RESIDENTIAL DEVELOPMENT ON THE NEW VOLCANICS: A CASE STUDY OF SUSPECTED BARIUM CONTAMINATION AND SOIL AMENDMENT

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1 INTRODUCTION

As Melbourne expands to the north and west in response to growing demand for residential accommodation, soils developed on the Lava Plains (Geological Survey of Victoria, 1967), otherwise known as the New Volcanics (Cochrane, Quick & Spencer Jones, 1999), will be exploited. These soils are commonly shallow, alkaline and duplex, whilst the interspersed grey cracking clays pose significant constraints on building foundations and urban infrastructure due to their high “shrink-swell” nature. Rock floaters, clay fissuring, calcareous layers, sodicity and high electrolyte levels can serve as additional impediments.

The aforementioned soil characteristics also constrain garden development, landscaping and revegetation due to the presence of relatively heavy B-horizons with poor internal drainage, a relatively flat landscape with poorly-defined surface drainage, shallow heavy finely-textured topsoils and shallow calcareous bands which limit root propagation. The range of native and exotic plant species that can be planted in this landscape is limited, despite the need to improve aesthetics in order to attract residents.

Whilst the geological characteristics of soils on the New Volcanics are well understood and their limited potential as plant growth media recognised, the impact of soil chemical properties on some foundations, plant growth and heavy metal availability is not.

This paper describes the outcome of an investigation into potential barium (Ba) contamination of a 15 ha site located 18 km west of the CBD which threatened to stop the proposed residential development. Barium, as a trace element, concentrates in intermediate and acid magmatic rocks and its occurrence is linked with alkali feldspar and biotite (Kabata-Pendias, 2001). In soils in the natural environment, barium will generally occur as barium sulphate ($BaSO_4$) due to the ubiquitous presence of sulphate ions. Some paint pigments contain barium salts and thus barium levels can be elevated on derelict land (Bridges, 1987). Barium is also associated with radio-active fall-out and nuclear waste. Barium sulphate is widely used as a safe tracer in medical practice due to the insolubility of the compound.

In conducting a soil survey for residential development where barium levels are found to be high it is essential to determine if possible why the levels are high, how widespread is the area impacted and whether anthropogenic input is likely. Of particular interest are the distribution of barium concentrations with depth and the association of barium with appropriate anionic concentrations. Evidence of site disturbance or encapsulation is also important as is the prospect of pseudo-stratification.

Knowledge of the availability of heavy metals for plants can assist the assessment of risk to humans from food chain transfers and contact with soil barium; fortunately there are well-defined relationships between pH and soil electrolytes that dictate this availability.

2 GEOLOGY AND GEOMORPHOLOGY

Parent material for the site under investigation was found to be vesicular Quaternary Basalt. The flat and gently sloping land surface is classified as “Lava Plains” (and also “Newer Volcanics”); this mafic parent material contains high levels of iron, magnesium and calcium with plagioclase the dominant feldspar.

The geomorphology of the New Volcanics is dominated by low volcanic cones and rolling plains on Quaternary basalt parent material. This terrain, with a poorly-defined surface drainage system, limited infiltration and relatively-low rainfall has favoured accumulation of some cations in the soil B-horizon and this can lead to elevated concentrations of trace elements (heavy metals such as chromium, copper, lead, nickel and others).

Jeffrey (1981) conducted a land-use study in the region and, based upon his work, the site is likely to be similar in landform to the Cottrell Land System. Assuming that the site possesses similar characteristics, then soil profiles are calcareous, sodic and duplex with a coarse structure derived from the weathering of Pleistocene basalt.

Sodicity in these types of soil profiles is usually found to increase with depth from an exchangeable sodium percentage (ESP) of about 2 (non-sodic) in the A-horizon to an ESP of about 20 (highly sodic) at the base of the B-horizon, with pH increasing correspondingly from between 5.5 and 6.0 to between 8.5 and 9.0. As the case study site possesses rocky rises and minor depressions the soil profile is likely to vary, with vertosols dominating the lower land and red duplex the slopes and rises, so the land is not wholly consistent with the Cottrell Land System. Alkaline clay subsoils are common, based on previous experience in the district.

