NETWORK FOR INDUSTRIAL
ENVIRONMENTAL MANAGEMENT (NIEM)

PHASE I FINAL REPORT

Volume 2

ANNEXES 1-6
MANUALS AND GUIDELINES

AUGUST 1989

SWEDISH
INTERNATIONAL
DEVELOPMENT
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ENVIRONMENT PROGRAMME
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BANGKOK, THAILAND

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The Report consists of three volumes. The Volume 1 is the "Main Report" which provides conclusions and recommendations about the NIEM Phase I programme as a whole. The Volume 2 includes the first six Annexes to the Report which are the "Manuals and Guidelines" produced during Phase I. The Volume 3 contains the Annexes 7-12 of the Report which include the six reports on the field studies carried out during Phase I. Additionally, a brief "Executive Summary" for the Phase I Report was also produced.

Contents

Annex 1

MANUAL ON DISCHARGE CHARACTERIZATION

PREFACE

This manual was prepared as part of the Phase I programme of the Network for Industrial Environmental Management (NIEM). The manual presents in detail the methodology and procedures to be used in conducting discharge characterization surveys at small pulp and paper mills. Network members, drawn from industry, government and academia of the Asia-Pacific region, conducted a series of coordinated projects on discharge characterization of pulp and paper mills based on the recommendations of this manual. The results and experience obtained during the course of the individual mill surveys was used to revise and update this manual to its present form.

The United Nations Environment Programme gratefully acknowledges the financial contribution by the Swedish International Development Authority that made fuctioning of the Network possible. Special thanks are extended to Mr. Gustaf Blidberg, Vice-President of Industrins Processkonsult AB, IPK, Sweden, who drafted the text. Suggestions for revisions to the draft were provided by Network members.

Contents

DISCHARGE CHARACTERIZATION

1. Objectives and Goals

The objective of this manual is to present a guideline for practical day-to-day pollution control and specific mill discharge surveys in pulp and paper mills situated in the NIEM countries. The major part of this industry consists of comparably small units with limited facilities for process and discharge control.

Therefore, the emphasis in this manual has been laid on simple, low-cost techniques giving acceptable and comparable results, while some precise and elaborate techniques have been omitted.

The manual outlines the appropriate methods for characterizing mill discharges with reference to:

- the characterization concept;
- flow methodology;
- sampling methodology;
- selection of parameters for characterization;
- analysis of parameters;
- presentation of results;
- cross checks on the reliability of results.

The goal of this manual is to help the NIEM members to harmonize procedures and provide reliable and comparable data, thus obtaining better basic information on mill operation and environmental impact from their own and other members' experience.

2. The Characterization Concept

Discharge characterization is essential for measuring effluent properties, for controlling pollution, and for obtaining the data that mill managers need to better utilize resources. Data obtained in discharge surveys also provides the information needed for the design of new production and pollution control systems. Discharge characterization refers to the measurement of flow rates and analysis of representative samples of the process streams throughout a mill. The techniques employed in this process should be chosen such that the date obtained are reliable. Cross checks should be carried out in order to confirm this reliability.

The analysis of discharges is often complex, requiring the expenditure of much effort and money. Establishment of a single procedure can be risky in view of the fact that different raw materials, processes, and standards are employed in the various kinds of mills found in the NIEM member countries. The underlying principles remain the same, however, and in order to characterize the discharges of a particular mill the following steps are necessary:

- measurement of total discharge;

- separation of various production stages into managable, well-defined blocks (usually representing processes);
- establishing proper procedures in order to characterize the block discharges;
- measurement of discharges from these blocks;
- correlation of discharges from various production stages (blocks) with the overall mill discharge (i.e. establishment of unit material balances and overall material balances).

The pulp and paper manufacturing process can be broadly classified into the following production stages:

- Raw material preparation;
- Fibre line (pulping);
- Bleaching and bleach chemicals preparation;
- Chemical recovery;
- Paper making;
- Utilities;
- Effluent treatment.

The block diagram should be based on the actual mill configuration and should be as simple as is adequate for the analysis. In the simplest case it may be just one block, although in a modern integrated mill the block diagram will consist of several blocks. Figure 1 shows an example of a block diagram for an integrated mill.

The measurement of various parameters to characterize the effluents is the key step in a mill survey. Measurements should characterize the effluent as fully as possible (be it total or sectional), be relatively easy to conduct, and result in information that is useful for process and discharge control. Whenever possible, flow measurement and sampling should reflect normal mill operation and production; any discrepancies should be noted on the sampling data sheet.

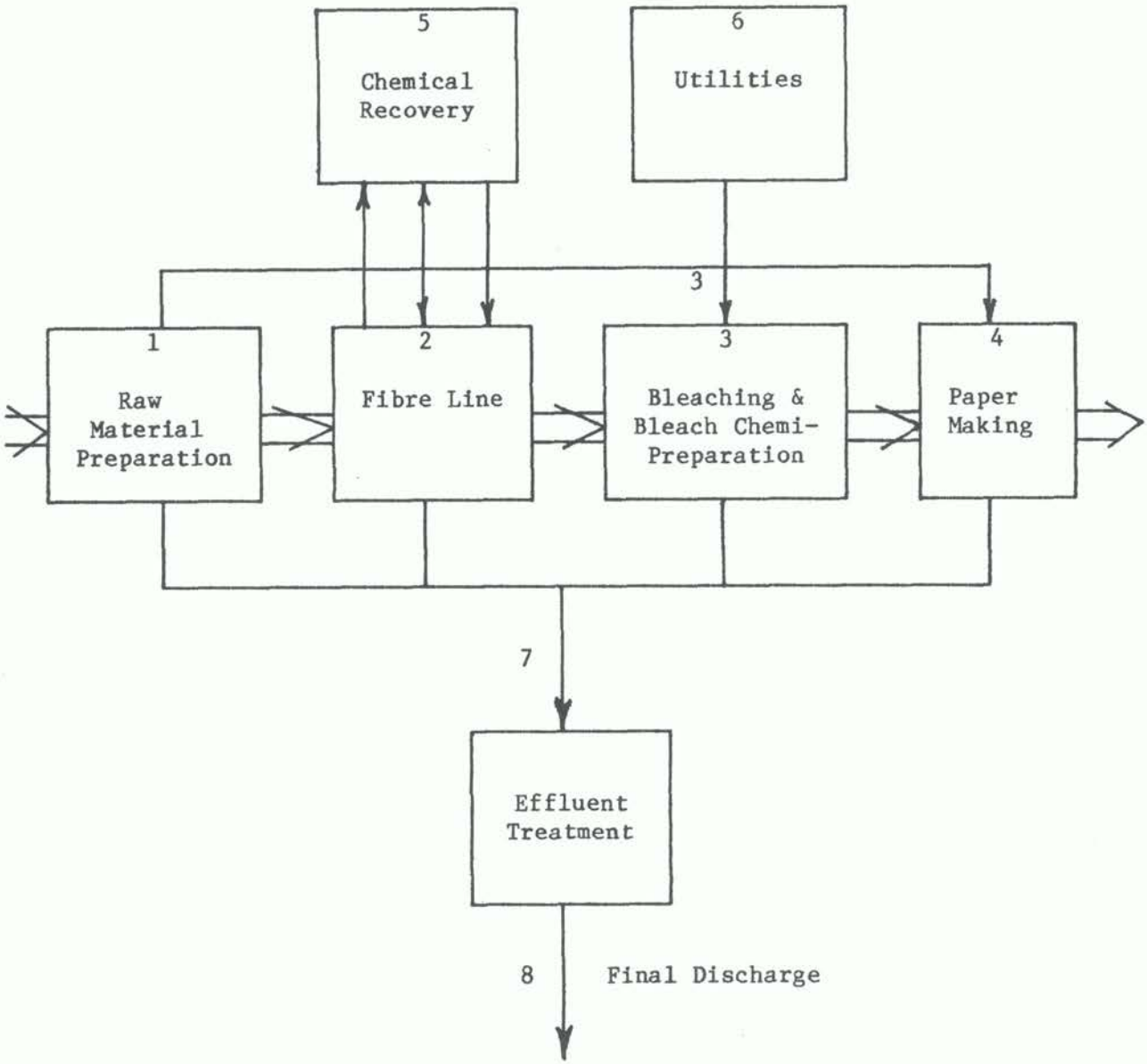


Figure 1 - Block Diagram Showing Processing Stages and Numbered Effluent Sampling Locations in a Pulp and Paper Mill

3. Check Point Location

The check point/points required to characterize a block or a mill should be located so that the flow data and samples collected represents the discharge of the unit in question in the best possible way. Therefore, the points should be carefully selected to ensure that representative data are collected. The following criteria should be satisfied:

- It should be possible to determine the flow rate using either direct or indirect means (Section 4);

- The effluent should have a homogeneous composition to ensure that the sample is representative (Section 5);

- Great care should be given in monitoring the final mill discharge. This check point/points should be selected and arranged to the highest possible degree of reliability and be used for cross-checking of the in-plant monitoring results (Section 10);

- The block discharges should be monitored at locations that give the maximum information about the function of the block taking in account interconnections between the blocks (e.g. spent liquor, white water, and diluted pulp streams). At locations having a relatively constant flow rate and composition, flow measurements and sampling can be done manually.

4. Flow measurement

At all check points, data on flow rates is essential and must be established either by direct or indirect measurement. Direct measurement of flow is preferred whenever possible.

The main methods of direct flow measurement are:

- weirs (channels or pipe ends);
- parshall flumes (channels);
- orifice plates (pipes);
- magnetic flow meters (pipes).

A brief description of these methods is given in Appendix 1.

Before choosing and designing a flow measuring device, it is important to have an idea of the magnitude and frequency of variations in the flow at the choosen check point. Design of flow measurement devices resulting in submerged flow situations should always be avoided.

The flow rate of the final mill discharge should preferably be measured and recorded continuously. The function and accuracy of the instrument should be checked at regular intervals. It is important to remember that, while most mill operation instruments are used for determination of trends and changes in relation to present values, these

instruments are used for determination of absolute values. Consequently, the accuracy required is higher.

Flows from blocks can be measured intermittently, but the frequency must be determined carefully in order that representative values of the average flow rates are obtained.

