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WATERS SAMPLING OF WASTE WATERS

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1. Introduction

The selection of sampling procedures is the basis of environmental study because any sample must be representative of the environment from which they are taken. In water sampling we must know all problems associated with sampling contamination from sampling equipment; sorption and leaching of contaminants by sampling tool materials; replication; frequency of sampling; nature of samples and problems associated with sample collection.

Perhaps the most critical element in environmental analysis is the sampling and analysis plan. Recently, some guidelines about the quality control in sampling for water analysis were reported [1].

Sampling plan objectives after Barcelo [2] are:

1. Definition of objectives Aims of the measurements
2. Select target analytes and analytical methods
3. Determine sampling locations
4. Fix number of increments and method of sampling
5. Select methods for sample preservation and pre-treatment
6. Prepare final plan.

A general book on this topics was republished in 1996 by Keith as Editor [3].

2. Types of samples

The two basic types of water and wastewater samples are: discrete and composite samples. In fig. 1 are illustrated the types of samples .

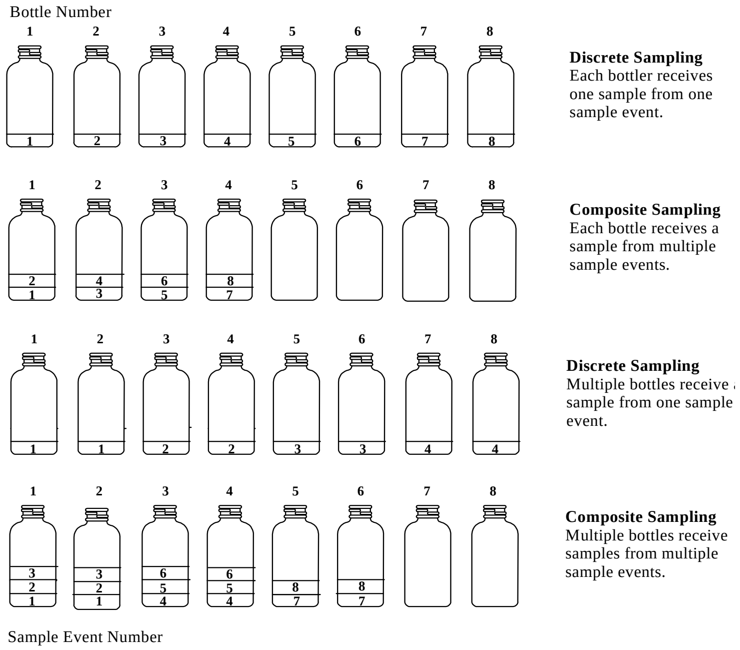

Figure 1. Types of water and wastewater samples

A *discrete sample* , also known as a *grab sample* , is an individual sample collected in less than 15 min. *Discrete sample* are recommended when the quality of the discharge is essentially constant.

A *composite sample*, consist of series of smaller samples collected over time and deposited into the same container. They are useful in calculating the average concentration and pollutant loading during the sampling period. Depending on the collection method, can be produced : a *time composite sample*; a *flow- proportional composite sample, a sequential composite sample.*

A single grab sample or a half-dozen grab sample over a 24-h period give representative sample only if the streams essentially constant-flow, spatially homogeneous in composition at any time and varying in composition gradually over an extended period of time. A modest series of grab samples may give a fair approximation of stream characteristics. Industrial wastewaters rarely meet the requirements for this idealised model

Particularly for a river ,the most practical river sampling program is accomplished from a boat at known sampling location. The sort of sample collected is almost always a *manual grab* or a series of manual grab sample composites prior to analysis.

There are various techniques for choosing appropriate locations. One technique especially appropriate for sampling rivers for chemical constituents is the *spatial gradient technique*.

3. Manual and Automatic Sampling

Discrete and composite sampling can be collected *manually or automatically*. The sample should be collected in a container which is compatible with both the analyte being determined and the sample matrix. USEPA has published requirements for selecting the right type of containers(Table 1) [4].

According the 1980s, manual sampling lost ground to automatic samplers with many advantages: rapidity, improved accuracy and reduce costs associated with manual collection.

The two basic types of automatic samplers are *portable and permanent samplers*.

The sample delivery system is a pump designed to transfer the sample from the liquid source to the bottles for storage. At the beginning was used vacuum pumping but now the most commonly used are peristaltic pumps and bladder pumps [5].

Sample volume inaccuracy in peristaltic pump samplers was solved with introduction of liquid detectors [6]. The detector used a thin piezoelectric film sensor. The piezoelectric film does not contact the water or wastewater to be sampled and does not depend on the conductivity, pH, or other characteristics of the water.