The terrain pattern for the site is accorded the Province No. 52.009 and Pattern 0 (Grant, 1972). The lithology is basalt with the flow possibly derived from Mt. Atkinson, a volcanic cone located nearby. Under the CSIRO PUCE classification system the site is close to the boundary between two Terrain Provinces and, based upon field observations, most of the site soil profiles are likely to be vertosol rather than duplex. Site drainage features and soil types were found after investigation to be consistent with the CSIRO classification.

3 INITIAL SUBSURFACE INVESTIGATIONS

The initial investigation comprised a conventional geotechnical and environmental survey of the residential development site using a drilling rig and auger hole logs supplemented by backhoe pits. Soil samples were collected from the surface of the profile (0–100 mm) and at 0.5 m and 1.0 m depths. This investigation concentrated on foundation characteristics but laboratory chemical analysis did reveal the presence of elevated soil barium levels at sampling depths of 0.5 m and 1.0 m. in one auger hole and an elevated concentration in another hole at a depth of 1.0 m. The results confirmed that the National Environment Protection Measure NEPM (EIL) criterion of 300 mg/kg for barium (NEPC, 1999) was exceeded, with the implicated soil test results ranging from 300 mg/kg to 900 mg/kg. It should be noted that although over 100 auger holes were installed in a grid pattern on the 15 ha site with associated soil testing, the exceedance criterion was triggered at only two locations at the depths indicated.

The supplementary investigation comprised two backhoe pits adjacent to the two incriminating auger holes to facilitate the collection of soil samples at 100 mm intervals from the natural surface to a basalt rock layer. Following contaminated site protocols the soil samples were despatched to a laboratory for assay.

4 SUPPLEMENTARY INVESTIGATIONS

The soil profile exposed by the first pit was between 1 m and 1.2 m deep, the excavation limited by weathered rock floaters of vesicular basalt. Layering in the profile was well-defined, with 600 mm of red-brown clayey-loam (A-horizon) overlying a calcareous grey heavy clay (B-horizon) – the latter being well aggregated and showing “slickensides” providing abundant evidence of shrinking and swelling with fluctuations in soil moisture content. The B-horizon was flecked with lime and underlain by an extensive calcareous layer about 100 mm thick.

The profile exposed by the second pit had better internal drainage, with more pronounced layering and more duplex in character; additionally, the rock was closer to the natural surface and the B-horizon thinner. Rocks were stockpiled nearby, possibly indicating that a rocky rise had been removed.

The magnitude of soil barium levels recorded in the initial investigation was confirmed by the results of the supplementary investigation; sampling and experimental errors were accordingly discounted.

5 SURFACE FEATURES AND SOILS

The property is dominated by a gilgai landform (wavy micro relief) and, whilst introduced pasture and weeds dominated one half of the property, Wallaby grass (Danthonia purpurascens) – a native species - dominated the other half, providing evidence of minimal cultivation or land disturbance. The heap of rocks in one corner indicated previous extraction activity; lesser disturbance was evident in the opposite corner, probably associated with a shallow layer of sheet rock.

On the basis of reconnaissance there was no evidence at either backhoe pit site of anthropogenic disturbance (apart from limited surface rock removal) or surface deposition of material containing barium. Encapsulation can be ruled out because the soil profiles exposed were formed by natural processes and did not show a layer of overburden or destruction of soil structure patterns; pseudo-stratification was also ruled out on the basis of previous chemical data. Accordingly, it must be assumed that the barium levels measured were derived from the parent rocks and may have been translocated within the soil profile by natural geomorphic processes dominated by leaching in this terrain.

6 SOIL PROFILE INFORMATION

For each of the backhoe pits the description of the soil profile was limited to noting the Munsell colours for each of the 100 mm intervals sampled; Table 1 records the details of these colours. It should be noted that, whilst colour is not used as an indicator of geotechnical characteristics, it is employed to assist the determination of agronomic potential and drainage state.

Table 1: Soil Profile Colours.

