**Obsolete Pesticides. Sampling and Analytical Procedures**

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The first stage in addressing chemical pollution in different environmental media typically involves sampling and analysis to understand the nature of the pollution, its extent, and potential effects.  A detailed sampling and analysis plan is a crucial component of this first stage; it not only ensures that data of appropriate quality will be obtained but also forces one to ask and address important questions about the range of potential data needs and the expected remedial objectives. The plan must specify the procedure(s), by which samples are collected, the sample locations, and the appropriate sample number. It must also describe how samples are to be handled, transported and analyzed. Proper consideration of these elements of the sampling plan will yield data that provide a solid foundation, on which are based all subsequent activities.

A well conceived plan for assessing the presence and/or extent of chemical pollution is a critical component of efforts aimed at environmental protection and remediation. The data obtained via the sampling and analysis plan provides the basis for all subsequent activities, including determining whether a problem exists, how significant the problem is, and how it is best remediated. Problems arising from a poorly designed sampling and analysis plan can therefore spread like ripples throughout all subsequent stages of environmental remediation and decision making.

A well thought out sampling and analysis plan tells you what, where, when and how to collect samples, and defines procedures for analyzing the samples once they have been collected. It also helps to ensure that the data collected are of appropriate quality. The sampling and analysis plan therefore serves as an instruction manual for field and laboratory staff. But the sampling and analysis plan serves another very important purpose – development of the sampling and analysis plan forces one to ask and attempt to answer many important questions about the site in question. Such questions may include:

General questions:

1. What types of chemicals are thought to be involved?

2. What is currently known about the site in terms of contamination of environmental media and past waste practices?

3. Is there a concern about past or future pesticide pollution?

4. How do you expect human health or ecological systems may be affected by this problem?

5. Is the work intended to comply with, or achieve regulatory requirements?

6. How will the data collected during sampling activities be used: to support risk assessment, to define the limits of contamination, to help develop a remedial action plan, or some combination of these?

Attempting to answer these questions may seem more difficult and time consuming than simply "going out and getting some data", however, the answers obtained will not only help develop a robust sampling and analysis plan, but may also ensure that the data obtained (usually at considerable time and expense) are of the greatest use.

Questions about the site to be sampled:

Another critical element in the design of the sampling and analysis plan is to take advantage of already available information about the site in question. Questions that can be asked include the following:

1. What have the past uses of the site been? Have past owners contributed to the problem? Is there a history of waste dumping at the site or nearby properties?

2. Are there potentially multiple sources of contamination (both in terms of time and place)?

3. Based on what is known about prior activities, what types of compounds might be expected? Based on the timeframes involved, are breakdown products of chemicals of concern also likely to be present in appreciable amounts?

4. Has the land been altered in ways (e.g., regraded, filled) which could influence pollutant movement or transformation?

5. What sampling and analysis data have already been collected? Can these be used to rule out the presence of certain chemicals? Were prior sampling and analysis plan’s deficient in some regard that can be remedied?

With respect to sampling and analysis specifically for obsolete pesticides, substantial information is available concerning their environmental properties. This information can be used to help understand pollutant movement in the environment and the types of environmental media that should be sampled (*the table on the next slide*). For example, if contamination with a relatively water soluble and readily degraded pesticide like 2,4-D is suspected then historical pollution may have left only residual traces in surface soils but groundwater would likely be affected. Due to its relatively low bio-accumulative potential (log BCF=0.3), 2,4-D would be unlikely to be present at high levels in biota (e.g., fish, soil invertebrates). Please, look on row 1 in the next table.

Environmental Properties of Some Obsolete Pesticides:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Pesticide** | **Half-life in soil (days)** | **Koc (L/kg)** | **Water solubility (mg/L)** | **H****(atm-m3/mole)** | **Log BCF (daphnia)** |
| **2,4-D** | 10 - 30 | 19.6 - 109.1 | 500 | 1.02 E-8 | 0.3 |
| **DDT** | 2000 | 677,934 | 0.025 | 8.10 E-06 | 4.2-4.4 |
| **Chlordane** | 4300 | 10,811 | 0.25 | 7.52 E-06 | 3.13-4.0 |
| **Chlorpyrifos** | 600 | 95,816 | 0.74 | 6.00 E-06 | 3.49-4.84 |
| **Dieldrin** | 1000 | 25,546 | 0.195 | 1.51 E-05 | 4.1 |
| **Heptachlor** | 250 | 30,200 | 0.18 | 1.09 E-03 | 4.08 |
| **Lindane** | 400 | 1,352 | 6.8 | 1.4 E-05 | 1.2 -3.2 |
| **Methoxychlor** | 350 | 51,310 | 0.056 | 4.86 E-05 | 4.4 |
| **Toxaphene** | 120 | 80,000 | 0.045 | 1.58 E-05 | “low” |

Conversely, while persistent and highly lipophilic pesticides such as chlordane and DDT would be expected to be bound preferentially in soil and present in biota, they would be expected to have relatively limited impacts on groundwater. In terms of air pollution, the Henry's Law Constant (H) provides an indication of the partitioning between air and water (including soil pore water). Consideration of the Henry's Law Constant suggests that a relatively volatile pesticide such as Heptachlor may be more likely to be present in soil gas samples than a pesticide such as DDT which will tend to remain dissolved in the aqueous phase. Information of this nature has to be also used in interpreting the results of soil sampling. For example, the finding of minimal concentrations of Toxaphene in groundwater samples says little about overall pollution levels at a site because most of the chemical would be expected to remain in the soil matrix.