According to the EPA more than 100 models of portable automatic sample collection devices existed. All of the portable samplers offer units that operate on ac and dc, weigh less than 20 kg empty, offer sampling intervals from 1 min to at least 4 h , are capable of flow-proportional or timed-interval sampling, have no metal parts in contact with the sample, operate over temperature range from -30 to 50^0C and purge the sample line before and after sampling.

Table 1.

Partial list of Parameters and Required Containers

Parameter	Container type
Acidity	Plastic(P), Glass(G)
Alkalinity	P, G
BOD	P, G
COD	P, G
Chlorinated hydrocarbons	G, Teflon-lined cap
Chlorine, total residual	P, G
Coliform, faecal and total	P, G
Colour	P, G
Cyanide	P, G
Fluoride	P
Nitrate	P, G
Metals	Polyethylene
Oil and grease	G, G
OD	G, G
Temperature	P, G

An ideal sampler after Newburn [7] should have include the following:

1. ac and dc operation with adequate dry battery energy for 120 h of operation at 1-h sampling intervals
2. suitability for suspension in a standard manhole and accessibility for inspection and sample removal
3. total weight including batteries under 18 kg
4. sample collection intervals from 10 min to 4 h
5. capability for flow-proportional and time-composite samples
6. capability for collecting a single 9.5 L sample or collecting 400-mL discrete samples in a minimum of 24 containers
7. capability for multiplexing repeated aliquots into discrete bottles
8. a single intake hose having a minimum ID of 0.64 cm
9. intake-hose liquid velocity adjustable from 0.61 to 3 m/s
10. explosion-proof materials and electronics
11. no metal parts in contact with waste souse or samples
12. an integral sample container compartment capable of maintaining samples from 4 to 6 ^{0}C for a period of 24 h in ambient temperature ranging from -30 to 50^{o}C
13. purge cycle before and after each collection interval
14. interchangeability between glass and plastic bottles, particularly indiscreet samplers
15. sampler exterior surface light in colour to reflect sunlight

4. **Preserving Sample integrity**

The main purpose of sampling project is to collect a sample that truly represents the source at the time of collection. It will be necessarily to preserve the integrity of the sample during and after sampling.

Ideally, the samples should be completely analysed immediately after collection. However, immediate analysis may not be done according to permit requirements, regulations and consist of refrigeration, chemical fixation or both. First step is to select the right automatic sampler (sample bottles and sample tubing. Harris and Keffer [8] concluded that vacuum sampler produced higher BOD and COD and solid concentration than sampler using peristaltic pumps. Vacuum samplers produced higher values than manual flow-weighted grab samples. In conclusion high-vacuum, high liquid intake velocity samplers were more effective in capturing solid than peristaltic pump samplers. Thomas and Eads [9] study about contamination of successive samples in portable sampling systems showed that a vacuum sampler produced more cross-contamination than peristaltic pump sampler. For a good recovery of VOC was recommended moderate speed peristaltic pumps [10].

The basic difference between one sampler over another is in liquid intake velocity and the wetted surface area of the liquid transport system. For toxic pollutants, the sample should contact only Teflon, glass and medical-grade silicone rubber if a peristaltic pump is being used in the sample transport system.

The type of contaminates contributed to water sample by material used in sampling tools are shown in table 2.

Contamination can be minimised by stream cleaning. If the water are transported through soldered pipes the most common contaminants are tin and lead [12]. Adsorption of metals at low concentration on container walls is determined by metal concentration, pH of the sample, length of contact with the container, sample and container composition [13, 14]. Sorption of dilute halogenated hydrocarbon mixture in water by various plastics and PVC was studied [15, 16]. Many samples start changing physically, chemically or biologically almost instantaneously. Sample preservation must be done immediately after collection. At the moment the sample is removed, the chemical processes that affect the sample may deviate from what occurs in situ. In process of collection, the sample is often exposed to ambient light and its temperature most likely has changed. Consequently, photochemical reactions may take place, and the temperature-dependent kinetics of other types of reactions will be altered. The presence of oxygen may initiate oxidation of some chemical species.

The vessel may contribute to the process by adsorbing certain components of the sample. This adsorption permits additional loss of volatile compounds or introduces extraneous compounds into the sample. Complete stability of the sample through preservation cannot be totally achieved for every constituent in a sample, nor can all constituents be stabilised with the same degree of success. The most common change that preservation technique attempt to minimise are *physical changes* such as *adsorption volatilisation, , diffusion* and *precipitatio*n, and *chemical changes* including air oxidation, *photochemical changes* and *microbiological degradation.*

Table 2.