Weirs are the most commonly used flow measuring device in channels. Construction and installation of and flow rate measurement with weirs is described in Appendix 2:1. The water level above the weir edge is usually measured indirectly from a fix-point. It should be noted that whenever the position of the weir edge is changed (e.g. during channel rinsing operations), a new fix-point location must be determined. Sedimentation in the channel and microbial growths on the weir may also interfere with the flow measurements and should be regularly removed.

For permanent flow measuring installations, a Pharshall flume is the best flue measuring device due to its standardized dimensions, etc. In Appendix 2.2, the design and installation of Pharshal flumes is further described.

At some check points, indirect flow measurements may be employed. These methods include:

- Calculation from water balances, mass balances and/or energy balances for unit operations or blocks. Example: The overflow from a drum washer in a bleach plant may be calculated from the pulp concentration before and after the bleaching stage, the pulp production, the amount of wash water applied, and the amount of reused filtrate;

- The flow may be diverted into a container of known volume and the time required to fill the container measured;

- If the system includes a tank where liquid levels can be measured easily, the flow may be calculated from the rate at which the level rises when the outlet valve is closed;

- Dilution measurements by injection of a salt solution or tracer dye at a constant rate. This type of measurement can only be performed irregularly, but can be carried out with very good accuracy;

- Velocity measurements by instantaneous injection of a tracer (salt, tracer, dye) into a channel or pipe with a known length and mean cross-sectional area between the injection and sampling points. Again, this type of measurement can usually only be performed irregularly. The data normally obtained in practice often show low accuracy, therefore the use of this method should preferably be restricted to pre-tests etc.

5. Sampling

The sample collected from a check point must reflect the variations that occur during the sampling period. At the final discharge point, the sample preferably should be collected automatically proportional to flow. At other check points, grab sampling methods may be employed to get a composite sample. The following points should be observed:

- The effluent should have a homogeneous composition at the point of sampling. Special care should be excercised if the effluent contains dense suspended particles;

- Difficulties can arise through a build-up of suspended particles in narrow or constricted sampling pipes or valves;

- In pipes containing pulp, it is necessary that the sampling pipe be extended into the transport pipe a distance equal to 30 percent of the larger pipe diameter in order to avoid wall effects;

- Samples from channels shall be taken at some distance from the bottom in order to prevent sediment particles from entering the sample in unrepresentative quantities;

- Automatic samplers should be easily accessible for inspection and maintenance. Furthermore, the function of the sampler should not be affected by corrosive media, suspended particles, or microbial growth;

- In the case of substantial variations in the flow rate, it is preferred that composite samples correspond to these flow variations. This can be achieved through the corresponding variation of sampling intervals when the sample volume is constant or variation of the sample volume when the interval is constant. In the case of manual grab sampling, it is easier to have a constant sampling interval and vary the volume added to have a constant sampling interval and the composite sample proportional to the flow;

- Composite shift samples preferably should be collected at block check points whenever large variations in the discharge might occur. This also helps in process control;

- Composite daily samples may be collected at regular time intervals if the flow rate and composition are relatively constant;

- The volume of each sample should be large enough to ensure that a representative sample was obtained. The volume of the composite daily sample should be in the range of 3-5 litres.

6. Sample Handling and Storage

Composite samples should be handled in such a way that the sample characteristics are not distorted before analysis. The following precautions should be observed to ensure correct results:

- The sampling bottles should be clean;
- Daily composite samples might require refrigeration during the sampling periods in order to minimize bacterial growth (at check points in a warm environment this should be checked);
- The composite sample should be mixed carefully before a portion (usually one litre) is withdrawn for analysis;
- The samples should be analysed as quickly as possible;
- Samples that cannot be analysed within an appropriate time should be refrigerated or frozen;
- The temperature and pH of the samples should be recorded immediately after sampling.

7. Selection of Parameters for Characterization

The parameters evaluated at any check point should properly characterize the discharge from the block in question. Parameters that are proposed to be evaluated at the check points shown in Figure 1 are indicated in Table 1. Parameters are classified as first and second priority for each check point. Final determination of priority for each parameter should be left to the discretion of individual mills and researchers.

The Priority 1 parameters at Check Point 8 should be evaluated daily using a composite sample. At the other check points, Priority 1 parameters preferably should be analysed once a week. Frequency for evaluating Priority 2 parameters will depend on the facilities available, but if possible should not be less than four times during the 12 month monitoring period. A toxicity test would preferably be carried out once during the monitoring period.

Table 1 - Proposed Parameters for Evaluation

I - First Priority
II - Second Priority

Check point / Parameter	1		2		3		4		5		6		7		8	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
flow	x		x		x		x		x		x		x		x	
temperature	x		x		x		x		x		x		x		x	
pH	x		x		x		x		x		x		x		x	
suspended solids	x		x		x		x		x		x		x		x	
dissolved solids														x		x
BOD, soluble														x		x
COD, soluble	x		x		x		x		x				x		x	
colour		x		x		x									x	
sulfides																x
total posphorus																x
Kjeldahl nitrogen																x
mercury																x
toxicity																x
washing losses			x													
sodium adsorbtion ratio (SAR)																x
chlorides																x

Section Legend

1. Raw material preparation discharge
2. Fiber line discharge
3. Bleaching and bleach chemicals preparation
4. Paper production
5. Chemical recovery
6. Utilities
7. Combined effluent to effluent treatment
8. Final discharge

8. Analysis of Parameters

All the parameters should be evaluated in accordance with well established standard analytical methods. In order to harmonize the results, a generalized procedure for each parameter is suggested for this phase of the work. The proposed methods are as follows (Standard Methods refers to Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Pollution Control Federation, 16th Edition):

NIEM Approved Analytical Procedures

pH	Standard Methods: Method 423, p. 429
Suspended solids	see text below
Dissolved solids	Standard Methods: Method 209B, p. 95
BOD, soluble	Standard Methods: Method 507, p. 525, but modified to 3-day, 30°C incubation time and temperature, see also text below
COD, soluble	see text below
Colour	Standard Methods: Method 204A, p. 67, see also text below
Sulfides	Standard Methods: Method 427C, p. 475
Total Phosophorus	Standard Methods: Method 424E, p. 446
Kjeldahl Nitrogen	Standard Methods: Method 420A, p. 408
Mercury	see text below
Toxicity	see text below
Washing losses	see text below
SAR	see text below
Chlorides	Standard Methods: Method 407A, p. 287, see also text below

Suspended Solids

At Check Point 1-8, the coarse fraction of the suspended material is determined by filtration through a 70 micron mesh wire cloth, which will retain fibres, bark particles and other relatively large-sized suspended matter. This determination is primarily for mill process control. The analysis is principally carried out according to the description in Appendix 4, but with the use of a 70 micron filter. At Check Point 8 an additional analysis of the effluent suspended solids should be conducted following Standard Methods, Method 209C, p. 96 and using a Whatman GF/C 1.2 micron filter instead of the grade 934-AH filter specified.

BOD

At Check Points 7-8, the BOD should, as the COD, be carried on the filtrate from the suspended solids analysis (BOD, soluble). Note also that in the case of secondary biological treatment, the BOD determinations of Points 7-8 might preferably be made First Priority. We have proposed BOD to be determined as BOD_3, 30 °C, however, it is also possible to apply the more commonly used BOD_5, 20°C. The results are, however, not comparable.

COD

At Check Points 1-8 (excluding Point 6), the analysis should be carried out on the filtrate from the suspended solids analysis (COD, soluble). Thus, the organic material is characterized by one coarse fraction (SS analysis) and one dissolved or finely dispersed fraction (COD analysis on filtrate). A description of the analysis is given in Standard Methods, Method 508A, p. 533. At Check Point 8, an additional COD test should be run on the unfiltered effluent following Standard Methods, Method 508A (COD, open reflux method).

Colour

The colour of forest industry waste waters is often very high and dependent on pH. In many cases, the content of suspended solids is also rather high. The colour determination should therefore be carried out on a filtrated sample (Whatman GF/C 1.2 micron filter) at a set pH. Standard Methods recommends a pH of 7.6. Normally the sample must be diluted before determination and that can preferably be done with a buffer solution (approx. 7.6). The determination is normally carried out on a spectrophotometer but it is also possible to use a colour comparator. However, in order to get comparable results, it is recommended that the colour is expressed in Pt-units.

Washing losses

In the case of efficient chemical recovery, the washing losses are the main source of discharge of dissolved organic substances from the fiber line. In order to check the efficiency of this important operation, pulp samples are taken out at the outlet of the last washing stage and the pulp is washed and the filtrate analysed with respect to dissolved organic substance, preferably as COD, and expressed as kg COD/t pulp. In order to cross check the results, the same sample can also be analysed with respect to the cooking base chemical (Na, Mg, Ca). The method is described more in detail in Appendix 3. The analysis of metal ions can be performed according to Standard Methods, Section 303A. p. 157.

Mercury

It is recommended that some checks are performed regarding the mercury content in final effluent in the case of chlorine and alkali use when these chemicals are manufactured by the mercury cell process. In the case of an integrated mill, the discharge from this block should also be checked. Samples for mercury determination require special preservation on storage according to Standard Methods: Section 105, p. 42. The determination should be done according to Standard Methods: Method 320A, p. 232, or by the use of a mercury analyzer.

Toxicity

It is recommended that the test is performed according to the NIEM "Guide on Determination of the Acute Lethal Toxicity of Pulp and Paper Mill Effluent to Freshwater Fish.

Sodium Absorption Ratio (SAR) and Chlorides

In the case that the pulp mill effluents are used for irrigation of crops, determination of SAR and the chloride concentration is important. This might also be valid if the recipient water is used for irrigation purposes and the initial dilution of the dischanges from the mill is limited.

The SAR value is defined as

$$SAR = \frac{(Na^{+})}{\sqrt{((Ca^{++}) + (Mg^{++}))/2}}$$

where (Na^{+}), (Ca^{++}), and (Mg^{++}) are the concentrations of the respective ions in milliequivalents per litre of water. The concentrations in meq/l are obtained by multiplying the concentrations in mg/l by 0.004, 0.050 and 0.082 for Na, Ca and Mg respectively. The analysis of the metal ions should be performed according to procedure outlined in Standard Methods, Section 303A, p. 157.

Portable test equipment is commercially available for in situ analysis of many constituents. Such equipment minimizes the costs and errors associated with sample storage, transport and handling. Portable test kits and equipment may be used in the NIEM studies provided that the accuracy and precision of the results obtained is checked to be comparable to the laboratory methods. It is important that all field instruments be checked and recalibrated in the laboratory at frequent intervals. Records of this should be kept for reference.

