures that included replacement of the equipment or removal of the leaded paint.

Table 5: Total (XRF) and physiologically-extractable Pb, Cr and Sb concentrations in selected paints sampled from a variety of structures in different playgrounds. BA refers to oral bioaccessibility and is derived from the ratio of extractable to total concentration in each case, and figures in bold represent the maximum values for each column.

		Pb			Cr			Sb		
structure	colour	XRF, μg g^{-1}	extractable, μg g^{-1}	BA, %	XRF, μg g^{-1}	extractable, μg g^{-1}	BA, %	XRF, μg g^{-1}	extractable, μg g^{-1}	BA, %
railing (ramp)	yellow	**129,000**	194	0.15	**24,800**	**205**	0.82	**6,080**		
interior (frame-slide complex)	yellow	50,000	566	1.13	4,020	90	**2.25**	4,230	**23.6**	**0.56**
support (ramp)	red	42,000	220	0.52	4,180	82	1.95	2,560		
gate	red	41,400	143	0.35	6,780	16.8	0.25	4,110	12.8	0.31
interior (frame-slide complex)	green	29,600	774	2.61	1,050	0.93	0.09	2,840	9.25	0.33
handle (climbing frame)	blue	27,100	21	0.08	1,580	5.14	0.33	313		
games (goal post)	white	16,300	**2,710**	**16.6**						
railing (climbing frame)	green	277	0.79	0.28						
support (climbing frame)	red	467	0.43	0.09						
support (swings)	red	40	1.44	3.61	42					

Figure 2: A ramp structure in a Plymouth playground, date stamped March 2009, that contained Pb, Cr and Sb at concentrations of 129,000 $\mu g\ g^{-1}$, 33,800 $\mu g\ g^{-1}$ and 6,080 $\mu g\ g^{-1}$, respectively, in the yellow railing paint (a), and concentrations of 42,000 $\mu g\ g^{-1}$, 5,050 $\mu g\ g^{-1}$ and 2,560 $\mu g\ g^{-1}$, respectively, in the red support frame coating (b).

