



## Evaluation of Site Contamination from Storage of Fertilizer

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**Abstract** Australia has extensive agricultural production of crops and livestock production. Regular fertilizer application maintains production rates of grain crops. Large quantities of phosphorus-based fertilizers are produced from phosphate rock by sulfuric acid extraction at designated production works at coastal locations and transported by train to distribution points in selected agricultural areas. Bulk fertilizer is stored in large sheds adjacent to railway lines and large or small trucks then make deliveries to farms. When such sites are disused or abandoned, contaminated soil may remain from fertilizer constituents. Occasionally fertilizer storage sites may have experience accidental contamination from railway engine or truck hydrocarbons. The objective of this study is to examine the extent of fertilizer contamination at agricultural storage sites, identify environmental risks associated with the handling practices of storage sites, and distinguish from other contamination from transport vehicles. Soil samples were collected at two locations using a grid-base sampling program to identify contaminants. Following preparation soils were analysed for phosphorus, sulfate, sulfur, petroleum hydrocarbons (aliphatic and aromatic), heavy metals and pesticides using standard procedures. A ‘within a target area’ was used to assess contamination levels by comparing the 95% Upper Confidence Limit (UCL) of the average concentration of each analyte of concern against respective ‘contamination’ criteria for industrial sites; exceedance of the 95% UCL against site criteria identified contamination. Statistical analysis of the data for different analytes in soil at fertilizer storage sites showed the relationship between contaminant levels and dispersion over respective sites and extent of contamination from fertilizer handling activity and other vehicle-related site contamination. In conclusion accurate estimation of contamination of sites can be provided using the grid-base sampling approach and 95% Upper Confidence Limit (UCL) criteria to distinguished transport vehicle-related contamination from phosphate-based fertilizer on site.

**Keywords** fertilizer storage, transport vehicles, contamination, risk management

## INTRODUCTION

Australia has extensive agricultural production of crops and livestock. Regular fertilizer application has maintained production rates over many years (Fitzpatrick, 1968). Phosphorus-based fertilizers are produced by sulfuric acid extraction at Australian coastal production works and transported by train to distribution points. Bulk fertilizer is stored in large sheds adjacent to railway lines and large or small trucks then deliver to farms. The storage sheds usually have bare soil floors and over periods of decades fertilizer levels can build up. The disused or abandoned sites may leave soil contaminated with fertilizer phosphate, sulfate and sometimes sulfur (FMA, 1998). Occasionally fertilizer storage sites have experienced contamination from railway engine derailment or truck hydrocarbons (NSW EPA, 1994). The Australian National Environmental Protection Measure (NEPM) soil contamination guidelines are risk-based Health and Ecological criteria (Noller, 2020) and some guidelines may be applicable for assessing fertilizer contamination.

## OBJECTIVE

The objective of this study is to examine the extent of fertilizer contamination from phosphate, sulfate and sometimes sulfur at agricultural storage sites, identify environmental risks associated with the handling practices of storage sites, and distinguish from other contamination due to transport vehicles.

## METHODOLOGY

Soil samples were collected using a grid-base sampling program to identify analytes of concern (NSW EPA, 1995) at two comparative fertilizer storage sites; one location (A) experienced contamination due to a rail derailment following fertilizer storage ten years earlier and another location (B) was used for fertilizer only storage for several decades (Noller, unpublished data). Following preparation, soils were analysed by Queensland Health Scientific Services laboratory, Coopers Plains, Queensland for phosphorus, sulfate, sulfur, petroleum hydrocarbons (aliphatic and aromatic), heavy metals and pesticides using standard procedures (ANZECC, 1992; NEPM, 1999; NSW EPA, 1994; NSW EPA, 1995).

The criteria from the NSW EPA (1998) Guidelines for the NSW Site Auditing Scheme were used, together with the assessment criteria of the Australian National Environmental Forum health-based soil investigation Levels for Soil and Groundwater NEPM (1999) at industrial sites. A ‘within a target area’ statistical evaluation was used to assess contamination levels by comparing the 95% Upper Confidence Limit (UCL) of the average concentration of each analyte against respective ‘contamination’ criteria for industrial sites; exceedance of 95% UCL against site criteria identified contamination using the assessment criteria of the NSW EPA Sampling Design guidelines (NSW EPA, 1995). “Hotspots” could be identified when analytical results from individual sites were 250% of the relevant criteria value, and when the standard deviation of data was <50% of the criteria.

The 95% upper confidence limit (UCL) of the arithmetic average concentration is calculated using Eq. (1) (NSW EPA, 1995) as follows:

$$\text{UCL average} = \bar{x} + t_{\alpha, n-1} \times \text{sd} / \sqrt{n} \quad (1)$$

UCL average = Upper confidence limit of the arithmetic average concentration of the sampling area at the 1- $\alpha$  confidence level.

