

# Soil Analysis --- What the Lab Certificate Doesn't Tell you

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There's an almost universal acceptance in the site assessment industry that the Certificate of Analysis from an accredited laboratory gives an accurate estimation of the concentrations of each parameter in the samples submitted. There are good reasons for this. All accredited labs are regularly checked by an outside agency (CALA) who send out performance testing samples twice yearly and conduct quality audits on a regular basis to ensure the lab's quality control system is both written down and being adhered to. The certificate of analysis issued by the lab lists the concentration of each parameter, the Government's acceptable limit for that parameter, the "Reporting Detection Limit" (RDL) for the lab method used, the lab's in-house quality control results, the date samples were taken, the date samples were received, the date the certificate was issued, "flags" against any anomalies or departures from accepted protocols and a host of other information. Even a single sample sent to the lab produces a 6-8 page certificate of analysis. So what's could be wrong with that? Unfortunately, lots!

*Does the sample sent to the lab have the same concentration of contaminants as the area of the site it was taken from?*

That's an impossible question to answer when you don't know how the contaminants are scattered throughout the site or even around the area being sampled! One thing for sure, contaminants in soil are never distributed evenly and every site is different but it's the consultant's job to find out where they are and then to remove them. It's how this is currently being done that desperately needs attention.

There are two problems that must be addressed before the results received from the lab can be accepted as reliable estimates of the levels in the field:

- Was the sample sent to the lab a *representative* sample of the area being sampled?
- Did the lab get a *representative* sample out of the bottle to run the analyses?

Actually, there's an even more fundamental question that needs to be addressed:

*Is it possible for lab-sized samples weighing ~100 grams to be representative of many tons of soil (millions of grams) in the field?*

Currently, these questions are essentially being ignored and the reason seems tied to the fact that either the legislators forgot to address the problem or it was an "inconvenient truth" that had no easy answer so they chose to give it only lip-service in their regulations. Ontario's Brownfields Regulation 153/04 says that the consultant "shall gather representative samples..." but gives no indication how this should be done and it says the consultant shall set Data Quality Objectives which "outline the overall level of uncertainty that a Qualified Person will accept in collecting field data in order to develop a Conceptual Site Model," but again it gives no instruction as to what is acceptable. Worse than that,

it instructs the consultant to sample soil piles by taking at least one sample every 50 cubic metres or, if importing fill to a site, at least one sample every 150 cubic metres! That's one lab sample every 80-100 tons of soil (80,000,000 to 100,000,000 grams) for soil piles and one lab sample for every 250 tons (250,000,000 grams) of imported fill. That's insane and even if you quadruple the number of samples, you are still not even in the statistical ballpark! A recent court-case in Ontario illustrates just how insane this approach is. A dig-and-dump site cleanup was underway when the Provincial Environmental Officer drove by and noticed a lump of black goo falling into the dump truck from the excavator bucket so he called in, climbed up of the truck and grabbed a sample of the goo. Presto! analysis of the goo showed it to be unfit for dumping with the rest of the hundreds of tons of soil in the local landfill to which it was being hauled. The company was charged and fined---wait for it--- \$125,000! The appeals court refused the appeal because the Regulation does not specify the SIZE of sample to be taken. This decision should make every consultant, contractor and site owner very nervous indeed! It's also very unfair.

These statements and decisions simply pass the buck from the legislators to the unwary consultant who is now legally responsible to defend his/her results should something go wrong such as a site formerly declared to be clean later being found to be dirty based on more lab tests. The normal practice in site investigations is to collect as many samples as the consultant deems necessary (but more often what the budget allows!) into laboratory-supplied containers and ship them off in ice-cooled coolers to an accredited lab for analysis. But how does a consultant know what's "necessary" when there's no information on how the contaminants are distributed throughout the site? The lab results are then used to plot the spread of the contaminants in three dimensions and to plan the cleanup but this is done without ever giving the above two questions any serious consideration whatsoever.