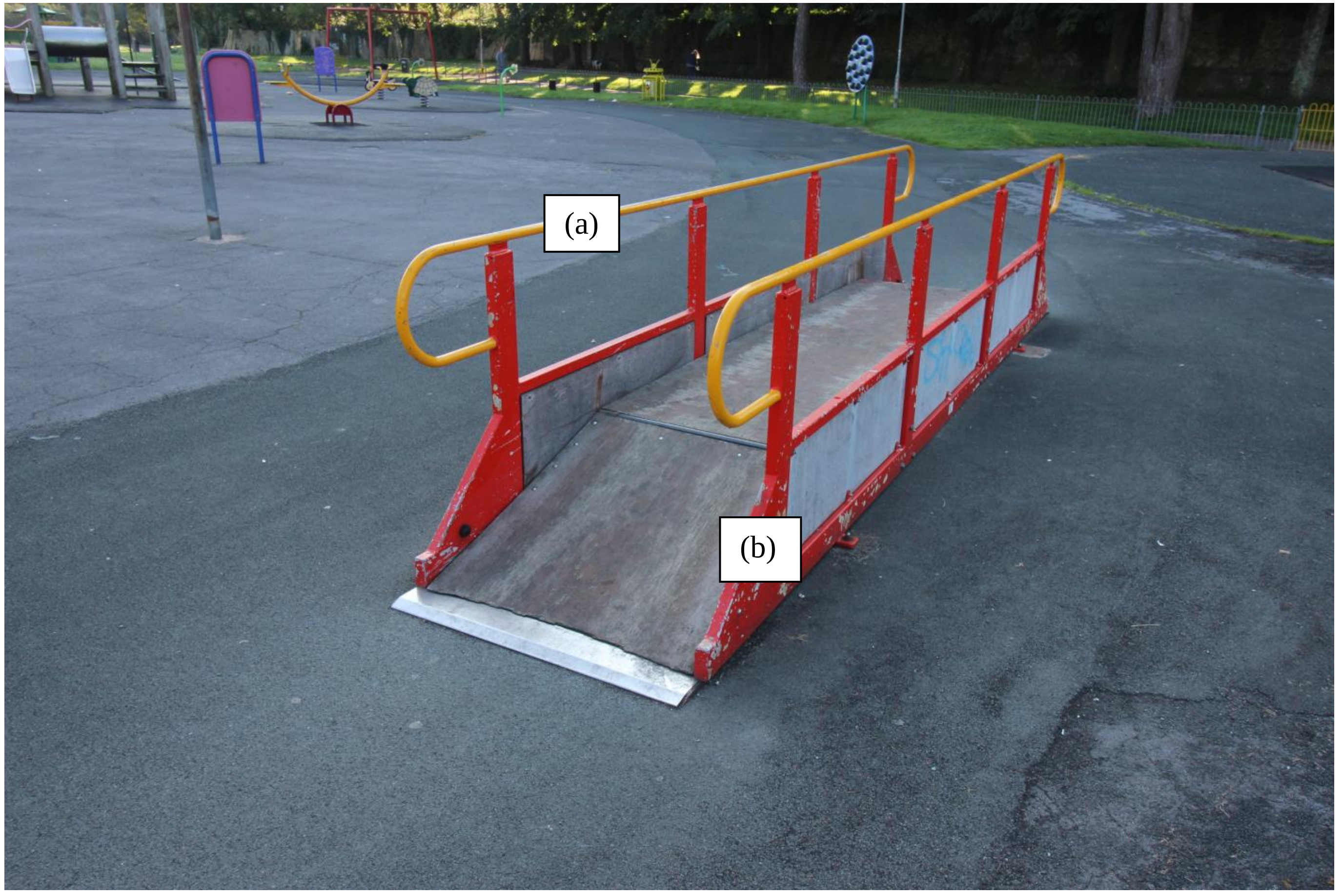
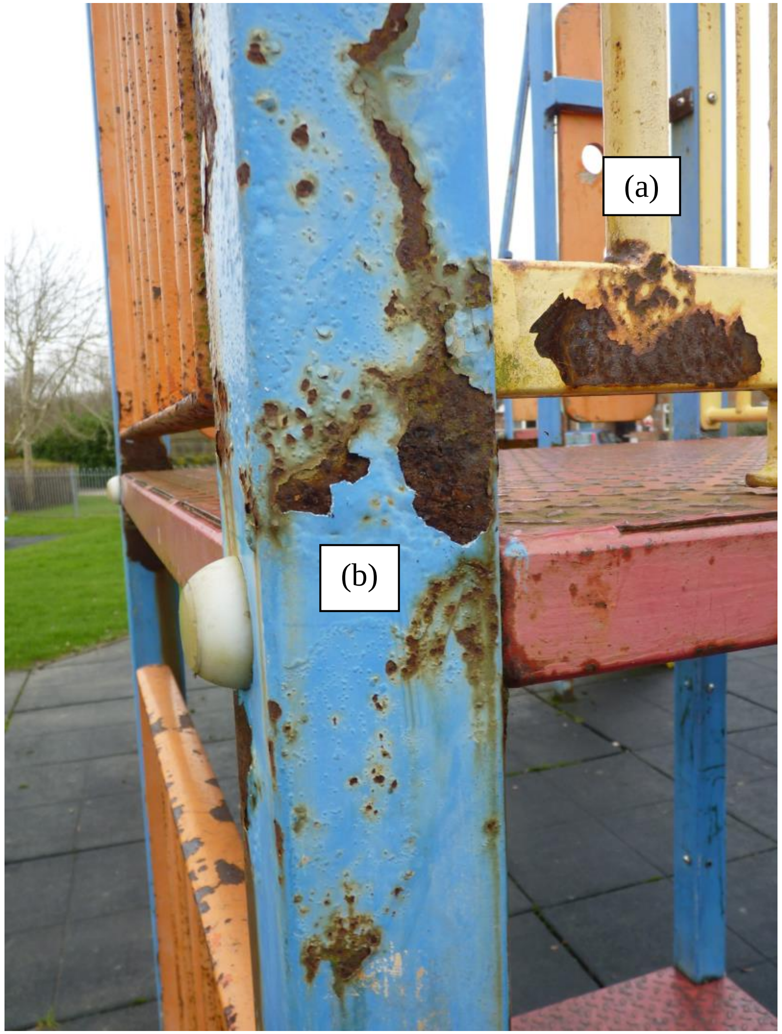


Figure 3: Poorly maintained paint on a frame-slide complex in a playground in Pennington. The yellow railing paint (a) contained Pb, Cr and Sb at concentrations of 89,300 μg g^{-1}, 9,590 μg g^{-1} and 4,340 μg g^{-1}, respectively, while the blue frame (and handle) paint (b) contained Pb and Cr at concentrations of 27,100 μg g^{-1} and 1,580 μg g^{-1}, respectively.