$\alpha$  = The probability that the ‘true’ average concentration of the sampling area might exceed the UCL average determined by Eq. (1).

n = Number of sample measurements.

n-1 = Degrees of freedom

$\bar{x}$  = Arithmetic average of all sample measurements.

$t_{\alpha, n-1}$  = The test statistic at an  $\alpha$  level of significance and degrees of freedom of n-1 obtained from table of values of Student’s t.

sd = Standard deviation of the sample measurements.

## RESULTS AND DISCUSSION

Table 1 gives results for soil sulfate, total phosphorus and elemental sulfur concentrations at the two fertilizer storage Locations (A and B). Both show extensive soil contamination, compared with contamination criteria, from sulfate, phosphorus and sulfur (B only) with higher concentrations observed at Location B due to extensive use over several years. Such contamination is quite different to low level contamination of agricultural soils (Noller, 2020), but significant over long-term accumulation in soil (Weissengruber et al., 2018). Comparison of the statistical evaluations using the 95% Upper Confidence Limit (UCL) of average concentration of each constituent (NSW EPA, 1995)

and exceedance of 95% UCL against the respective contamination criteria against site criteria (ANZECC, 1992; NEPM, 1999) enabled the following features of ‘hotspots’ to be identified:

- Location A Sulfate. The difference of samples below the contamination criteria from all samples showed that 7 sites are contaminated and indicated the extent of the ‘hotspot’ for sulfate.
- Location A Total phosphorus. The difference of samples below the contamination criteria from all samples showed that 13 sites are contaminated and indicated the extent of the ‘hotspot’ for total phosphorus and was more extensive than for sulfate.
- Location B Sulfate. The difference of samples below the contamination criteria from all samples showed that 7 sites are contaminated and indicated the extent of the ‘hotspot’ for sulfate.
- Location B Total phosphorus. The difference of samples below the contamination criteria from all samples showed that all 10 sites are contaminated and indicated the extent of the ‘hotspot’ for total phosphorus was also more extensive than for sulfate.
- Location B Sulfur. The difference of samples below the contamination criteria from all samples showed that 2 sites are contaminated and indicated the extent of the ‘hotspot’ for sulfur, was much less than for sulfate.

**Table 1 Soil sulfate, total phosphorus and elemental sulfur concentrations at fertilizer sites**

Test	Sulfate as S (mg/kg)	Total phosphorus as P (mg/kg)	Elemental sulfur as S (mg/kg)
<b>A. Once only storage site (600 m<sup>2</sup>) followed by train derailment contamination of soil</b>			
Number of samples (n-all)	20	20	-
Mean	4509	6132	-
Range	61-33400	130-25200	-
SD	8458	6935	-
Students $t_{\alpha=0.05}$	1.729	1.729	-
95% UCL mean	1239	9850	-
Contamination criteria	2000 <sup>a</sup>	2000 <sup>a</sup>	-
Number of samples (n<Contamination criteria)	13	7	-
Mean	527	926	-
Range	61-1600	130-1700	-
SD	532	631	-
Students $t_{\alpha=0.05}$	1.782	1.943	-
95% UCL mean	792	1389	-
Contamination criteria	2000 <sup>a</sup>	2000 <sup>b</sup>	-
<b>B. Storage site (5800 m<sup>2</sup> used continuously for 40 y with only fertilizer contamination</b>			
Number of samples (n-all)	10	10	10
Mean	28542	10470	3615
Range	520-100100	2400-22700	100-32300
SD	33124	7277	10087
Students $t_{\alpha=0.05}$	1.833	1.833	1.833
95% UCL mean	47756	14691	9466
Contamination criteria	2000 <sup>a</sup>	2000 <sup>b</sup>	600 <sup>b</sup>
Number of samples (n<Contamination criteria)	3	0	8
Mean	11732	-	225
Range	520-1600	-	100-500
SD	575	-	183
Students $t_{\alpha=0.05}$	2.353	-	1.8603
95% UCL mean	1954	-	345
Contamination criteria	2000 <sup>a</sup>	-	600 <sup>b</sup>

Source: a. ANZECC (1992) and b. NEPM (1999)