9. Presentation of Results

The presentation of all experimental and evaluated results should be on a common form for easy understanding and comparison. A tentative form for the presentation of results is given in Appendix 5.

In the case that discharge permits are expressed in mg/l such data should also be specified. It should, however, be observed that in order to get an understanding of the relation between discharges and production process, figures expressed in kg/d and kg/t product must be used. Kg/t figures are also comparable with data from other mills.

The accuracy in final results of discharge surveys are very seldom better ±10%, therefore never report more than two digitals.

10. Cross Checks on the Reliability of Results

It is necessary to check results by cross checking values. This will establish the reliability of the procedures. Cross checks can be made on the basis of expected values, mass balances, or technical data from own or other mills experience. Some examples are indicated for reference in Appendix 6. However, each mill must ultimately establish its own system of cross check methodologies.

Relevant data on effluent discharges in specificly non-wood pulping are rather difficult to obtain from other mills or the literature. However, some data and guidelines are given in Appendix 7. It is one of the goals of the NIEM project that, through the work of the members, a common bank of such data shall result, thus, improving the know-how and understanding of the relation between the processes used and their impact on the environment.

APPENDIX 1

1.1 Flow rate measurements of liquids

1.1.1 General

There are several methods used for the measurement of flow rates and which one to choose will depend on the type of sewer (channel, pipe etc), the accessibility for installation of measuring equipment and the properties of the effluent, especially corrosiveness and the presence of suspended solids. The methods may be divided into two groups according to the type of system. Open systems include open channels, floor channels etc, and closed systems are mainly pipes. For the relevant calculations of flow in either case, reference is made to the literature.

1.1.2 Flow rate measurements in open systems

There are three main methods of flow measurements in open systems:

1) Methods based on the change of water level

2) Methods based on the determination of the area and the velocity of the liquid

3) Methods based on dilution.

Flow rate measurements based on water level change

The most commonly empolyed methods in the first group are weirs or parshall flumes which are placed in a channel etc as a dam or constriction causing changed level and velocity of the water.

The use of a weir is one of the best and accurate methods for measuring flow rate. **A weir is a dam placed in a channel, flume or pipe outlet and over which the water flows freely** (Figure 1.1) **. The flow is calculated from the geometry of the weir and the water level upstream of it. Weirs are made of steel plate, planed wood or plastic material. The edges of the weir plates in contact with the flowing medium should be sharp and cut so as to form an angle of 45° to the direction of flow.**

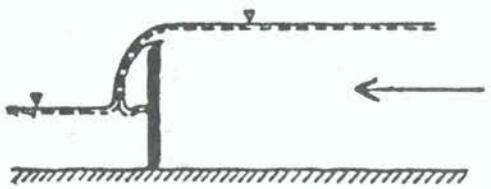


Figure 1.1 Flow over a weir

The choice of a suitable weir is made on the basis of the channel width, the accessible dam height and the range within which the flow is expected to vary. Some basic information in this respect is therefor required before the design of the weir. Rectangular weirs without end contractions (Figure 1.2) hve their edge extending across the entire width of the channel. This type is used for high flow rates.

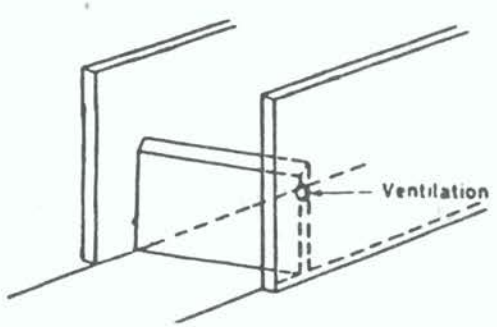


Figure 1.2 Rectangular weir without end contractions

Rectangular weirs with end contractions (Figure 1.3) are weirs being combined with a contraction of the channel. This type is used for moderate flow rates. V-notched weir (Thompson weir) (Figure 1.4) consists of a V-shaped notch in the dam. This type is normally used for varying flow rates.

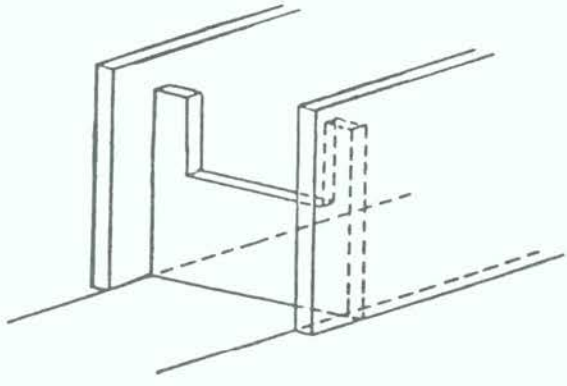


Figure 1.3 Weir with end contraction

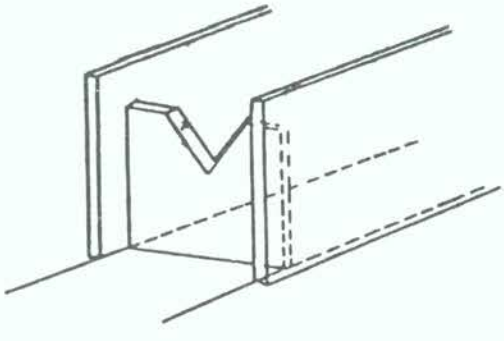


Figure 1.4 Thompson weir

Because of the simple mounting, weirs can be recommended for temporary installation in channels, flumes and pipe outlets. Provided that sedimentation and microbial growth are controlled and that the sensing device is protected against corrosion, weirs are extremely reliable in their operation. See also Appendix 2 :1

A constriction in a channel causes an increase in the water level. For a suitably shaped constriction, the flow rate can be obtained with sufficient accuracy by measuring the level upstream of the constriction.

The Parshall flume (Figure 1.6) is a modified Venturi flume of standardized dimensions.

Measuring flumes are usually cast on site, in concrete, but standardized flumes made of stainless steel or plastic are manufactured. When designing the flume, attention should be given to any future increases in flow, for instance as a result of a rise in production. The measuring device should be mounted in a separate measuring chamber.

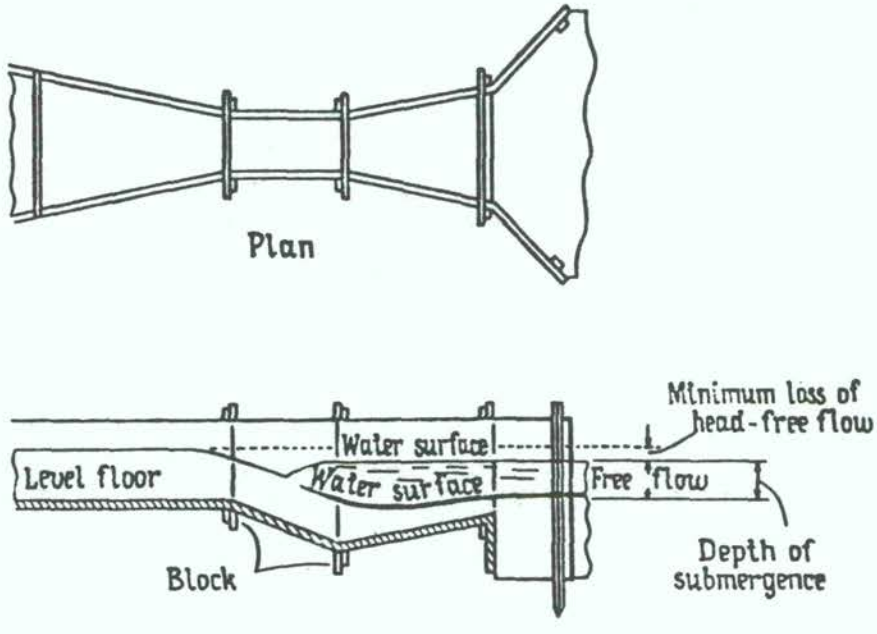


Figure 1.6 Parshall flume

As they are self-cleaning, flumes are reliable in their operation and little maintenance is called for. For waste water systems conducting fibres, flumes are preferred to weirs. For satisfactory operation flumes require a slightly smaller drop in level than weirs, but they are more expensive to install, especially in already existing channels.
(see also appendix 2:2)

To calculate the flow rate, the water level relative to the weir edge or the bottom of the flume must be measured. To achieve this a gauge is placed upstream of the measuring device.

For permanent installations it is preferable to place the gauge in a separate cylindrical measuring chamber close to the channel and communicating with it; when the channel is accessible for inspection the water level can be measured directly. This method is suitable for temporary installations where for some reason automatic recording is not arranged for.

A bubble tube for measuring the water level consists of a narrow vertical tube submerged in the channel. The tube is fed with compressed air via a reduction valve, so that there is a steady air flow from the orifice. The pressure in the tube is measured and, after conversion, transmitted to a recording instrument. The bubble tube can be recommended for temporary installation because it can easily be mounted directly in the channel, or in case of measuring flumes in a separate chamber communicating with the flume.

Measurement of level by means of a float should always be carried out in a separate measuring chamber. The level is transmitted by a cable to a meter or, preferably, to a

recorder. With a mechanical transmission system a float will be sensitive to corrosion. Provided that there is no interference from growth in the measuring chamber or from corrosion, the float yields reliable and accurate measurements.

Flow rate measurement based on velocity

If the flow area is known, the flow rate can be calculated from the velocity of flow, as measured with a velocity indicating instrument. Since the velocity varies over a cross section of the flow, it is necessary to know the approximate velocity distribution across the section. From the velocity distribution the mean velocity is calculated.

For estimating the order of magnitude of a flow it will suffice to measure the velocity at one point, preferably in the centre of the flow where normally the velocity is a maximum. The approximate mean velocity is then calculated.

The velocity can be measured with a pilot tube, which measures the difference between dynamic and static pressure in the system. The pilot tube is connected to a differential manometer, however the tube tend to clog to fiber containing waters.

If a salt solution or tracer dry is injected and the time for it to reach a given point or to pass between two given points is measures, the flow can be calculated from the result.

Flow rate measurements based on dilution

A concentrated solution of a substance (inorganic salt or dye tracer) that can easily be determined in low concentrations, is injected into the medium at a constant, known rate. The concentration of the tracer is then measured far enough downstream for complete mixing to have taken place.