More recently, general ‘safe’ limits on Pb concentrations in consumer paints have been revised downwards and, although there are no health-based standards for lead concentrations in paint, the international consensus is that paints without added Pb compounds should have concentrations of less than 90 $\mu g\ g^{-1}$ (Kessler, 2014). It is also worth noting that the Global Alliance to Eliminate Lead Paint (GAELP) has a goal of eradicating Pb in paint by 2020 (UNEP/WHO, 2011), and that, since May 2015, lead chromate pigments have been banned from use in the EU unless application had been granted before November 2013 (FIRA, 2012).

Lead and other toxic metals are also regulated in toys and all products intended for use by children. For example, ATSM F963 and the US Consumer Product Safety Improvement Act require that products designed or intended mainly for use by children under 12 years of age contain no more than 100 $\mu g\ g^{-1}$ Pb in any accessible component and that the maximum concentration of Pb in paint or surface coating on such products must not exceed 90 $\mu g\ g^{-1}$ (Mercan et al., 2015). The European Standard for safety of toys, EN 71-3:1994, which also has the status of a British Standard (BSI, 1995), provides figures for the maximum migration (or bioavailability, in μg) of metals and metalloids on a daily basis (including 0.7 for Pb, 0.3 for Cr, 0.6 for Cd and 0.2 for Sb). Figures are based on the assumption of an ingestion rate of 8 mg per day and are equivalent to maximum migratable concentrations on a weight basis of 90, 60, 75 and 60 $\mu g\ g^{-1}$ for Pb, Cr, Cd and Sb, respectively.

The results of the present study are both surprising and concerning in that metals (and in particular, Pb and Cr) and chemicals (e.g. lead chromates) that have been phased out, restricted or banned are so prevalent in paints on play equipment facilities and other structures used by young children in contemporary playgrounds in the UK. Thus, with respect to Pb, 26 paints on playground structures exceeded 5,000 $\mu g\ g^{-1}$ on a dry weight basis, despite being sampled-analysed nearly forty years after the implementation of the 1977 EC Directive; 33 paints exceeded the 2,500 $\mu g\ g^{-1}$ European standard specifically recommended for playgrounds, and 86 paints exceeded the current consensus concentration of 90 $\mu g\ g^{-1}$. Based on the results of the physiological extractions of eleven paints in the current study (Table 5), six samples exceeded the European threshold for maximum migratable Pb and three samples exceeded the respective limit for Cr.

One of the biggest concerns of the present study was play equipment that had evidently been installed or repainted relatively recently but that contained concentrations of Pb in surface coatings that far exceed any current or historical limits. For example, among the structures analysed, a ramp that contained the second highest concentration of Pb (129,000 $\mu g\ g^{-1}$ on its painted railing), as well as the highest concentration of Cr (> 10,000 $\mu g\ g^{-1}$ in the same paint) was date stamped March 2009 (Figure 2). Although it is unclear whether this specific structure was painted before being shipped and secured at its current location or painted after being installed, the recent application of hazardous formulations on public equipment designed for children requires prompt investigation and remediation by the appropriate authorities and suppliers.

3.6. Comparison with earlier studies

Although the present study appears to represent the first published investigation of toxic metals in playground paints in the UK, and indeed in Europe, investigations of Pb in playground paints in a number of other countries have reported similar findings, suggesting that the problem is generic, widespread and pervasive. For example, in the US, the Consumer Product Safety Commission (1996) assessed 26 playgrounds in 13 cities and found that equipment from 16 playgrounds had Pb concentrations in surface coatings in excess of 5,000 $\mu g\ g^{-1}$ by weight. Additional studies undertaken by state and local authorities revealed that paint on equipment from 125 playgrounds in 11 additional cities had Pb concentrations ranging from 900 to 290,000 $\mu g\ g^{-1}$. Mathee et al. (2008) measured Pb in paint from 49 playgrounds in central South Africa and found variable concentrations up to 10.4 mg cm^{-2} (equivalent to > 50,000 $\mu g\ g^{-1}$ on a weight basis), while Takaoka et al. (2006) found that paint chips from playgrounds in Tokyo were as high as 89,000 $\mu g\ g^{-1}$. In a Canadian disease report (Health Canada, 1984; see below), Pb concentrations measured in paint chips sampled from a park in the Montreal region ranged from about 100 to 100,000 $\mu g\ g^{-1}$.