Contaminates of Water Samples from Materials Used in Sampling Device.

Material	Contaminants
PVC - threaded joints	Chloroform
PVC - cemented joints	Methyl ethyl ketone, toluene, acetone, methylene chloride, benzene, ethyl acetate, tetrahydrofuran, cyclohexanone, three organic Sn compounds, and vinyl chloride
Teflon(polytetrafluoroethylene)	Nothing detectable
Polypropylene or polyethilene	Plasticizers and phthalates
FRE(Fiberglas-reinforced epoxy material)	Nothing detectable
Stainless steel	Cr, Fe, Ni, and Mo
Glass	B and Si

Table 3 illustrate a partial list of Preservatives and maximum holding time in water analysis.

Table 3.

A Partial List of Preservatives and Maximum Holding Time

Parameters	Preservative	Maximum Holding Time
Acidity and Alkalinity	4^oC	14 days
BOD	4^oC	48 h
COD	4^oC; H_2SO_4 to pH<2	28 days
Chlorinated hydrocarbons	4^oC	7 days until extraction
Coliform, faecal and total	4^oC	6 h
Oil and grease	4^oC, H_2SO_4 or HCl to pH<2	28 days
VOCs	4^oC	14 days
SVOC, pesticides, dioxins	4^oC	7 days until extraction
Metals	2 ml HNO_3 50% to pH<2	6 months
Cyanide	2 ml NaOH 50% to pH<12	14 days
Sulfide	4^oC, 1 ml $Zn(Ac)_2$, 1 ml NaOH 50% to pH<9	7 days
Fluoride	4^oC	28 days

Rapid cooling down to 4^oC reduces microbiological activity and the potential for volatilisation of dissolved gases and organic substances contained in the sample [17].

Some parameters, such as temperature, pH, DO, and residual chlorine cannot be preserved. They must be measured on-site during sampling. Proper preservation requires a co-ordination of activities between the field crew and the laboratory staff.

Holding time is defines by ASTM as " *the time during which a water sample can be stored after* collection and preservation without significantly affecting the accuracy of analysis [18]. In fact, evidence suggests that holding times can be extended for some parameters [19]. The maximum time that a sample can be held before compromising the integrity of the analysis is dictated by the matrix (e.g. surface, ground or wastewater), the properties and concentration of the substance being determinate, and preservation technique employed.

Oak Ridge National Laboratory (USA) conducted holding time studies [20, 21] for 17 VOCs and four explosives in three waters types (distilled, ground and surface water) and three soil matrices. With respect to VOCs in water preservation with sodium bisulphate provides considerable stability (>28 days) and is considerable safer than hydrochloric acid.

A concept called ***practical reporting time*** (PRT) was introduced, which provides a technically valid approach for assessing the data usability of samples analysed after the regulatory holding time has expired [22].

The PRT is defined as the day when there is a probability of 15% that the measured analyte will be below the CC. A critical concentration (CC) is determined on the first day of the holding time study; the CC is the concentration below which there is only a 5% chance, due to measurement error, that a measure concentration will be observed.

5. Replication

The number of replications is determined by the purpose of samplings: a) determination of chemical composition of water body and b) sampling for the purpose of monitoring.

Table 4.

Chemical Results from Various Water Sampling Techniques

Number of Sub-samples Replicated 10 Times	Ca mg/L	Mg mg/L	Sr µg/L	P µg/L	Pb µg/L
Three aliquots 1-L samples	53(4.5)	30(8.3)	130(20)	20.4(5.1)	2.4(0.5)
1 aliquot/three 1-L samples	29.7(5.0)	11.8(3.8)	64(20)	72(30)	13(4)
χ^2, P<	0.02	0.05	0,001	0.001	0.01
Three 2-L samples	55(10.0)	56.2(10.0)	155(25)	100(25)	5(3,0)
Three 5-L samples	40(11.0)	22(10.0)	120(21)	110(25)	10(3.1)
Three 20-L samples	30(3.0)	12(2.1)	75(10)	75(10)	15(2.4)
Three 30-L samples	31(2.8)	14(2.1)	70(10)	80(8)	18(2.1)

Note: The depth sampled was from the surface to 2,5 m below the surface. The numbers in parentheses denote the standard deviation.

The percent coefficient of variations are dependent of the number of aliquots analysed and is always lower when more aliquots per litter are analysed than when one sub-sample is analysed [23]. Table 3 containing results from various sampling techniques.