The flow is calculated from the formulate:

$$Q = q \cdot \frac{c}{C-Co}$$

where Q = flow in check point, l/min
q = injected flow, l/min
C = concentration of tracer element in check point, mg/l
c = concentration of tracer element in injected flow, mg/l
Co = concentration of tracer element in zero sample in check point, mg/l.

Good tracer elements are Li- and K-salts. LiCl has been commonly used for this type of investigations with good results. In this case the resulting concentration in check point should preferably be above 1 mg/l during a sampling time of about 10 minutes.

In some cases it is also possible to use the make-up chemical concentration in different mill flows in the same way in order to obtain approx flow data.

1.1.3 Flow rate measurements in closed systems

Several methods have been developed for flow rate measurements with a good degree of accuracy in closed systems. The methods may be divided into three main categories.

1) Measurement of a pressure difference

2) Determination of the velocity and area of the liquid

3) Methods based on dilution

In addition there are some miscellaneous methods.

Pressure difference methods

The most common types of measuring devices used for continuous flow measurement are orifice plates, flow nozzles, and venturi tubes. Constriction of a pipe results in an increase in the speed of the flowing medium and a corresponding drop in its static pressure. The pressure difference is measured manometrically.

A standardized orifice plate consists of a thin plate with a central, sharp edged hole which is mounted perpendicularly to the direction of flow (Figure 1.7). The flow rate is highest and the contraction greatest just below the orifice.

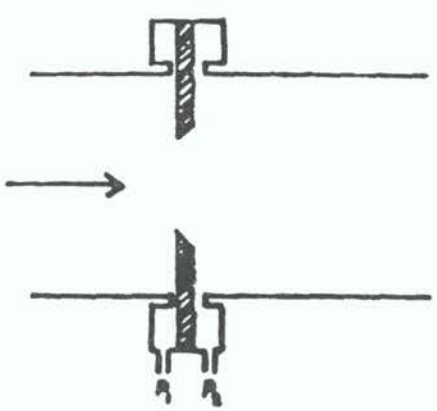


Figure 1.7 Orifice plate

Orifice plates give a high level of accuracy but at the expense of a large pressure drop, which increases the pumping costs. They do not function satisfactorily in the presence of suspended particles and are therefore unsuitable for permanent installation in systems with fibres. The fact that orifice plates can sometimes be easily inserted at pipe flange connections in existing systems renders them suitable for temporary installations.

The liquid in a pipe can be measured by a magnetic flow meter which consist of a straight pipe section fitted with standard flanges. An electric coil around the tube imposes a magnetic field which changes with the velocity of the liquid. Magnetic flow meters are resistant to corrosion and unaffected by the presence of suspended particles.

The supersonic meter is based on the measurement of the velocity according to the Doppler principle, i.e. the frequency of the sound wave is changed by reflexion on air bubbles or particles in the fluid.

Methods based on dilution

The dilution methods used (salt solutions, chemical and dye tracers) can be applied to flow rate measurements also in closed system as described above.

Miscellaneous measuring methods for flow rate

When, as is often the case, the flow cannot be measured directly, usually because the system is inaccessible for the installation of measuring equipment, other methods must be resorted to.

If the system includes vats or containers where the level can be measured the flow can be calculated from the rate at which the level rises on closing the outlet valve.

Where feasible the effluent may be diverted to a suitable container and the time required to fill can be measured.

If the concentration of the liquor before and after e.g. an evaporator and either the inlet or the outlet flow can be measured by any suitable method, the other flow can be calculated. Foaming introduces an error.

If no other method is possible the flow of pulp suspensions can be calculated from the pulp concentration before and after a thickener or filter unit and the rate of pulp output. The largest source of error is the determination of the inlet pulp concentration. If water is added to the system between the sampling points, these flows must be measured.

APPENDIX 2:1

FLOW RATE MEASUREMENTS WITH WEIRS

2.1 General

Flow measurement with weirs is one of the most commonly employed methods of measuring flows in open systems, e.g. channels, flumes or pipe outlets. This is due to the fact that the use of weirs gives a comparatively accurate reading of water flows.

2.2 Principle

A weir is a dam or constriction placed in the channel etc, over which the water falls freely (Figure 2.1. The weir causes changed level and velocity of the water and the flow can be calculated from the geometry of the weir and the water upstream of it. In order to obtain an accurate flow measurement it is essential that there is an ambient air pressure under the overfall. See the ventilation hole in Figure 2.2

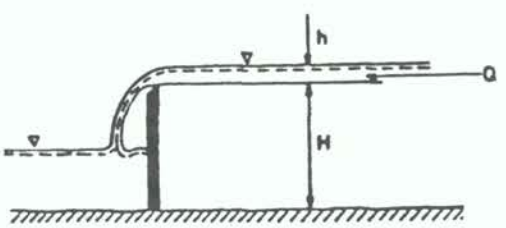


Figure 2.1 Flow over a weir.

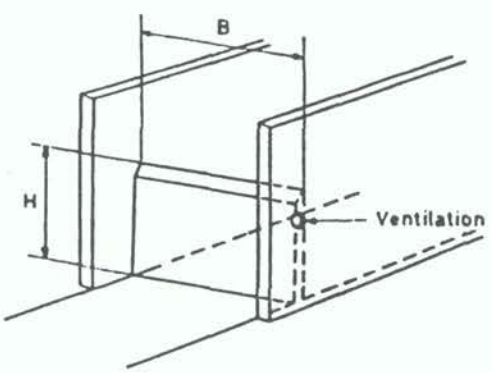


Figure 2.2 Weir without end-contractions with external ventilation hole.

2.3 Construction and installation

Weirs are made of steel plate, planed wood or plastic. The edge of the weir plates in contact with the flowing medium should be sharp and cut so as to form an angle of 45° to the direction of flow.

Weirs are mounted accurately at right angles to the direction of flow and with the upper edge horizontal (spirit-level). The mounting can be carried out by one of the following methods, care being taken to ensure tight seals against the walls and the bed of the channel.

1. The weir is mounted between rails or bolts. For temporary installations it will often suffice to bolt strong strips to each channel wall (the water pressure will normally be large enough to keep the weir in position), and to seal with machine felt, foam rubber or foam plastic. The sealing material is chosen with regard to the properties of the flowing medium.

2. The weir, which shall be made slightly wider than the channel, is forced into position, care being taken to avoid damaging the edges.

3. The weir can be secured with wooden wedges, but this method entails problems in sealing.

In general alternative 1 is to be preferred.

2.4 Types of weir; formulae

The following symbols are used

Q = flow (m^3/s)
g = acceleration due to gravity (m/s^2)
B = width of channel (m)
b = width of weir opening (m)

H = distance from the channel bed to the edge of the weir (m)

h = upstream water level relative to the edge of the weir (m)

μ = coefficient of discharge

2.4.1 Choice of weir type and size

The choice of a suitable weir is made on the basis of the channel width, the accessible dam height and the range within which the flow is expected to vary. It is therefor important to get a good understanding of the approx flow and the range of variations to be expected in the chosen check point prior to the design of the weir. Insertion of these values into the formulae below will indicate what type is suitable or alternatively, what changes are required in the existing system to make measurements possible. It is highly recommended to avoid designs resulting in submerged flow situations.

2.4.2 Weir without end-contractions

The edge of the weir extends across the entire width of the channel (figure 2.2) This type is used for heavy flows. The flow is given by

$$Q = \frac{2\mu}{3} \cdot b \cdot h^{1.5} \cdot \sqrt{2g}$$

$$\frac{2\mu}{3} = 0.4224 + 0.00053/h$$

2.4.3 Weir with end-contractions

The weir is combined with a constriction of the channel (Figure 2.3. This type is used for moderate flows.

$$Q = \frac{2\mu}{3} \cdot b \cdot h^{1.5} \cdot \sqrt{2g}$$

$$\frac{2\mu}{3} = 0.3838 + 0.0386b/B + 0.00053/h$$

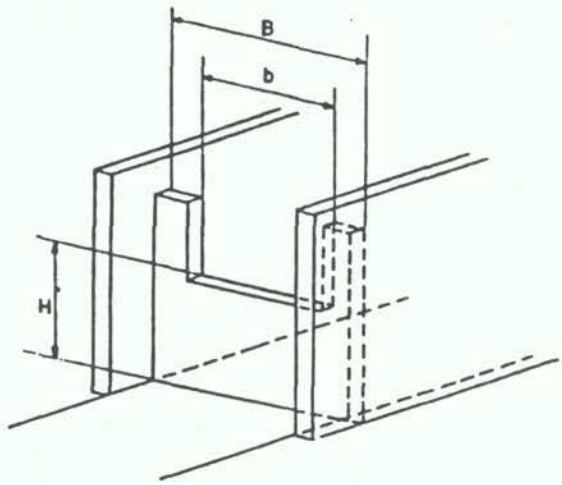


Figure 2.3 Weir with end-contractions.

2.4.4 V-notched weir (Thompson weir)

The weir consists of a V-shaped notch (Figure 2.4) in the dam. This type is used for light flows.

$$Q = \frac{8}{15} \cdot \mu \cdot h^{1.5} \cdot \sqrt{2g} \cdot \tan\frac{\theta}{2}$$

$$\mu = 0.5650 + 0.00868 \cdot \sqrt{\frac{1}{h}}$$

where θ is the angle of the notch. (When, as is usually the case, $\theta = 90°$, $\tan \theta/2 = 1$.)

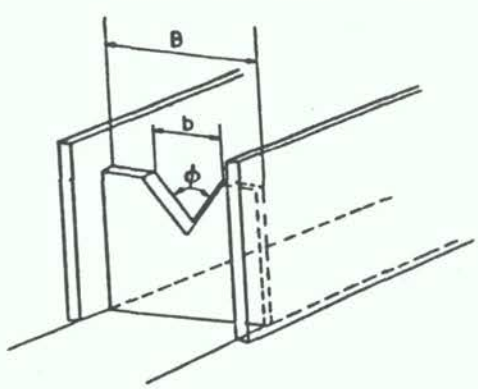


Figure 2.4 V-notched weir (Thompson weir).