*What if it can be shown that the sampling and analysis program for the site investigation is severely flawed and many results are essentially meaningless?*

There's a gaping chasm between what the contaminant distribution demands as necessary for sample size and sampling frequency and what the legislation deems as necessary. Sending a 100-150 gram sample from a borehole to the lab for contaminant analysis and expecting the answer to be an accurate description of what's in the many tons of soil around the borehole is not just faulty, it's insane, especially when you consider the lab only takes small sub-samples from the sample bottle to perform the various analyses. For example, 5 - 10 grams from the bottle are taken for metal analysis but only 1-1.5 gram of this is actually analyzed after pulverizing; 3 - 4 grams are sent in a separate bottle for VOC analysis or for BTEX/F1 analysis and ~10 grams are taken for PAHs. Remember, these sampling and analysis rules follow the Regulation's recommended protocols and they are a clear indication of what happens when you choose to ignore the most fundamental rule of soil sampling: "make sure your sample is representative of the whole". If the sample sent to the lab is not representative of the area from which it was taken, no amount of careful analysis at the lab will produce a meaningful result.

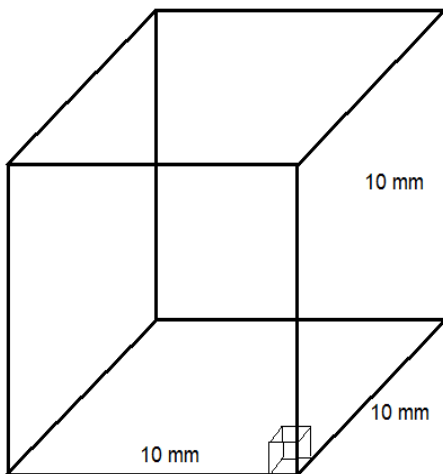
*Contaminant levels in soil can vary wildly even in samples taken within a few feet of each other!*

Some contaminants enter the soil as solid particulates and others as liquids which can be adsorbed and absorbed by the soil. Common examples of the former are sand-blasting operations where lead paint is being removed from steel equipment and falls on to the soil. The sand-blasting material itself can be a major source of contaminants since the older ones were produced from nickel-refining slag. For the latter, the most common example would be retail fuel outlets (gas stations) where fuel spillage around the pump island or leakage from the storage tanks and delivery lines contaminate the soil. In no case does the contaminant uniformly distribute itself throughout the soil but follows a variety of pathways of least resistance depending on the soil types; former site activities such as building construction/ demolition and many others but it is up to the consultant---usually with very limited historical information---to estimate or guess how the contaminants are spread across the site both horizontally and vertically. Keeping in mind the current use of the "one-size-fits-all" model for the size of samples sent to the lab, let's examine following scenario:

### *Real-life Scenarios*

Here's an example of the problem: A former metal fabrication site which used sand-blasting and paint-spraying for many years is to undergo a phase 2 environmental site assessment and the site history reveals that following many years of this type of use it was redeveloped as a warehouse. No one is quite sure where the blasting sand was dumped so the consultant drills a number of boreholes, collects samples into the laboratory-provided bottles. Screen analysis indicates that the site soil is coarse sand with an average particle size of  $1\text{ mm}^3$ . Samples are collected into 100 mL soil jars and submitted for analysis.

The lab screens the soil through a 2 mm sieve, discards the +2 mm fraction then withdraws 5 - 10 grams from the bottle and pulverizes this to pass a  $300\ \mu\text{m}$  (0.3 mm) sieve. *Question:* How many soil particles were taken from the sample bottle for pulverizing?



If all the soil particles, including the lead paint particles are perfect 1 mm cubes, then 1 cc of soil (~ 1.5 grams) contains a maximum of 1000 particles (10 x 10 x 10). In reality, due to air-space, there are about half this number or 500 particles. So, if the lab withdraws a 7 gram sub-sample from the bottle for pulverizing to minus 300 µm before withdrawing a cut for analysis, there are 3500 particles in the sample. Here's where it gets interesting.