3.7. Factors affecting risk of paint ingestion and Pb intoxication

Given that the total tolerable daily intake of Pb for a child under six years of age is 6 μg (Mielke et al., 2001), the results of this study suggest that the ingestion of as little as 60 μg of paint is required to exceed this limit. Despite this quantity, however, it is important to appreciate that the overall risks and hazards associated with metals in paints are dependent on a number of additional factors. For example, paint that is visibly chalking, cracking and peeling is more susceptible to being deliberately or inadvertently handled, ingested or chewed by a child and more liable to contaminate the playground flooring and local soil than coatings that are intact. Moreover, surfaces that engage friction or impact with children, such as railings, rungs, poles and handles, will increase the overall contact with paint while accelerating the deterioration of a flaking surface and the generation of inhalable and ingestible paint dust (Dixon et al., 2007).

In the current study, the apparent age and visible condition of the structure or painted surface was not a good indicator of the concentrations of the hazardous elements in the paints. Thus, coatings that were in a poor state of repair and with visible accumulations of paint on the ground sometimes contained no measurable Pb, Cr, Cd or Sb, but in other cases, and as exemplified in Figure 3, contained one or more elements at concentrations among the highest recorded for the corresponding structural category. Likewise, paint on the newest structures or that appeared to have been recently applied contained highly variable concentrations of Pb, Cr, Cd and Sb, including those among the highest recorded (Figure 2).

Because of their tendency to mouth non-food objects and absorb relatively high proportions of ingested Pb in their gastro-intestinal tract, children under six years of age, and in particular those under 72 months old, are at significantly greater risk of Pb poisoning than older children (Kennedy et al., 2014). While it is difficult to attribute poisoning directly to paint on playground equipment because the effects of Pb are cumulative and children may be exposed to a multitude of sources of Pb in the domestic and urban settings, it is worth citing a case described in a disease report published by Health Canada (1994). Thus, a 5-year old boy undergoing assessment for autistic behaviour was found to have elevated blood level Pb and paint chips in his intestines. His mother revealed that he would occasionally eat paint flakes stripped or bit from metallic playground equipment. Subsequent measurements of paint samples revealed Pb concentrations of less than 600 $\mu g\ g^{-1}$ in the family apartment but concentrations up to 100,000 $\mu g\ g^{-1}$ on playground structures, strongly suggesting that the latter were the source of the child's intoxication.

3.8. Recommendations

Based on recommendations provided by various authorities and international standards, we suggest the following regarding paint on equipment and structures in children's playgrounds:

1. Surfaces should be monitored regularly for condition, and in particular for flaking and cracking paint; if Pb cannot be measured, the safest option is to assume that Pb, and likely Cr, are present
2. Paint in poor condition should be carefully removed and structures stabilised and repainted with Pb-free paint, or equipment replaced
3. Stricter controls should be applied to domestic and imported paints used for playgrounds, and for equipment that is pre-painted before installation
4. Parents should be made aware of the dangers of children sucking or biting painted surfaces or ingesting paint chips.

Acknowledgements

We acknowledge the support of Mr Joe Levermore, Mr Andy Arnold and Dr Andrew Fisher (UoP) during sampling and analysis of the play-park paints. This study was funded partly by a UoP Marine Institute grant.

References

Abel, A.G., 2000. Pigments for paint. In: Paint and Surface Coatings: Theory and Practice (ed. R. Lambourne and T.A. Strivens). Woodhead Publishing, Cambridge, UK, pp.91-165.

Ayres, D.C., Hellier, D.G., 1998. Dictionary of important chemicals. Blackie Academic and Professional, London, 332pp.

BSI, 1995. Safety of toys – part 3: Migration of certain elements. British Standard BS EN 71-3:1995, London.

Consumer Product Safety Commission, 1996. Recommendations for Identifying and Controlling Lead Paint on Public Playground Equipment. US CPSC, Washington, 12 pp.

Davies, R., Heseltine, P., 2008. An essential guide to BS EN 1176 and BS EN 1177: Children's playground equipment and surfacing. Wicksteed, Kettering, UK, 20pp.

Dixon, S., Wilson, J., Galke, W., 2007. Friction and impact surfaces: Are they lead-based paint hazards? Journal of Occupational and Environmental Hygiene 4, 855-863.

Farfel, M.R., Orlova, A.O., Lees, P.S.J., Rohde, C., Ashley, P.J., Chisholm Jr, JJ., 2005. A study of urban housing demolition as a source of lead in ambient dust on sidewalks, streets, and alleys. Environmental Research 99, 204-213.

FIRA, 2012. REACH substance sheet 4: lead chromate and related derivatives. FIRA International, Stevenage, UK.

Furl, C., Mathieu, C., Roberts, T., 2012. Evaluation of XRF as a screening tool for metals and PBDEs in children's products and consumer goods. Environmetnal Assessment Program Report No. 12-03-009, Washington State Department of Ecology, Olympia, WA, 69pp.