2.5 Gauges

According to the above the calculation of flow over weirs only requires measurement of the water level relative to the weir edge. For this a gauge is placed upstream of the

weir and distant from it (if possible) at least 2.5 times the maximum level (h) above the weir (Figure 2.5)

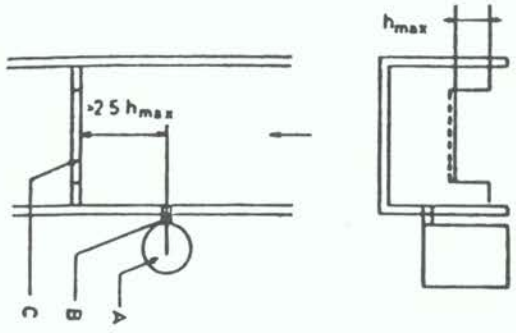


Figure 2.5 Arrangement of measuring chamber on a weir. A. Measuring chamber (internal diam. 300-400 mm with float; 100-150n mm with bubble tube). B. Connecting tube. C. Weir.

For permanent installations it is preferable to place the gauge in a separate, cylindrical measuring chamber (stilling well) close to the channel and communicating with it. The tendency for microbial growth in the measuring chamber can be counteracted by admitting a tangential stream of fresh water, small in relation to the diameter of the communicating pipe.

2.5.1 Scale

When the channel is accessible for direct inspection the water level can be observed directly on a scale on the channel wall. This method is suitable for temporary installations where for some reason automatic recording cannot be arranged. The accuracy of measurement is limited to the accuracy with which the scale can be read; the presence of foam in the channel can be a nuisance.

2.5.2 Bubble tube

This device for measuring the water level consists of a narrow vertical tube (internal diameter c. 10 mm) submerged in the channel with its orifice on a level with the weir edge. (For temporary installations the orifice should be as near this level as possible; the position should be determined with a spirit level.) The tube is fed with compressed air via a reduction valve, so that there is a steady flow from the orifice of 1 or 2 bubbles per second. The pressure in the tube is converted and transmitted to a recording instrument.

2.5.3 Float

Measurement of level by means of a float should always be carried out in a separate measuring chamber with a diameter of the order of 300 to 400 mm. The level is transmitted by a cable to a meter or, preferably, to a recorder. With a mechanical transmission system a float will be sensitive to corrosion and therefore unsuitable for systems in which the waste water containse sulphide, sulphite and chlorine.

Provided that there is no interference from growth in the measuring chamber or from corrosion, the float yields reliable and accurate measurements.

APPENDIX 2:2

PARSHALL FLUME MEASUREMENT

The Parshall flume is a convenient device for measuring the flow in existing sewers and consists of three parts; a converging section, a throat section, and a diverging section. The dimensions and capacities of Parshall flumes are shown in Figure 1. The level of the floor in the converging section is higher than the floor in the throat and diverging sections. The head of the water surface in the converging section is a measurement of the flow through the flume.

The elevation of the water surface should be measured back from the crest of the flume at a distance equal to 2/3 of the length of the converging section. The crest is located at the junction of the throat and converging section. The head should be measured in a stilling well instead of in the flume itself as sudden changes in flow are dampened in a stilling well. The size of the Parshall flume should be determined during the preliminary survey. The general formula for computing the free discharge from a Parshall flume is as follows:

$$Q = 4\ WH^{n}$$

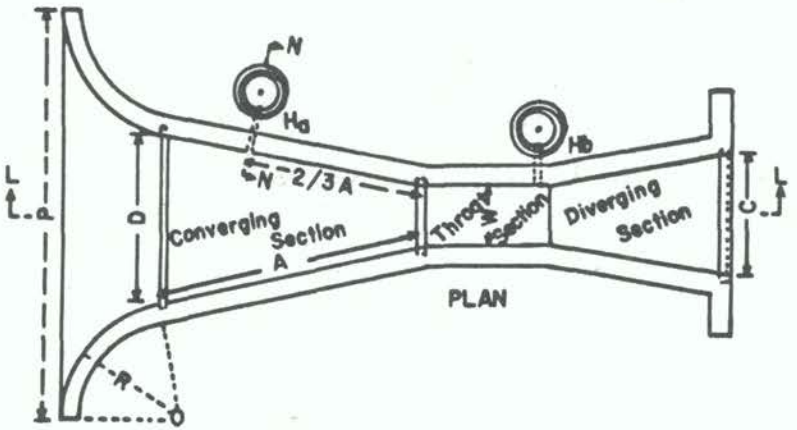
where:

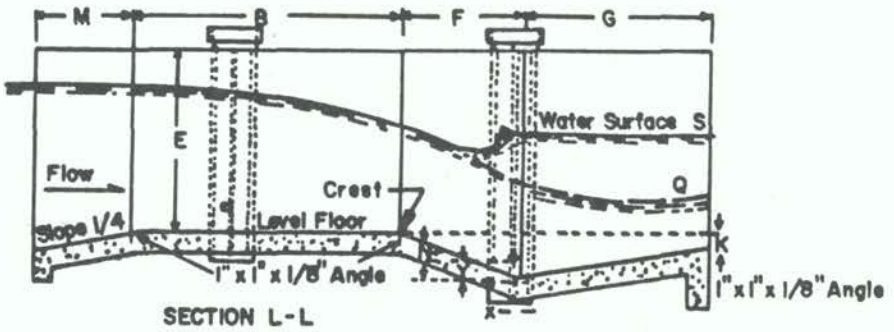
Q = discharge, cfs
W = throat width, ft
H = head of water above the level floor in ft in the converging section
$n = 1.522\ W^{0.026}$

The flume may be built of wood, fiberglass, concrete, plastic or metal and can be installed at convenient locations, such as a manhole. The Parshall flume is used for sewer lines where continuous-flow measurements are desirable. The main advantage of the Parshall flume over a weir is the self cleaning properties of the flume. Accurate measurements can be made even if the flow is submerged as shown by the water levels in Figure 2.

The flow can become submerged due to high water elevations downstream. If the flow is submerged, a velocity reduction in the flow occurs. The degree of submergence must be determined in order to measure the flow accurately since the flume is calibrated for free flow conditions. The condition of submerged flow is evidenced by a ripple or wave formed just downstream from the end of the throat. A reduction in the velocity of the water leaving the flume may lessen the effects of erosion downstream. In order to determine the degree of submergence, a stilling well must be built in the throat section. The crest elevation in the throat section is H_b and the head in the converging section is H_a and the ratio H_a/H_b, is a measurement of the submergence. The stilling well used to measure H_b should be located near the downstream end of the throat section and the datum for H_a and H_b is the level floor of the converging section. However, it is recommended to avoid submergence situations as far as possible by proper design.

In appendix 1 is presented design data and flow tables for Parshall Flumes in the most normally used sizes 1/4-3 feet specified in metric system.





W		A		½ A		B		C		D		E		F		G		K	N	R		M		P		X	Y	Free-Flow Capacity (Second-Foot *)	
Ft	In.	Ft	In.	Ft	In.	Ft	In.	Ft	In.	Ft	In.	Ft	In.	Ft	In.	Ft	In.	In.	In.	Ft	In.	Ft	In.	Ft	In.	In.	In.	Minimum	Maximum
0	3	1	6⅜	1	¼	1	6	0	7	0	10⅜	2	0	0	6	1	0	1	2¼	1	4	1	0	2	6¼	1	1½	0.03	1.9
0	6	2	1/16	1	4⅜	2	0	1	3½	1	3⅜	2	0	1	0	2	0	3	4½	1	4	1	0	2	11½	2	3	0.05	3.9
0	9	2	10⅜	1	11¼	2	10	1	3	1	10⅜	2	6	1	0	1	6	3	4½	1	4	1	0	3	6½	2	3	0.09	8.9
1	0	4	6	3	0	4	4⅞	2	0	2	9¼	3	0	2	0	3	0	3	9	1	8	1	3	4	10⅜	2	3	0.11	16.1
1	6	4	9	3	2	4	7¼	2	6	3	4⅜	3	0	2	0	3	0	3	9	1	8	1	3	5	6	2	3	0.15	24.6
2	0	5	0	3	4	4	10⅛	3	0	3	11½	3	0	2	0	3	0	3	9	1	8	1	3	6	1	2	3	0.42	33.1
3	0	5	6	3	8	5	4⅝	4	0	5	1⅛	3	0	2	0	3	0	3	9	1	8	1	3	7	3½	2	3	0.61	50.4
4	0	6	0	4	0	5	10⅝	5	0	6	4¼	3	0	2	0	3	0	3	9	2	0	1	6	8	10⅜	2	3	1.3	67.9
5	0	6	6	4	4	6	4½	6	0	7	6⅝	3	0	2	0	3	0	3	9	2	0	1	6	10	1¼	2	3	1.6	85.6
6	0	7	0	4	8	6	10⅝	7	0	8	9	3	0	2	0	3	0	3	9	2	0	1	6	11	3½	2	3	2.6	103.5
7	0	7	6	5	0	7	4¼	8	0	9	11⅝	3	0	2	0	3	0	3	9	2	0	1	6	12	6	2	3	3.0	121.4
8	0	8	0	5	4	7	10⅛	9	0	11	1⅝	3	0	2	0	3	0	3	9	2	0	1	6	13	8¼	2	3	3.5	139.5

* Equals 1 cu ft per sec.

LEGEND:

W	Size of flume, in inches or feet.
A	Length of side wall of converging section.
⅔ A	Distance back from end of crest to gage point.
B	Axial length of converging section.
C	Width of downstream end of flume.
D	Width of upstream end of flume.
E	Depth of flume.
F	Length of throat.
G	Length of diverging section.
K	Difference in elevation between lower end of flume and crest.
N	Depth of depression in throat below crest.
R	Radius of curved wing wall.
M	Length of approach floor.
P	Width between ends of curved wing walls.
X	Horizontal distance to H_a gage point from low point in throat.
Y	Vertical distance to H_a gage point from low point in throat.

Source: *ORSANCO* (1952).