Backhoe pit # 1 Soil Profile 1			Backhoe pit # 2 Soil Profile 2		
Depth (cm)	Munsell Colour		Depth (cm)	Munsell Colour	
0-10	10YR 3/1	Very dark grey	0-10	7.5YR 3/4	Dark brown
10-20	10YR 3/3	Dark brown	10-20	7.5YR 3/4	Dark brown
20-30	10YR 3/2	Very dark grey brown	20-30	7.5YR 3/2	Dark brown
30-40	10YR 3/2	Very dark grey brown	30-40	7.5YR 4/2	Brown
40-50	10YR 3/2	Very dark grey brown	40-50	7.5YR 4/4	Brown
50-60	10YR 3/3	Dark brown	50-60	7.5YR 4/4	Brown
60-70	10YR 4/3	Brown	60-70	2.5Y 3/2	Very dark greyish brown

On the basis of profile colour, the profile at backhoe pit #2 has better natural drainage and is better oxidised than the profile at backhoe pit #1; however, neither indicates significant waterlogging during the year, therefore the evidence is that reducing conditions can periodically occur but that sulphates should remain in sulphate form.

7 BARIUM BEHAVIOUR IN THE SOIL

Barium is likely to concentrate in intermediate and acid magmatic rocks, although in this case the barium is derived from mafic (or “basic”) rocks; commonly, the concentration range is 400 ppm to 1200 ppm (A.K. & H. Pendias, 2001). World average natural abundance of barium in basaltic rocks is 250 mg/kg, but some basalts have much higher barium levels e.g. tholeite basalt in north-east Ireland contains 1,350 mg/kg of barium (Krauskopf K.B. 1967). As far as is known, there is no systematic survey of Victorian basalts that provide data on barium levels in these rocks and hence it is unknown what barium levels may be expected in the rocks from which these soils have developed.

Barium released from weathering is not very mobile and readily precipitated as sulphates and carbonates as long as sulphates and carbonates are available in a profile or can be applied as amendments. It must also be remembered that, as other rock constituents are lost by leaching in the soil formation process, those constituents that are less likely to be lost become proportionally more abundant in the residue. The soil barium levels derived from laboratory tests, although exceeding the threshold value (NEPC, 1999) were within typical range measured from soils in their natural state around the world. The elevated concentrations recorded at this site are associated with depths of between 0.5 m and 1.0 m in well-defined soil profiles that possess a rock basement with little colonisation of plant roots beyond 450 mm due to the presence of a calcareous clay-dominated B-horizon. The barium accumulations also occur in the profile where free lime is omnipresent and the pH high, thereby limiting plant availability.

Barium precipitates in the presence of sulphate (SO_4^{-2}) to form barite ($BaSO_4$) which is extremely insoluble; thus sulphate can be employed to assess the actual level of risk to health and control mobility (Lehr, Hyman; Gass & Seevers, 2002) and as gypsum it can be used as an amendment to limit barium availability. Further barium, like carbon, hydrogen, phosphorus and sulphur, is a common constituent of plants around the world; it is also present in the form of a radioactive isotope – the result of past atomic weapons testing in the open air gradient (Pierzynski, Sims & Vance, 2000) - but there is no likelihood that the material found at the site is derived from fall-out due to the observed barium concentration.

Plant toxicity is possible at the levels indicated if the barium were more soluble, but the roots would need to penetrate to 0.5 m to exploit the soil profile to the depth where elevated barium levels are recorded in soil samples; at this depth, high soil pH levels would limit the availability of barium to plant uptake for introduction to the food chain. In addition, the substantial lime layers in the B-horizon and particularly at the top of the C-horizon will pose a major impediment to root penetration for all but the most lime-tolerant deep-rooted vegetation, so it is unlikely plant roots could reach the depth where elevated barium levels are measured.

8 INITIAL SOIL BARIUM AND GROUNDWATER TEST RESULTS

The results of supplementary soil barium tests conducted on backhoe pit samples are shown in Table 2.

Table 2: Results of Validation Sampling.