**Table 2 Soil sulfate, total phosphorus, cadmium, lead and zinc concentrations at 9 sites, Location A**

Site A (surface 0cm)	Sulfate-S (mg/kg)	Total phosphorus-P (mg/kg)	Cadmium (mg/kg)	Lead (mg/kg)	Zinc (mg/kg)
Site 1	33,400	20,800	9.7	98	170
Site 2	5,600	10,200	2.2	43	160
Site 3	120	400	<1	25	32
Site 4	19,000	25,200	45	790	460
Site 5	360	6,300	4.3	62	220
Site 6	160	4,100	3	36	130
Site 7	930	8,600	7.7	78	220
Site 8	1,200	2,200	1.3	34	110
Site 9	250	1,700	1.3	400	240
Contamination criteria	2,000 <sup>a</sup>	2,000 <sup>b</sup>	100 <sup>b</sup>	1500 <sup>b</sup>	35,000 <sup>b</sup>

Source a. ANZECC (1992) and b. NEPM (1999)

**Table 3 Soil total petroleum hydrocarbon, polynuclear aromatic hydrocarbons, benzo(a)pyrene, and organo phosphorus pesticides concentrations at 9 sites, Location A**

Site (surface 0cm)	Total petroleum hydrocarbon (mg/kg)	PolyAromatic hydrocarbons (total) (µg/kg)	Benzo(a)pyrene (µg/kg)	Organo phosphorus pesticides (µg/kg)
Site 1	142	2,255	2,255	<10
Site 2	194	1,460	1,460	<10
Site 3	48	450	450	<10
Site 4	336	5,330	5,330	<10
Site 5	108	1,510	1,510	<10
Site 6	23	320	320	<10
Site 7	46	830	830	<10
Site 8	13	255	255	<10
Site 9	67	1,370	1,370	<10
Contamination criteria	28,000 <sup>b</sup>	100,000 <sup>a</sup>	100,000 <sup>a</sup>	10,000 <sup>a</sup>

Source a. NEPM (1999) and b. NSW EPA (1994)

Tables 2 and 3 give comparative data for soil sulfate, total phosphorus, petroleum hydrocarbons (aliphatic and aromatic), benzo(a)pyrene, heavy metals (cadmium, lead and zinc), and organo-phosphorus pesticide concentrations for 9 sites at Location A with rail derailment contamination being close to the railway line. Based on historical use of the agricultural storage site (Location A) for fertilizer, the type and concentration of contaminants found should be consistent with storage of phosphorus-based fertilizers. Therefore the presence of cadmium, lead, zinc, total petroleum hydrocarbon (TPH) and BTEX (all at detection limit; benzene <0.5 mg/kg, toluene <0.5 mg/kg, ethylbenzene <0.5 mg/kg and xylene <0.5 mg/kg), polyaromatic hydrocarbons (PAHs) comprising benzo(g,h,i)perylene, dibenz(a,h)anthracene, indeno(123c,d)pyrene, benzo(a)pyrene, benzo(b+k)fluoranthene, chrysene, benz(a)anthracene, pyrene, fluoranthene, phenanthrene, fluorene, acenaphthalene, acenaphthene and naphthalene, benzo(a)pyrene itself as a key carcinogen from fuel combustion, organo phosphorus pesticides, and are inferred collectively as not being consistent with the presence of phosphate-based fertilizers; cadmium is also present in phosphate rock used in fertilizer manufacture but is associated with zinc additives used in engine oils.

The data in Tables 2 and 3 is intended to show how fertilizer contamination can be displayed at the same sites at Location A together with rail derailment contamination. Sulfate and total phosphorus concentrations (Table 2) are consistent with the identification from Table 1 that some sites at Location

A are contaminated with fertilizer by comparison against the contamination criteria and comprise 'hotspots'. None of the cadmium, lead, zinc, total petroleum hydrocarbon (TPH) and BTEX, polyaromatic hydrocarbons (PAHs), benzo(a)pyrene or organo phosphorus pesticides (OCPs) concentrations given in Tables 2 and 3 exceed respective contamination criteria and cannot be described as 'hotspots' at Location A or as being environmentally significant. However, the association of engine fuel and oil constituents with a rail engine derailment is clear.

## **CONCLUSION**

Accurate estimation of contamination of sites has been demonstrated using the grid-base sampling approach and 95% Upper Confidence Limit (UCL) criteria to distinguish transport vehicle-related contamination from phosphorus-based fertilizer at two locations. Statistical analysis of the data for different constituents in soil at the fertilizer storage sites showed the relationship between contaminant levels and dispersion over respective sites (ANZECC, 1992; NEPM, 1999; NSW EPA, 1994; NSW EPA, 1995). Dispersion of constituents of phosphorus –based fertilizers can distinguish extent of contamination during the operational phases of fertilizer handling activity from other vehicle-related contamination. "Hotspots" were identified when analytical results from individual sites were 250% of the relevant criteria value, and when the standard deviation of the data set was <50% of the criteria.

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