Figure 1 DIMENSIONS AND CAPACITIES OF THE PARSHALL MEASURING FLUME, FOR VARIOUS THROAT WIDTHS, W(4)

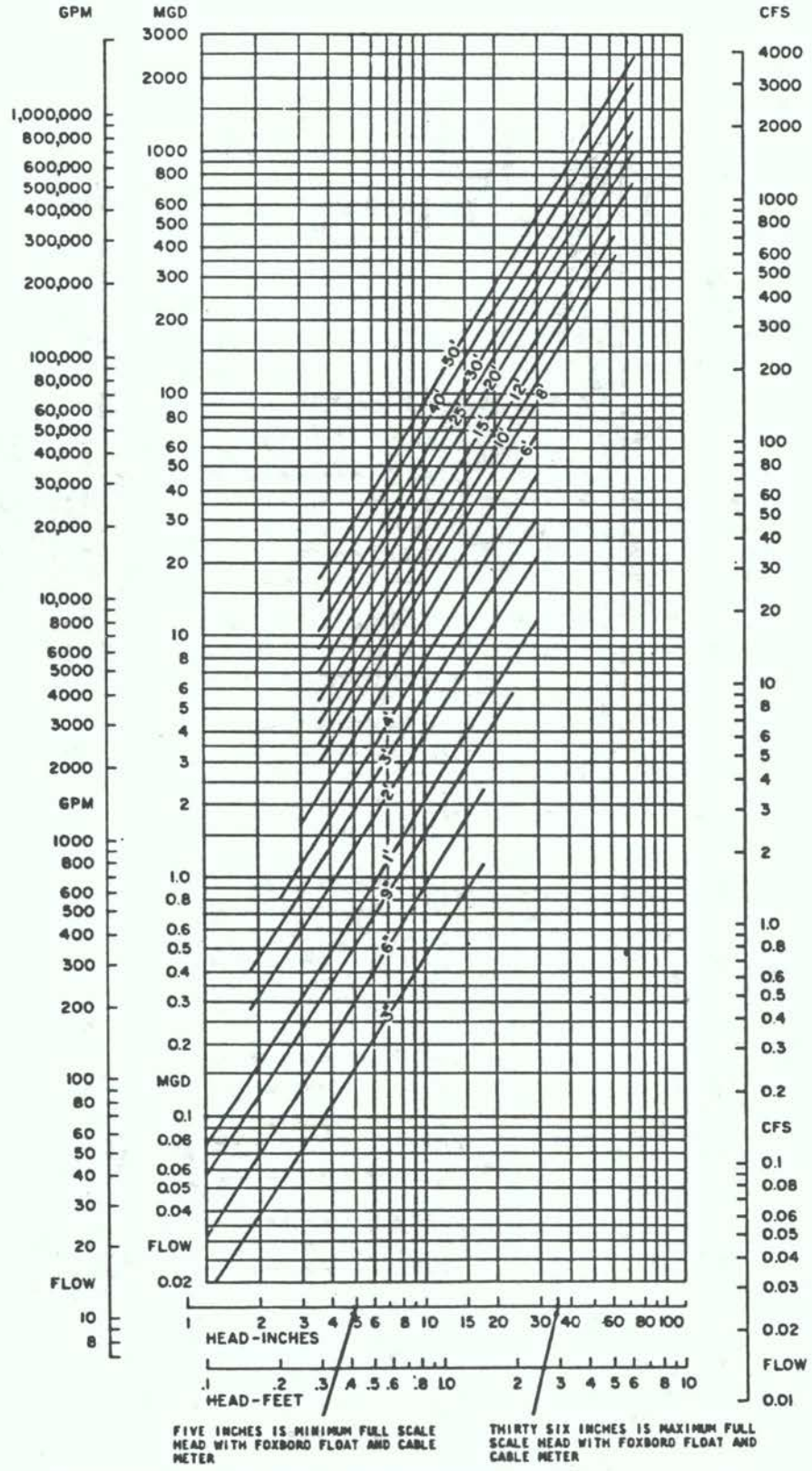
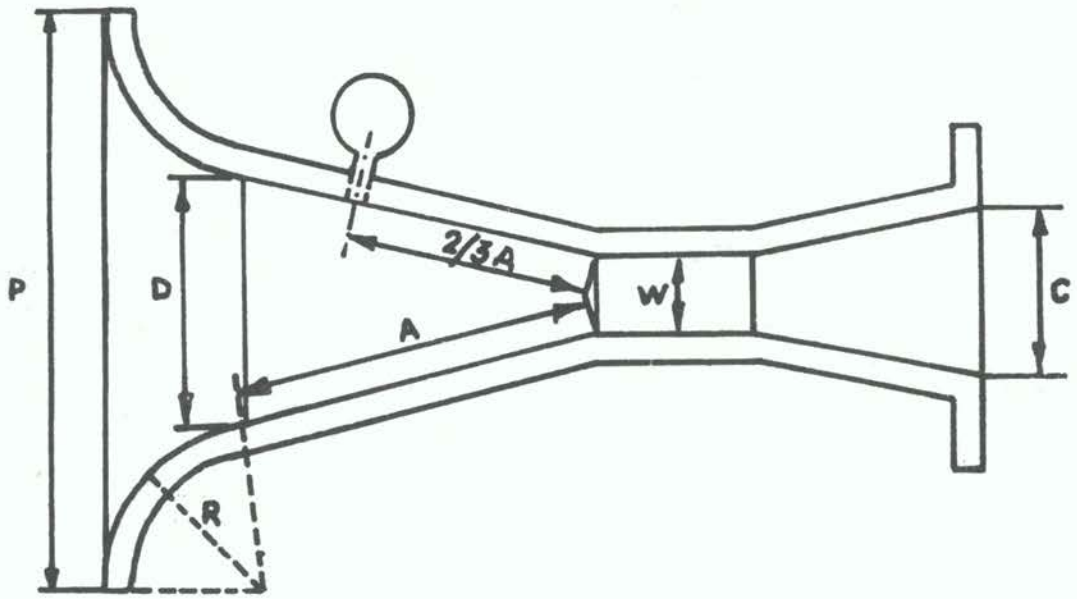
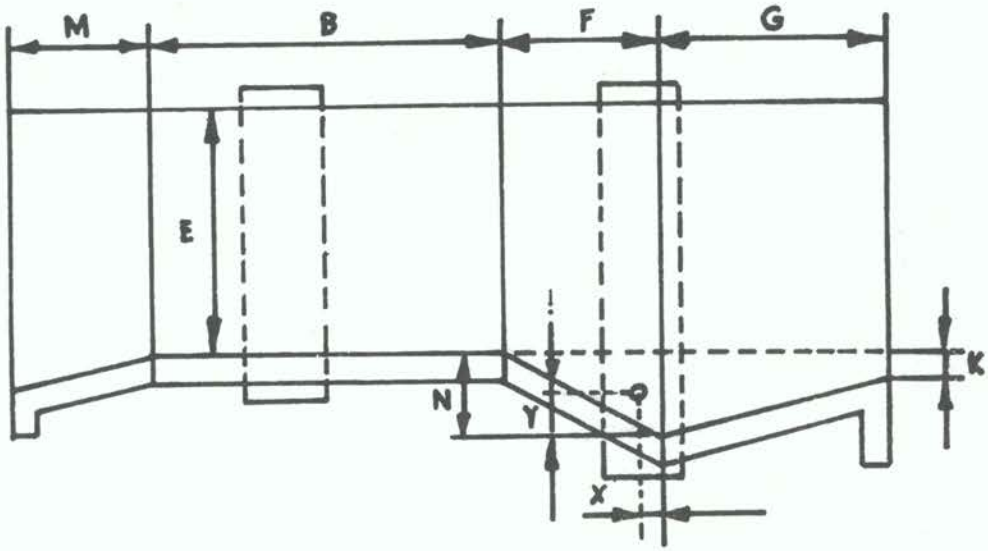


Figure 2 FLOW CURVES FOR PARSHALL FLUMES





IVL

PARSHALL FLUME

RITAD K.Å

INDUSTRINS VATTEN- OCH LUFTVÅRD AB

RITNINGSNR

Parshall flumes, capacity and dimensions

W ft	W mm	A mm	2/3A mm	B mm	C mm	D mm	E mm	F mm	G mm	K mm	N mm	R mm	M mm	P mm	X mm	Y mm	M+B+F+G mm	Q (l/min) when h is in m.
1/4	76	467	311	457	178	259	610	152	305	25	57	406	305	768	25	38	1219	$h^{1,468} \cdot 9711$
1/2	152	621	414	610	394	397	610	305	610	76	114	406	305	902	51	76	1830	$h^{1,495} \cdot 20052$
3/4	229	879	587	864	381	575	762	305	457	76	114	406	305	1080	51	76	1931	$h^{1,511} \cdot 30660$
1	305	1372	914	1343	610	845	914	610	914	76	229	508	381	1492	51	76	3248	$h^{1,522} \cdot 41424$
1 1/2	457	1448	965	1419	762	1026	914	610	914	76	229	598	381	1676	51	76	3324	$h^{1,539} \cdot 63369$
2	610	1524	1016	1495	914	1207	914	610	914	76	229	508	381	1854	51	76	3400	$h^{1,549} \cdot 85578$
3	914	1676	1118	1645	1219	1572	914	610	914	76	229	508	381	2216	51	76	3550	$h^{1,566} \cdot 130957$
4	1219	1829	1219	1794	1524	1937	914	610	914	76	229	610	457	2711	51	76	3775	$h^{1,578} \cdot 178141$
5	1524	1981	1321	1943	1829	2302	914	610	914	76	610	457	3080		51	76	3924	$h^{1,587} \cdot 223796$
6	1829	2134	1422	2092	2134	2667	914	610	914	76	229	610	457	3442	51	76	4073	$h^{1,595} \cdot 271042$
7	2134	2286	1524	2242	2438	2032	914	610	914	76	229	610	457	3810	51	76	4223	$h^{1,601} \cdot 318497$
8	2438	2438	1626	2391	2746	3397	914	610	914	76	229	610	457	4172	51	76	4372	$h^{1,607} \cdot 366658$

Parshall flume

W = 1/4 ft = 76 mm

$h^{1,468} \cdot 9711$ l/min

mm wc	l/min
20	38
30	56
40	86
50	120
55	137
60	156
65	176
70	196
75	217
80	238
85	260
90	283
95	307