*Assume the true lead concentration in this area of the site is 600 mg/Kg (5 times the allowable Ontario limit of 120 mg/Kg)*

If just ONE of the 3500 particles is lead paint, the lab certificate will report the lead concentration as 1620 mg/Kg which is more than 13 times the true value. This is calculated as follows:

1 mm<sup>3</sup> of lead (1 "soil" particle) weighs 11.34 mg. Therefore, 11.34 mg of lead in a 7 gram sample represents a concentration of 1620 mg/Kg of lead. If two particles of lead are present, the lab will report 3240 mg/Kg and if no lead particles are present, the lab will report a "non-detect" but remember, THE TRUE VALUE FOR THE AREA IS 600 mg/Kg! You can pulverize the 7 g sub-sample to the consistency of fine flour but it won't correct your seriously wrong result and please note that it is impossible for ANY 7 g sample to give you a correct result because THE SAMPLE IS TOO SMALL TO BE ABLE TO PRODUCE THE CORRECT ANSWER! It doesn't matter how careful the lab is or how many quality control samples they run or how tightly they control the measurement uncertainty, the sample taken cannot produce the correct answer! In order to have a hope of getting the correct answer, the sample size analyzed would have to be at least 18.9 grams and you would have to be sure that you collected only one lead particle into the 18.9 g sample (11.34 mg lead in 18.9 g of sample = 600 mg/Kg). Thus, for the lab analysis to indicate something close to a correct result, the sample size should be 50 - 100 grams and ALL of it should be analyzed for lead! The problem, of course, is that labs cannot handle anywhere close to these sample sizes and that, unfortunately, sums up the reason so many consultants are left scratching their heads when duplicate samples from the same location produce widely different results and re-sampling from the field simply compounds the confusion. Note that in this example, the true value for the lead is 600 mg/Kg but how much worse does it get when the same sample size is used to investigate cadmium or beryllium with allowable limits of only a few mg/Kg? The current approach of fixed sample size is simply not working because it can't!

### *What needs to be done?*

Ignoring the problem is not the answer because it only gets worse as the allowable levels of contaminants in soil get lower and lower. The lead limit in soil is 120 mg/Kg but for cadmium in a potable groundwater site it is 1.9 mg/Kg and for benzene it is 0.32 mg/Kg. Trying to get meaningful results at these levels from small soil samples is futile and the evidence to this fact is the common occurrence of duplicate field samples at near-limit concentrations producing greatly different results. The analysis results often disagree by well over 100% as shown in the following "real life" examples of site cleanups where duplicate soil samples were taken for analysis. The first table shows PAH results for a medium fine sandy soil. The second table shows the results of duplicate confirmation samples for BTEX/F1-F4 PHC's analysis taken from the floor of an excavation pit in a clay soil. Note the very large

Relative Percent Differences (RPD) in the clay soil despite the fact that the particle size is extremely fine, so there are other factors in play helping to make it impossible to get the "right" answer with such small samples (for BTEX components, the total sample analyzed is only 3 - 5 grams). The third table shows the results for 12 composite samples taken from around the soil pile in the picture.

These are quite common examples among many others, all of which make site assessment and cleanup a very "hit-and-miss" exercise, especially at near-limit levels. While these issues are serious at the lab end of the process, they are much greater in the field when you have no foreknowledge of the contaminant distribution across the site and are having to rely on the lab results to get it for you.

Parameter	Unit	G/S	BH-3 @ 2 - 4 ft	BH-3 @ 2-4 ft
Naphthalene	µg/g	9.6	<0.05	0.17
Acenaphthylene	µg/g	0.15	0.05	0.15
Acenaphthene	µg/g	96	0.05	0.25
Fluorene	µg/g	62	<0.05	0.36
Phenanthrene	µg/g	12	0.58	2.6
Anthracene	µg/g	0.67	0.14	<b>0.75</b>
Fluoranthene	µg/g	9.6	0.89	2.2
Pyrene	µg/g	96	0.78	1.9
Benz(a)anthracene	µg/g	0.96	0.44	0.96
Chrysene	µg/g	9.6	0.37	0.80
Benzo(b)fluoranthene	µg/g	0.96	0.53	<b>1.3</b>
Benzo(k)fluoranthene	µg/g	0.96	0.14	0.47
Benzo(a)pyrene	µg/g	0.3	<b>0.43</b>	<b>0.78</b>

*Duplicate soil samples for PAH analysis taken from the same location on a site. Note the 5-fold difference in anthracene, the 2-fold difference in benzo(b)fluoranthene and the 2-fold difference in benzo(a)pyrene.*

The next table shows duplicate clay soil samples for BTEX/F1-F4 analysis taken from the floor of an excavation. Note the number of RPD's (relative percent differences) that are well over 100% and remember that ANY exceedence of a regulatory limit by ANY amount needs to be cleaned up or risk-assessed. What does this say about the current practice of digging out contaminated soil until the lab confirmation samples show less than the allowable limits?