6. Nature of Samples

Type of water body (e.g. lakes, rivers, oceans, streams or aquifer) and physical state of sample (e.q. snow, ice, rain, fog or dew) have problem associated with sample collection.

The chemical composition of a following liquid, like a river, may vary with accordance to the changes in a number of parameters such as temperature, flow rate, distance from the source among others; none of them can be controlled during sampling. The full information may be available after a large number of samples have been taken an analysed.

Surface waters include a wide range of different types of waters: *surface run off*, *ditches*, *creeks*, *rivers*, *lakes*, *estuaries*, *seas*, *industrial areas*, *effluents*, *piped water*.

There is no single way or devise that is adequate to sample such a variety of situations. An overwiew of the different details was published [3, 24].

In many water bodies, the stratum from which the sample is gathered is very important from the standpoint of chemical composition. Data presented in table.4. illustrate this point [25].

Most of the variability is reasonable consistent within the deeps sampled. Position of sample collection is also important in the collection of ice and snow [26, 27]. Ideally snow should be sampled at the time of snowfall ,because its composition changes on standing. The oceans present sampling problems because the chemical composition is far more variable than any composition in freshwater bodies [28]

Table 5.

Variation in Chemical Composition in Relation to Sampling Strata in a 33-m Drinking Water Well

Strata m	Mo $x10^{-2}\mu g/L$	V $x10^{-4}\mu g/L$	Bi $x10^{-2}\mu g/L$	Hg $\mu g/L$	Be $x10^{-2}\mu g/L$
19 - 21	15(2.5)	0.8(0.2)	8.5(1.7)	1.6(0.4)	0.7(0.2)
24 - 26	10(2.0)	30(4.0)	4.5(1.0)	18.3(1.7)	18(3.0)
29 - 31	28(3.5)	1115(97.3)	18.2(2.0)	3.0(0.5)	11(1.0)

Note: The numbers in parentheses denote the standard deviation.

A general recommendation is that samples from a stream, should be collected 30 cm below the surface and similar distance above the bottom. If systematic sampling takes place in a lake or reservoir then locations in the lake should be planned, generally by dividing the surface in squares or grids and sampling in each on of these imaginary squares.

Water samples collected from the wells follow a protocol that consists of purging water standing in the well prior to the sampling. Usually the water is purged till the pH and conductivity remain constant. Various protocols of groundwater residue sampling were described [29] . The description of multilevel samplers and the pipe diameters, between 38 to 50 mm are given. The distance to the water table should also be defined when groundwater monitoring is performed. In general, when ground or well water monitoring is performed it is very important to know the history of the cultivated field, crops and chemicals used in the land which is above the wells.

Industrial wastewaters are never pure solutions. Substantial suspended particulate are present and rarely are these suspension stable. Sampling of such sedimentary materials used two categories: *bottom grab sampling and core sampling*. Abundant variants and devices of each type are available.

For the sampling of wastewater discharges the three major sampling techniques are available: *grab sampling*, *composite sampling* and *continual sampling*. A continuous sampler, should give the most nearly representative sample of a wastewater flow. This statement is especially true for those proportional to stream flow. Such samples, however, generally require large collection containers and present a more challenging routine maintenance problem that the somewhat simpler automatic composite samplers.

Groundwater is one of the most important natural resources, and has a very complex matrix. Although each aquifer represents a different water quality all groundwater has two unique properties for natural water system:

1. the movement of groundwater through the aquifer precludes the transport of chemicals by particulate. Only the substances soluble in the groundwater matrix are mobile within the aquifer.

2. Groundwater is nearly oxygen free and dissolved ions tend to be in their most reduced state.

Groundwater sample cannot contain any particulate matter, and must be protected from air at all times if the sample is to be truly representative.

Techniques for proper groundwater sampling must include the following [30]:

- purge-volume test
- consistent sampling protocol
- anaerobic sampling and sample handling conditions
- filtration of all samples

One of the least consistent elements of groundwater sampling is the time between the purging of the well and the sample removal from the well. Various methods for determining the necessary extent of well purging have been recommended [29-32]. The US Geological Survey recommended pumping the well until temperature, pH, and specific conductance are constant. The USEPA recommends removal of three well-casing volumes prior to sampling. The position of well water sampling should be as close as possible to the point of well purging. From sampling to sampling the sampling point within the well water column must be the same.

In the next review we will present techniques for extraction of the trace analytes (organic compounds and metals) from various water samples.

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