Summary

$h_{max.}$ = 450 mm wc

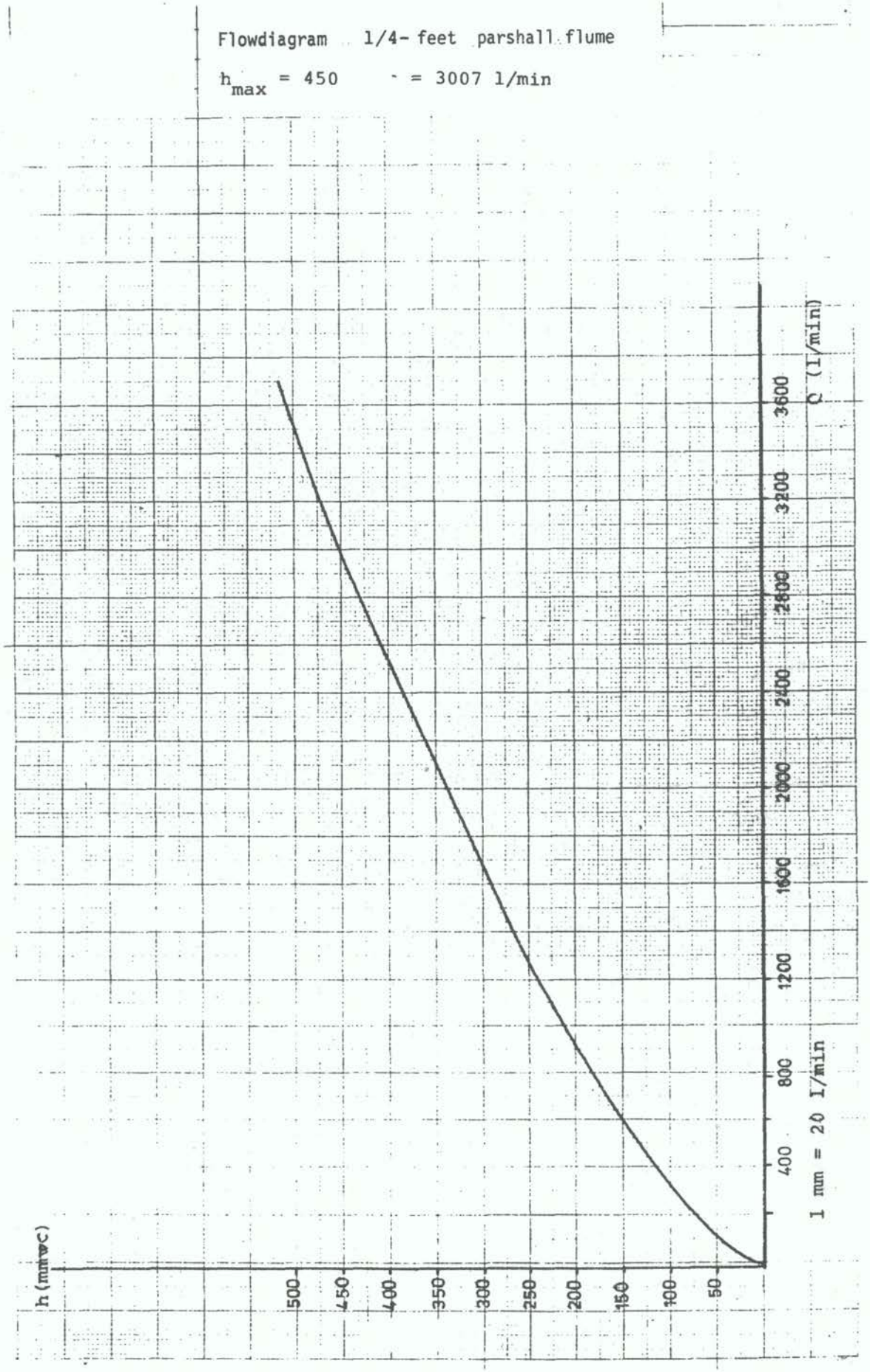
25	mm	= 43	l/min
50	"	= 120	"
100	"	= 331	"
150	"	= 599	"
200	"	= 916	"
250	"	=1269	"
300	"	=2079	"
400	"	=2530	"
450	"	=3007	"

mm wc	l/min
100	331
2	340
4	350
6	360
8	370
10	380
2	390
4	401
6	411
8	421
20	432
2	443
4	453
6	464
8	475
30	486
2	497
4	508
6	519
8	530
40	542
2	553
4	565
6	575
8	588
50	599
2	611
4	623
6	635
8	647
60	659
2	671
4	683
6	695
8	707
70	720
2	733
4	746
6	758
8	771
80	784
2	796
4	809
6	822
8	835
90	848
2	861
4	874
6	888
8	902

mm wc	l/min
200	916
2	930
4	944
6	958
8	972
10	986
2	1000
4	1014
6	1028
8	1038
20	1052
2	1066
4	1080
6	1094
8	1108
30	1128
2	1137
4	1151
6	1166
8	1181
40	1195
2	1210
4	1224
6	1234
8	1254
50	1269
2	1284
4	1299
6	1314
8	1330
60	1345
2	1360
4	1375
6	1390
8	1405
70	1420
2	1435
4	1450
6	1465
8	1480
80	1495
2	1511
4	1527
6	1543
8	1559
90	1575
2	1591
4	1607
6	1626
8	1642

W = 1/4 ft = 76 mm

mm wc	l/min	mm wc	l/min	mm wc	l/min
300	1658	400	2530	500	
2	1675	2	2548	2	
4	1691	4	2567	4	
6	1707	6	2586	6	
8	1724	8	2604	8	
10	1746	10	2623	10	
2	1756	2	2642	2	
4	1773	4	2661	4	
6	1796	6	2680	6	
8	1807	8	2699	8	
20	1823	20	2718	20	
2	1840	2	2737	2	
4	1857	4	2756	4	
6	1874	6	2775	6	
8	1890	8	2794	8	
30	1907	30	2813	30	
2	1924	2	2832	2	
4	1941	4	2852	4	
6	1959	6	2871	6	
8	1976	8	2890	8	
40	1993	40	2910	40	
2	2010	2	2929	2	
4	2027	4	2949	4	
6	2045	6	2968	6	
8	2062	8	2988	8	
50	2079	50	3007	50	
2	2097	2		2	
4	2114	4		4	
6	2132	6		6	
8	2150	8		8	
60	2167	60		60	
2	2185	2		2	
4	2202	4		4	
6	2221	6		6	
8	2238	8		8	
70	2256	70		70	
2	2274	2		2	
4	2292	4		4	
6	2310	6		6	
8	2328	8		8	
80	2346	80		80	
2	2364	2		2	
4	2383	4		4	
6	2401	6		6	
8	2419	8		8	
90	2438	90		90	
2	2456	2		2	
4	2474	4		4	
6	2493	6		6	
8	2511	8		8	


Flowdiagram 1/4- feet parshall flume
h_{max} = 450 = 3007 l/min
Q (l/min)
3600
3200
2800
2400
2000
1600
1200
800
400
1 mm = 20 l/min
h (mmwc)
500
450
400
350
300
250
200
150
100
50

Parshall flume

W = 1/2 ft = 152 mm $\qquad$ $h^{1,495} \cdot 20052$ l/min

mm wc	l/min	mm wc	l/min	mm wc	l/min
		100	641	200	1808
20	58				
		2	661	2	1835
30	106	4	680	4	1862
		6	700	6	1890
40	163	8	720	8	1917
		10	740	10	1945
50	228	2	760	2	1973
		4	780	4	2000
		6	801	6	2028
55	262	8	822	8	2057
		20	842	20	2085
60	299	2	864	2	2113
		4	885	4	2142
65	337	6	906	6	2170
		8	928	8	2199
70	376	30	950	30	2228
		2	971	2	2257
75	417	4	994	4	2286
		6	1016	6	2316
80	459	8	1038	8	2345
		40	1061	40	2375
85	503	2	1084	2	2404
		4	1106	4	2434
90	548	6	1129	6	2464
		8	1153	8	2494
95	594	50	1175	50	2524
		2	1200	2	2554
		4	1223	4	2585
		6	1247	6	2615
		8	1271	8	2646
		60	1295	60	2676
		2	1319	2	2707
		4	1344	4	2738
		6	1368	6	2769
		8	1393	8	2800
		70	1418	70	2831
		2	1443	2	2863
		4	1468	4	2895
		6	1493	6	2926
		8	1519	8	2958
		80	1545	80	2990
		2	1570	2	3022
		4	1596	4	3054
		6	1622	6	3086
		8	1648	8	3118
		90	1675	90	3151
		2	1701	2	3184
		4	1728	4	3216
		6	1754	6	3249
		8	1781	8	3282

