A scenario evaluation approach to assess exposure and health risk of potentially harmful elements in outdoor dusts collected in urban recreational areas used by children: the case study of the Bassin Minier de Provence

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- Geochemistry and mineralogy of outdoor dusts collected in urban recreational areas used by children
- Oral bioaccessibility testing of potentially harmful elements (PHE) in the dust samples
- Exposure through ingestion/dermal contact and health risk assessment for the PHE of concern in the outdoor dusts
- Children are particularly vulnerable to PHE due to their behavioural characteristics:
  - Spend significant amounts of time playing outdoors;
  - Show hand-to-mouth/object-to-mouth (involuntary soil/dust ingestion) behaviour

## THE MODEL



U.S. Environmental Protection Agency (EPA), 2004. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual. National Center for Environmental Assessment, Washington, DC

# **SAMPLING SITES**

#### Westwern part of the BMP



#### **Outdoor dust**

Mixture of displaced urban soil, pavement debris and airborne particles that settle at ground-level

Dust settled at ground-level was collected using small brushes and plastic shovels.

Samples were collected mainly in sport facilities, playgrounds and schoolyards

# SAMPLING SITES



# **MATERIALS & METHODS**



# CONCEPTS

Geoavailability	<ul> <li>susceptibility and availability of its resident mineral phase(s) to alteration and weathering reactions</li> <li>the binding of PHE to solid phases in soils may render them unavailable for absorption</li> </ul>
Human Bioavailability	• fraction of the inorganic contaminant that will be absorbed by the receptor
Oral Bioaccessibility	<ul> <li>fraction that is soluble in the gastrointestinal environment and available for absorption;</li> <li>bioaccessibility can be used as a conservative measure of bioavailability</li> </ul>

#### **EXPOSURE AND RISK ASSESSMENT FOR THE INGESTION ROUTE**

- For non-cancer effects the potential exposure is expressed in the form of the Average Daily Intake
- Where,
  - ADI = Average Daily Intake (mg kg<sup>-1</sup> day<sup>-1</sup>)
  - C = Total Concentration (mg kg<sup>-1</sup>)
  - $IR = Intake Rate (mg day^{-1})$
  - *ED* = Exposure Duration (years)
  - EF = Exposure frequency (days year<sup>-1</sup>)
  - *Averaging Time= ED*×365 days
- The *ADI* was estimated for 3 age groups
- The exposure estimate is adjusted when calculating the hazard quotient
- Where,
  - *RfD* oral reference dose
  - Bf- bioaccessible fraction
- *HQ*=1 is considered the safety level

$$ADI = \frac{C \times IR \times ED \times EF}{Body \, Weight \times Averaging \, Time}$$

$$HQ = \frac{(ADI \times Bf)}{RfD}$$

Reference Values	2 - <3	3 - <6	6 - <12
$IR (mg dust day^{-1})$	60	60	60
ED (years)	1	3	5
EF (days year <sup>-1</sup> )	19	27	33
AT (days)	365	1095	1825
Body Weight (kg)	12.6	18.6	31.8

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# RESULTS

#### ALUMINIUM AND LEAD



### **ALUMINIUM IN THE OUTDOOR DUSTS**

#### **GEOCHEMISTRY**

#### **CORRELATIONS**

- Total concentrations range from 0.25 to 8.71% and are higher near the alumina plant
- The element shows some correlations:
  - Gallium
  - Vanadium (excepting samples near the power plant)
  - Chromium for samples near the plants
  - Content in organic matter of the dust (excepting samples near the plants)
- Aluminium is not correlated with the pH of the dust



# GEOCHEMISTRY AND HEALTH DATA

Total concentration, bioaccessible concentration in the G-phase, bioaccessible concentration in the GI-phase



#### The bioaccessible fraction (BAF)

- Bioaccessible concentrations in the G-phase vary between 207-2974 mg kg<sup>-1</sup>
- Strong decrease to the GI–phase (higher pH of the GI environment promotes complexation and precipitation of Pb)
- The bioaccessible fraction was calculated using data from the Gphase
- BAF ranges from 1.7 to 38.6%