Depth (m)	Sample #	Ba mg/kg	Sample #	Ba mg/kg	Sample #	Ba mg/kg	Sample #	Ba mg/kg
Surface	#1/1-1	51	#1/2-1	33	#1/3-1	37	#1/4-1	45
0.5	#1/1-2	210	#1/2-2	300	#1/3-2	320	#1/4-2	150
1.0	#1/1-3	390	#1/2-3	160	#1/3-3	360	#1/4-3	350
Surface	#2/1-1	28	#2/2-1	29	#2/3-1	22	#2/4-1	36
0.5	#2/1-2	70	#2/2-2	190	#2/3-2	84	#2/4-2	240
1.0	#2/1-3	220	#2/2-3	270	#2/3-3	250 & 190 (dupl.)	#2/4-3	910

These results show, with one exception, that the barium levels increase with depth, and therefore resemble other well-known depth functions of salts in soils. The heavy clay soils on basalt often, but not always, show a zone of calcium carbonate concentration lower down in the soil profile, which indicates the maximum depth at which there was enough percolating rainwater to keep calcium carbonate in solution. As during the process of water percolation the vegetation removes water from the soil so that the remaining solution becomes more concentrated, at the point where the solubility of the calcium carbonate is exceeded, it will precipitate out from the solution and form solid calcium carbonate.

It is known that, when the soil profiles are deep enough and gypsum is present, there will also be a gypsum layer in the profile. That layer will be found below the calcium carbonate layer, because gypsum is more soluble in water and hence the soil needs to dry out more before gypsum precipitates.

As the likely forms of barium in the soil are barium sulphate and/or barium carbonate, the barium distribution in the laboratory data is suggestive of a similar down-profile enrichment of the soil with barium. Unfortunately, these samples were not analysed for either sulphate or carbonate as generally the focus of environmental testing is on the potential toxicant and ignores any other compounds that can render it harmless. Thus environmental testing often disables itself when a risk assessment has to be the final outcome. Groundwater samples were analysed both for barium and sulphate; the results of this analysis are as shown in Table 3.

Table 3: Relevant Groundwater Analytes With Regard To Barium Behaviour.

Groundwater Samples	A	B	C	D	E	F	G
Barium (mg/L)	0.061	0.048	0.044	0.031	0.02	0.042	0.046
(mmole/L)	0.000,45	0.000,35	0.000,32	0.000,23	0.000,15	0.000,31	0.000,34
Sulphate (SO4) (mg/L)	230	54	170	92	270	130	120
(mmole/L)	2.396	0.563	1.771	0.958	2.813	1.354	1.250
Bicarbonate alkalinity (CaCO3) (mg/L)	500	560	550	600	820	360	320
pH	7.7	8.2	8.5	8.1	8.0	7.6	7.6
Total Dissolved Solids (mg/L)	10,000	2,600	6,300	4,200	9,311,000	5,400	5,300

By expressing the concentrations of barium and sulphate in the groundwater as molar quantities (mmole/L = millimole/L) it can be seen that the sulphate ion concentration is many times greater than the barium concentration. The geometric mean barium concentration of groundwater samples in these seven monitoring wells is 0.0397 mg/L or 0.000,29 mmole/L. The geometric mean sulphate concentration is 135 mg/L or 1.406 mmole/L. In other words, the sulphate anions were found to outnumber the barium cations by about a factor of 5,000. Therefore, any solid phase barium sulphate in the earth/rock materials below the groundwater table at equilibrium with the dissolved species will be a system in which the dissolved barium concentration of groundwater samples is minimised by the great excess of dissolved sulphate. This is illustrated in Figure 1.