The ultimate goal of sampling is to gather reliable information about the pesticide pollution of a particular environmental media region or site, in order to provide sufficient data for further chemical analysis and future decision-making for the scope of possible remediation actions.

1.How many samples to collect from a site?

The goal in determining sample number is a balance b/n the level of certainty required with the limitations imposed on available resources.

2. Decision for the order and placement of samples across the area of interest, depending on the level of knowledge and characteristics of the site.

The different approaches include in brief: Preliminary Search sampling for identification of the source of pesticide pollution and estimation of the borders of the polluted region or site, Judgemental sampling, Systematic sampling, Random sampling, Stratified sampling, and definition of the sampling grid, which depends on the chosen approach of sampling.

3. Sample handling and transport. The sample handling, labeling are important issues when the chemical analysis is performed in laboratory conditions.

Judgmental Sampling

This technique is based on using personal judgement and opinion to select sample locations. Samples are placed where one thinks they ought to be based on what is known about the site and the particular interests in defining the contamination. The advantages of judgmental sampling are that it takes advantage of site-specific knowledge and experience and is fairly easy and straightforward to implement. It is the most intuitive approach to sampling. On the negative side, this method is subjective and depends on one’s knowledge being accurate and complete. What if some other source of pollution, not readily apparent, is also involved? This would likely be missed by judgmental sampling.



Systematic Sampling

Under this approach, one allocates samples in a consistent and pre-determined pattern. samples are located every 10 meters from a preselected starting point in all directions (the sampling interval could be expanded as one moves further out, the important factor is for it to be consistent). The advantages of systematic sampling are that it is largely unbiased and objective (entirely objective aside from the selection of starting point) and the strategy is easy to explain. The negatives are that it either requires a substantial number of samples (e.g., to sample every square in the grid) or supplies only limited coverage of the area in concern. Hot spots of potential contamination can be easily missed.



Random Sampling

Random sampling is generally preferred as a sampling technique because it produces an unbiased data set that can be analyzed using standard statistical techniques. In random sampling, one starts at a randomly chosen point in the sampling grid and then uses a random number generator to identify the locations to be sampled (random number generators are easily found on the internet). In addition to the advantage of being able to reliably perform statistical operations on the collected data, random sampling is also recognized by regulators as being objective and unbiased. Use of random sampling cannot, however, make up for having extremely small sample numbers. One is just as likely to miss a hot spot with small numbers of random samples as with small numbers of systematic samples.



Stratified Sampling

Stratified sampling combines several of the best features of the prior three approaches. Using site specific knowledge, one can divide the site in question into different strata and then use different sampling strategies, as appropriate, with each. Thus for identifying the extent of contamination, systematic sampling might be appropriate whereas to determine if the much larger remaining area of the site is affected, a random approach might be preferred. Specific samples could also be located via judgmental sampling to address specific concerns, in this case children's exposure during play and possible sediment contamination. Stratified sampling has the advantage of reflecting site-specific information (in terms of how the site is stratified) while still providing unbiased samples where appropriate. It does require site specific knowledge and depends on that knowledge being correct; otherwise the strata selected may be inappropriate.



Auger Hand Sampling Heads



Sample Analysis

The final step to specify is how the samples are to be analyzed.  It makes little sense to carefully specify the procedures for locating and collecting samples if unclear directions to the analytical laboratory result in unsatisfactory data. The directions should include not only the analytical method, but also whether any sort of pre-analysis digestion or treatment (*e.g.,* compositing, extraction) is required.  Analysis methods (GC-MS, ICP, HPLC) should ideally reference specific protocols unless some specialized analysis is being requested.  When specifying the analytical procedures to be followed, one should  consider whether breakdown products or contaminants should also be included (*e.g.,* 2,4, 5-T, 2,4-D and dioxins).  It is vital that the Sampling and Analysis procedure specify the necessary detection limits for all analyses to be conducted.  Data reported by the laboratory as below the detection limit will be useless if the detection limit is higher than the relevant regulatory or risk criterion.  Finally, analytical data quality objectives (percent recoveries, acceptable results for blanks, *etc.*) should be specified.

Summary

In summary, a well-designed sampling and analysis plan is a critical component of any remedial strategy. Such a plan provides the fundamental data on which additional assessments and decisions can be made. Successful design and implementation of such a plan requires the participation and input from all involved stakeholders, to the extent that such parties can be identified earlier in the remedial process. By maximizing the use of pre-existing information, determining the sample location strategy that best fits with the project needs, and thorough attention to the details of sample collection, handling and analysis, a sound sampling and analysis plan can be developed and carried out.

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