Health Canada, 1994. Lead intoxication in a child related to the ingestion of playground paint chips – Quebec. Canada Communicable Disease Report 21-2, F1-F3.

Horner, J. M., 2004. Lead in house paints – still a health risk that should not be overlooked. Journal of Environmental Health Research 3, 2-6.

Kennedy, C., Lordo, R., Sucosky, M.S., Boehm, R., Brown, M.J., 2014. Primary prevention of lead poisoning in children: a cross-sectional study to evaluate state specific lead-based paint risk reduction laws in preventing lead poisoning in children. Environmental Health 13, 93; DOI: 10.1186/1476-069X-13-93

Kessler, R., 2014. Lead-based decorative paints: Where are they still sold – and why? Environmental Health Perspectives 122, A96-A103.

Laidlaw, M.A.S., Zahran, S., Pingitore, N., Clague, J., Devlin, G., Taylor, M.P., 2014. Identification of lead sources in residential environments: Sydney Australia. Environmental Pollution 184, 238-246.

Le Bot, B., Arcelin, C., Briand, E., Glorennec, P., 2011. Sequential digestion for measuring leachable and total lead in the same sample of dust or paint chips by ICP-MS. Journal of Environmental Science and Health Part A 46, 63-69.

Lucas, J.-P., Bellanger, L., Le Strat, Y., Le Tertre, A., Glorennec, P., Le Bot, B., Etchevers, A., Mandin, C., Sebille, V., 2014. Source contributions of lead in residential floor dust and within-home variability of dust lead loading. Science of the Total Environment 470-471, 768-779.

Mansson, N., Bergback, B., Sorme, L., 2009. Phasing out cadmium, lead and mercury. Journal of Industrial Ecology 13, 94-111.

Martinez, L., 2000. Unusually high lead and chrome contents of paints in Mexico. Materials Technology 15, 80-84.

Mathee, A., Singh, E., Mogotsi, M., Timothy, G., Maduka, B., Olivier, J., Ing, D., 2009. Lead-based paint on playground equipment in public children's parks in Johannesburg, Tshwane and Ekurhuleni. South African Medical Journal 99, 819-821.

Mercan, S., Ellez, S.Z., Türkmen, Z., Yayla, M., Cengiz, S., 2015. Quantitative lead determination in coating paint on children′s outwear by LA-ICP-MS: A practical calibration strategy for solid samples. Talanta 132, 222-227.

Mielke, H.W., Gonzales, C., 2008. Mercury (Hg) and lead (Pb) in interior and exterior New Orleans house Paint films. Chemosphere 72, 882-885.

Mielke, H.W., Powell, E.T., Shah, A., Gonzales, C.R., Mielke, P.W., 2001. Multiple metal contamination from house paints: consequences of power sanding and Paint scraping in New Orleans. Environmental Health Perspectives 109, 973-978.

RoSPA, 2004. Information sheet number 15: Lead in paint on children's playgrounds. The Royal Society for the Prevention of Accidents, Birmingham, UK, 2pp.

Su, M., Barrueto, F., Hoffman, R.S., 2002. Childhood lead poisoning from Paint chips: a continuing problem. Journal of Urban Health 79, 491-501.

Schwab, A.P., Lewis, K., Banks, M.K., 2006. Lead stabilization by phosphate amendments in soil impacted by paint residues. Journal of Environmental Science and Health Part A 41, 359-368.

Takaoka, M., Yoshinaga, J., Tanaka, A., 2006. Influence of paint chips on lead concentration in the soil of public playgrounds in Tokyo. Journal of Environmental Monitoring 8, 393-398.

Turner, A., Sogo, Y.S.K., 2012. Concentrations and bioaccessibilities of metals in exterior urban paints. Chemosphere 86, 614-618.

Turner, A., Comber, S., Rees, A.B., Gkiokas, D., Solman, K., 2014. Metals in boat paint fragments from slipways, repair facilities and abandoned vessels: an evaluation using portable XRF. Talanta 131, 372-378.

UNEP/WHO, 2011. Operational framework global alliance to eliminate lead paint. United Nations Environment Program and World Health Organization.

White, K., Detherage, T., Verellen, M., Tully, J., Krekeler, M.P.S., 2014. An investigation of lead chromate (crocoite-$PbCrO_4$) and other inorganic pigments in aged traffic paint samples from Hamilton, Ohio: implications for lead in the environment. Environmental Earth Science 71, 3517-3528.