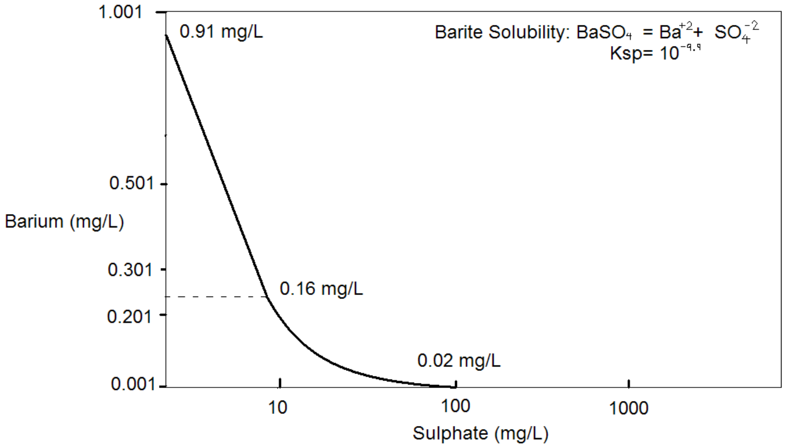

Figure1. Barite (BaSO4) Solubility Function

9 INTERPRETATION OF SUPPLEMENTARY SOIL ANALYSES

The results of analyses of soil samples for sulphate and barium are presented in Table 4, these results confirm the relative abundance of sulphate compared with barium as well as flagging the need for more information on total and leachable barium levels as well as linkages with soil pH and soil salinity. The Electrical Conductivity (EC) results in Table 5 indicate that salinity increases with depth until it reaches a more or less constant maximum level at 50 to 60 cm depth. This indicates that, in the main, rainwater does not percolate much below this level and the net equilibrium with regard to transport of salt in the soil profile is that below 60 cm salt levels remain constant.

The pH of the soil is influenced by the proportion of the exchangeable cations on the clay taken up by sodium, compared to calcium, magnesium and hydrogen, as well as by the possible occurrence of sodium bicarbonate, which is very soluble and hence more easily transported to lower portions of the soil.

Total barium levels were obtained by a standard method that is relatively insensitive but can detect concentrations above 500 mg/kg. In profile # 1 only one sample had just over 500 mg/kg at 510 mg/kg. Profile #2 had four samples exceeding 500 mg/kg and, at 80-90 cm depth, a value of 2,000 mg/kg.

Barium released by extraction with 1 molar hydrochloric acid shows depletion of the surface layers and accumulation below causing a bulge between 40-60 cm depth and continuing elevated levels deeper down. This barium is the fraction that will largely consist of barium carbonate.

Water soluble sulphate, expressed as sulphur (S), is abundant throughout both profiles and increases sharply below approximately 40 cm depth. As this represents free SO_4^{-2} anions, it means that water soluble barium concentrations must be depressed. Even acknowledging that the water in the soil is not pure water, but a rather saline aqueous system, the relationship is still of general validity in predicting that soluble, mobile barium levels must be low also.

Leachable barium levels are very low. The leachable barium may be equated with the water-soluble barium as the extractant is a buffered solution of acetic acid and sodium acetate with a pH that does not depart from normal soil pH values. These concentrations can be compared to the concentrations of water-soluble sulphate, with both expressed on a molar basis. This comparison indicates that the sulphate concentrations exceed the barium concentrations by between 5 and 6 orders of magnitude (Table 4).

Applications of gypsum to the soil profile would reduce the presence of soluble barium in the topsoil but, given the abundance of sulphate in the soil, its main benefits would be the improvement of the agronomic potential of the soil to support the growth of a greater range of garden and street plants, as well as enhancing soil workability. It is definitely not needed for controlling barium availability.

Table 4: Comparison of Concentrations of Water Soluble Sulphate with Leachable Barium.

	Depth (cm)	Sulphate as S (mg/kg)	Sulphate as SO4 (mole/kg)	Ba Leach. (mg/kg)	Ba Leach. (mole/kg)	Molar Ratio Sulphate to Barium
Soil Profile # 1	0-10	630	0.210	0.43	3.1 x 10-6	6.7 x 104
	10-20	<100		0.17	1.2 x 10-6	
	20-30	<100		0.08	5.8 x 10-7	
	30-40	410	0.137	0.19	1.4 x 10-6	9.9 x 104
	40-50	1400	0.467	0.34	2.5 x 10-6	1.9 x 105
	50-60	780	0.260	0.31	2.3 x 10-6	1.2 x 105
	60-70	550	0.183	0.29	2.1 x 10-6	8.7 x 104
	70-80	680	0.227	0.23	1.7 x 10-6	1.4 x 105
	80-90	1100	0.367	0.29	2.1 x 10-6	1.7 x 105
	90-100	1700	0.567	0.29	2.1 x 10-6	2.7 x 105
Soil Profile # 2	0-10	240	0.080	0.08	5.8 x 10-7	1.4 x 105
	10-20	980	0.327	0.07	5.1 x 10-7	6.4 x 105
	20-30	670	0.223	0.06	4.4 x 10-7	5.1 x 105
	30-40	1400	0.467	0.28	2.0 x 10-6	2.3 x 105
	40-50	1600	0.533	0.72	5.2 x 10-6	1.0 x 105
	50-60	1800	0.600	0.4	2.9 x 10-6	2.1 x 105
	60-70	1900	0.633	0.33	2.4 x 10-6	2.6 x 105
	70-80	3100	1.033	0.38	2.8 x 10-6	3.7 x 105.
	80-90	2400	0.800	0.4	2.9 x 10-6	2.7 x 105
	90-100	n.s.	n.s.	n.s.	n.s.	n.s.