Parameter	Initial Result	Duplicate Result	%RPD
Benzene	6.02	1.61	116
Toluene	16.8	2.19	154
Ethylbenzene	10.5	0.75	173
Total Xylenes	60.7	10.8	140
Fraction F1	754	17	191
Fraction F2	301	229	27
Fraction F3	314	266	17
Fraction F4	95	65	38

*Which result is correct and what would the %RPD be at near limit levels?*

The last table shows the results of 12 composite soil samples taken from the same soil pile and analyzed for arsenic.

#### Results of Analysis of 12 Composite Soil Samples taken from the soil pile

Sample #	Arsenic
1	4
2	5
3	<b>34</b>
4	<b>86</b>
5	<b>20</b>
6	<b>140</b>
7	<b>72</b>
8	<b>55</b>
9	6
10	16
11	13
12	<b>32</b>

*Where would you dispose of this soil? Based on the current rules under O. Reg. 153/04, you would have to analyze at least ONE sample. If that sample was #1 or 2 or 9 to 11, you would put it back in the pit and may end up getting sued for failure to perform. If it was #3 to 8, you would leach-test it and send it, at high cost, to the landfill.*

Ontario Reg 153/04 mandates the minimum number of lab samples to be taken from soil piles as shown in the next table. For the pile in the picture, that number is ONE sample for up to 50 m<sup>3</sup> (3 truck loads). If you are bringing soil on to a site, it gets even worse, since you only need one lab sample for up to 150 m<sup>3</sup> (10 truck loads).

### O. Reg 153/04 Sampling Protocol for Sampling Soil Piles

Pile Volume	Field Screening Samples	Samples for Laboratory Analysis
< 50 m <sup>3</sup>	A minimum of 5 samples	A minimum of 1 sample
>50 m <sup>3</sup> to 150 m <sup>3</sup>	A minimum of 15 samples	A minimum of 3 samples
>150 m <sup>3</sup> to 500 m <sup>3</sup>	A minimum of 30 samples	A minimum of 5 samples
>500 m <sup>3</sup> to 1500 m <sup>3</sup>	A minimum of 50 samples	A minimum of 10 samples
>1500 m <sup>3</sup>	A minimum of 75 samples	A minimum of 15 samples

NOTE: 50 m<sup>3</sup> of soil = 3 Dump-Truck loads (~85 Tonnes or 85,000,000 grams) so the minimum sampling requirement is ONE LAB SAMPLE OF ~150 GRAMS of which only 5 - 10 grams actually gets analyzed! A typical picture of a 30 m<sup>3</sup> soil pile is shown below. How on earth can a 150 g sample be representative? 12 composite samples were gathered from around this pile and submitted for analysis of arsenic. The results vary from a low of 4 ug/g to a high of 140 ug/g---almost eight times the allowable limit.



These examples may seem to be extreme but they are not uncommon and every consultant has had the frustrating experience of having lab results that just don't seem to make sense when the duplicates are varying widely, contaminants that weren't in the original now exceed the limits in the duplicate (and vice versa) and the Regulation mandates that any exceedence of any limit must be accepted as "real" and dealt with according to the Reg. The current protocols are based on very flawed reasoning and the effort for ever-increasing accuracy and quality control at the laboratory is quite misplaced when the samples submitted are incapable of producing meaningful results. This does not mean that every site investigation is deeply flawed because many sites are quite "clean" to begin with but the coarser the soil and the lower the allowable limit, the greater the risk of declaring dirty sites clean and clean sites dirty.

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