 $Bf\% = rac{highest \, UBM \, extracted \, concentration}{pseudo-total \, concentration} imes 100$ 

### **ALUMINIUM IN THE BMP DUSTS**







Dusts near the alumina plant have elevated concentrations and low *BAF* 

A major fraction of aluminium in the dusts near the alumina plant was not solubilised by the G-fluids, meaning that is not available for absorption

#### ALUMINIUM BIOACCESSIBILITY AND DUST PROPERTIES

ID	Al(%)	Aluminous phases	
1	0.77	n.d.	
2	0.66	n.d.	
3	1.15	n.d.	
4	0.88	n.d.	
5	0.42	n.d.	
6.1	0.57	n.d.	
6.2	0.25	n.d.	
7	0.91	n.d.	
8	0.32	n.d.	
9	0.47	n.d.	
10	0.77	n.d.	
11	0.27	n.d.	
12	0.65	n.d.	
13	0.84	n.d.	
14.1	2.25	16	
14.2	2.19	20	
15	1.73	22	
16.1	8.71	88	
16.2	3.42	22	
17	5.26	47	
18	3.37	33	
19	2.28	30	



Positive linear association between the concentration of Al and the contents in aluminous minerals in the dusts – Al in the dust is hosted by the aluminous mineral phases

The Al-minerals do not seem to be soluble in the G-fluids

# SEM

I- Al-hydroxide (sample 16.1 alumina plant)

II- Al-Fe oxyhydroxide (sample 16.2, alumina plant)

Other aluminium mineral phases:

-Al-Fe-Cr oxides

- Al-Fe-Ti oxides





### NON-CARCINOGENIC RISK FOR THE DUST INGESTION ROUTE

- Only 4 sites have *HQ* above the safety level
- On average, the studied sites can be considered safe for all age groups
- However, considering a chronic exposure through childhood, the urban sites of the Western part of the BMP cannot be considered safe for the health of the children
- The *RfD* used to estimate the risk was established by the US EPA for aluminium phosphide

Ref.	HQ 1- <3	HQ 3- <6	HQ 6- <12	HQ chronic
1	0.56	0.59	0.42	1.57
2	0.95	1.00	0.71	2.65
3	0.70	0.74	0.53	1.97
4	0.96	1.01	0.72	2.68
5	0.21	0.22	0.16	0.60
6.1	0.57	0.60	0.43	1.60
6.2	0.16	0.17	0.12	0.44
7	0.95	1.00	0.72	2.67
8	0.12	0.12	0.09	0.33
9	0.53	0.56	0.40	1.50
10	1.68	1.77	1.27	4.72
11	0.13	0.14	0.10	0.38
12	0.55	0.58	0.42	1.55
13	0.57	0.60	0.43	1.61
14.1	1.30	1.37	0.98	3.65
14.2	0.66	0.70	0.50	1.86
15	0.98	1.04	0.74	2.76
16.1	0.86	0.91	0.65	2.41
16.2	0.50	0.53	0.38	1.40
17	1.68	1.77	1.27	4.73
18	1.19	1.25	0.89	3.33
19	0.64	0.67	0.48	1.79
average	0.75	0.79	0.56	2.10

### NON-CARCINOGENIC RISK FOR THE DUST INGESTION ROUTE

- Vulnerable sites:
  - 10 schoolyard
  - 14 sports facility
  - 17 schoolyard
  - 18 residential "patio"
- Chronic exposure through childhood
  - the results indicate that exposure to outdoor dusts can become a longterm health problem for the population
  - But these results should be regarded only as an indication that other studies are necessary to confirm the health risk associated to aluminium in the BMP





#### **LEAD** IN THE OUTDOOR DUSTS

#### **GEOCHEMISTRY**

- Total concentrations range from 7 to 353 mg kg<sup>-1</sup>
- The element is not correlated with other major, minor or trace elements
- Lead is correlated with the content in organic matter of the dust only for samples collected near the power plant
- Lead is not correlated with the pH or any mineral phase of the dust