As the sulphate concentration far outstrips that of the leachable barium, the bulk of the solid phase barium in the soil will be in the barium sulphate form and will be inert.

Table 5: Second Stage Soil Test Results.

Depth (cm)	Sample Site # 1					
	EC (μS/cm)	Water Soluble Sulphate (as S) (mg/kg)	pH (H2O)	Ba Total (mg/kg)	Ba 1 M HCl extract. (mg/kg)	Ba Leachable (mg/kg)
0-10	76	630	6.9	<500	100	0.43
10-20	260	<100	7.0	<500	89	0.17
20-30	300	<100	7.1	<500	42	0.08
30-40	650	410	7.3	<500	110	0.19
40-50	940	1400	7.6	<500	130	0.34
50-60	1200	780	8.0	510	140	0.31
60-70	1300	550	8.2	<500	120	0.29
70-80	1300	680	8.3	<500	110	0.23
80-90	1300	1100	8.5	<500	110	0.29
90-100	1400	1700	9.0	<500	97	0.29
	Sample Site # 2					
0-10	130	240	6.8	<500	27	0.08
10-20	220	980	7.5	<500	31	0.07
20-30	520	670	8.0	<500	29	0.06
30-40	830	1400	8.4	<500	110	0.28
40-50	950	1600	8.5	610	180	0.72
50-60	1100	1800	8.9	540	160	0.40
60-70	1100	1900	9.2	<500	130	0.33
70-80	1100	3100	9.5	570	110	0.38
80-90	1100	2400	9.6	2000	84	0.40
90-100	n.s	n.s	n.s	n.s	n.s	n.s

n.s = No sample taken as bedrock occurred at this depth.

10 GEOTECHNICAL RESULTS

The high “shrink-swell” character of the clays in this region is well recognised but the alkaline soil conditions and the presence of free lime in the soil profile must also be considered in the context of foundation design. High sulphate levels are seen as a boon to barium immobility but in order to avoid the employment of sulphate-resistant cement the foundation depth should be restricted whilst soil EC and pH levels should be reviewed to assist foundation design and material selection. Plant root penetration will be severely restricted by the heavy subsoil and deep calcareous layers and knowledge of root propagation will help the assessment of risk of plant uptake of undesirable metals as well as the risk of foundation damage.

11 CONCLUSIONS

Supplementary tests of soil barium and sulphate levels confirmed the abundance of sulphate in soil samples which guaranteed the insolubility of barium, rendering the need for gypsum amendment obsolete. Based on detailed soil testing as a component of supplementary investigations in association with the original groundwater data the following observations can be made:-

(a) The barium in the soil is native barium.
(b) The barium has become concentrated in the subsoil through losses in the topsoil by normal geochemical process over many thousands of years.
(c) The barium in the soil is present as $BaSO_4$ - an inert solid compound.
(d) The barium is of nil environmental and public health risk.

Environmental assessments and audits should be based on more than routine soil sampling and analyses of contaminants in the soil and groundwater only; analyses should also include those other chemical factors that are well known to control solubility, mobility and toxicity of each contaminant. A sound understanding of geochemistry and soil chemistry is essential.

Geotechnical investigations in this landscape should also include an assessment of soil chemistry as it could impact on structural integrity. The major parameters are soil salinity, sulphate levels and pH.

Whilst soil amendment using gypsum would have agronomic benefits and enhance soil workability it has limited utility for controlling barium mobility which is already controlled by existing soil conditions.

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