#### **CORRELATIONS**



# GEOCHEMISTRY AND HEALTH DATA FOR LEAD

#### Total concentration, bioaccessible concentration in the G-phase, bioaccessible concentration in the GI-phase



#### The bioaccessible fraction (BF)

- Total concentrations vary between 7 - 353 mg kg<sup>-1</sup>
- Bioaccessible concentrations in the G-phase vary between 1.4 - 235.9 mg kg<sup>-1</sup>
- Strong decrease to the GI–phase (higher pH of the GI environment promotes complexation and precipitation of Pb)
- The bioaccessible fraction was calculated using data from the Gphase
- BAF ranges from18 to 100%

### **LEAD IN THE BMP DUSTS**





Lead total concentrations are not elevated but major fractions of the PHE are in bioaccessible forms

for dusts near both plants total concentrations are positively correlated with bioaccessible concentrations

High total concentrations do not correspond to high BAF



### **LEAD IN THE BMP DUSTS**



Sample 18



# LEAD BIOACCESSIBILITY AND DUST PROPERTIES



# **SEM - lead bearing** compounds

I – Pb-carbonates (sample 9, traffic)

II – Pb- aluminosilicates (sample 16.2, alumina plant)

Other Pb-bearing compounds:

Pb-Fe sulphides

Pb-Sn sulphates

Pb-Ti barium sulphátes





### NON-CARCINOGENIC RISK FOR THE DUST INGESTION ROUTE

- Only 1 site has a HQ above the safety level
- On average, the studied sites can be considered safe for all age groups
- However, considering a chronic exposure through childhood, 3 sites of the Western part of the BMP cannot be considered safe for the health of the children
- The *RfD* used to estimate the risk, indicated by the WHO is strongly protective of human health

Ref.	HQ 1- <3	HQ 3- <6	HQ 6- <12	HQ chronic
1	0.22	0.23	0.16	0.61
2	0.22	0.23	0.16	0.61
3	0.50	0.53	0.38	1.41
4	0.22	0.23	0.17	0.62
5	0.11	0.11	0.08	0.29
6.1	0.43	0.46	0.33	1.21
6.2	0.11	0.12	0.08	0.31
7	0.39	0.42	0.30	1.11
8	0.02	0.02	0.02	0.06
9	0.19	0.20	0.15	0.54
10	0.25	0.27	0.19	0.71
11	0.01	0.01	0.01	0.03
12	0.09	0.10	0.07	0.25
13	0.14	0.15	0.11	0.40
14.1	0.18	0.19	0.13	0.50
14.2	0.17	0.18	0.13	0.49
15	0.10	0.11	0.08	0.28
16.1	0.09	0.09	0.07	0.25
16.2	0.09	0.10	0.07	0.26
17	0.14	0.14	0.10	0.38
18	1.78	1.88	1.34	5.00
19	0.15	0.16	0.11	0.42
average	0.25	0.27	0.19	0.72

### NON-CARCINOGENIC RISK FOR THE DUST INGESTION ROUTE

- Vulnerable sites:
  - 18 residential "patio"
  - Sample 18 has elevated concentrations of Al, Ga, Zn and Pb
  - It is probable that the configuration of the buildings acts as a trap for metal-laden atmospheric dust that settle at ground-level
- Chronic exposure through childhood
  - Samples 3, 6.2 and 7 are schoolyards, which indicates that the source of lead should be identified
  - But in general the outdoor dusts of the BMP can be considered safe for human health in terms of lead contamination



### CONCLUSIONS

- The dusts near the alumina plant have elevated aluminium concentrations
- The host phases of the element are aluminous mineral phases that do not seem to be soluble in the G-fluids
- Total concentrations of lead are not very high but the element occurs in the dusts mainly in bioaccessible forms
- The content in organic matter seems to control the fixation of lead in the dust but not its bioaccessibility

### CONCLUSIONS

- Considering a chronic exposure through childhood, the urban sites of the Western part of the BMP can be hazardous for the health of the children if exposure to Alrich dust is likely to occur
- In general the outdoor dusts of the BMP can be considered safe for the health of the children if exposed to Pb-rich dust while playing outdoors

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