Summary

h_{max} = 650 mmwc

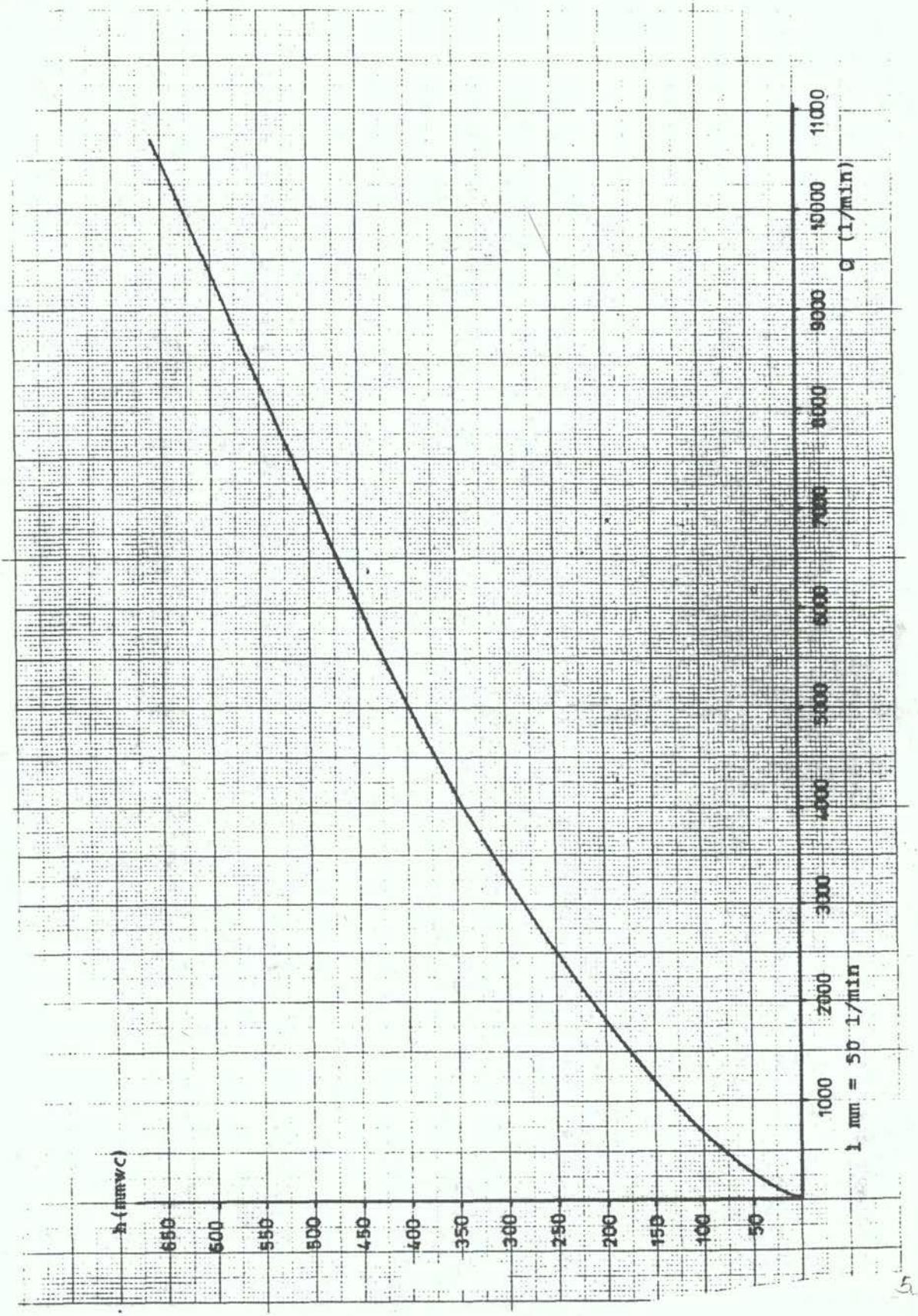
25 mm	= 81	l/min
50 "	= 228	"
100 "	= 641	"
150 "	= 1176	"
200 "	= 1808	"
250 "	= 2524	"
300 "	= 3314	"
350 "	= 4174	"
400 "	= 5096	"
450 "	= 6077	"
500 "	= 7114	"
550 "	= 8204	"
600 "	= 9343	"
650 "	=10531	"

W = 1/2 ft = 152 mm

mm wc	l/min	mm wc	l/min	mm wc	l/min
300	3314	400	5096	500	7114
2	3347	2	5134	2	7157
4	3381	4	5172	4	7199
6	3414	6	5210	6	7242
8	3448	8	5249	8	7285
10	3481	10	5288	10	7328
2	3514	2	5326	2	7371
4	3549	4	5365	4	7414
6	3583	6	5404	6	7457
8	3616	8	5443	8	7500
20	3651	20	5482	20	7544
2	3685	2	5520	2	7587
4	3719	4	5560	4	7631
6	3753	6	5599	6	7674
8	3788	8	5639	8	7718
30	3822	30	5678	30	7762
2	3857	2	5718	2	7805
4	3892	4	5757	4	7849
6	3927	6	5797	6	7893
8	3962	8	5837	8	7937
40	3997	40	5877	40	7982
2	4032	2	5916	2	8026
4	4067	4	5957	4	8070
6	4103	6	5997	6	8114
8	4138	8	6037	8	8159
50	4174	50	6077	50	8204
2	4210	2	6118	2	8248
4	4245	4	6158	4	8293
6	4281	6	6199	6	8338
8	4317	8	6240	8	8383
60	4353	60	6280	60	8428
2	4390	2	6321	2	8473
4	4426	4	6362	4	8518
6	4462	6	6403	6	8563
8	4499	8	6444	8	8608
70	4535	70	6486	70	8653
2	4572	2	6527	2	8699
4	4609	4	6568	4	8744
6	4646	6	6610	6	8790
8	4683	8	6665	8	8836
80	4720	80	6693	80	8881
2	4757	2	6735	2	8927
4	4794	4	6776	4	8973
6	4832	6	6818	6	9019
8	4869	8	6860	8	9065
90	4907	90	6902	90	9111
2	4944	2	6945	2	9158
4	4982	4	6987	4	9204
6	5020	6	7029	6	9250
8	5058	8	7072	8	9297
				600	9343

Flowdiagram 1/2- feet Parshall flume

h_{max} = 650 mmvp = 10531 l/min



Parshall flume

W = 3/4 ft = 9 inc = 229 mm $h^{1,511} \cdot 30660$ l/min

mm WC	l/min	mm WC	l/min	mm WC	l/min
		100	945	200	2694
20	83				
		2	974	2	2735
30	153	4	1003	4	2776
		6	1032	6	2817
40	236	8	1062	8	2859
		10	1092	10	2900
50	331	2	1122	2	2942
		4	1152	4	2984
		6	1183	6	3026
55	383	8	1214	8	3069
		20	1245	20	3112
60	435	2	1277	2	3154
		4	1308	4	3197
65	493	6	1340	6	3241
		8	1373	8	3284
70	551	30	1405	30	3328
		2	1438	2	3372
75	612	4	1471	4	3416
		6	1504	6	3460
80	677	8	1538	8	3504
		40	1572	40	3549
85	739	2	1606	2	3594
		4	1640	4	3638
90	806	6	1675	6	3684
		8	1709	8	3729
95	875	50	1744	50	3775
		2	1780	2	3820
		4	1815	4	3866
		6	1851	6	3912
		8	1887	8	3958
		60	1923	60	4005
		2	1960	2	4052
		4	1996	4	4098
		6	2033	6	4145
		8	2070	8	4193
		70	2108	70	4240
		2	2145	2	4288
		4	2183	4	4335
		6	2221	6	4383
		8	2259	8	4431
		80	2298	80	4479
		2	2336	2	4528
		4	2375	4	4577
		6	2414	6	4625
		8	2453	8	4674
		90	2493	90	4723
		2	2533	2	4773
		4	2573	4	4822
		6	2613	6	4872
		8	2654	8	4922

Summary

h_{max} = 650 mm wc

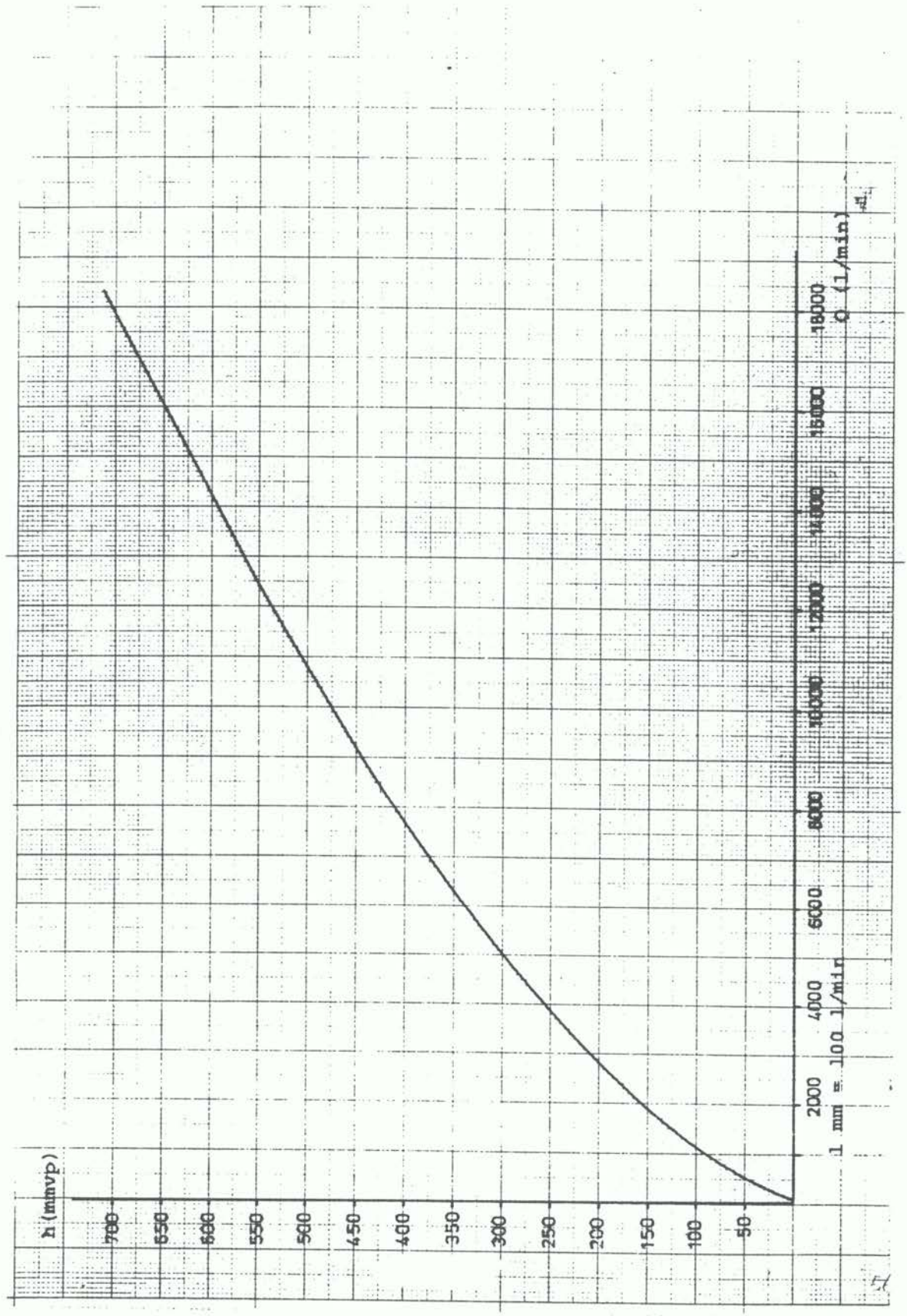
25 mm	=	116 l/min
50 "	=	311 "
100 "	=	945 "
150 "	=	1744 "
200 "	=	2694 "
250 "	=	3775 "
300 "	=	4972 "
350 "	=	6276 "
400 "	=	7679 "
450 "	=	9174 "
500 "	=	10758 "
550 "	=	12424 "
600 "	=	14170 "
650 "	=	15991 "

W = 3/4 ft = 9 inc = 229 mm

mm wc	l/min	mm wc	l/min	mm wc	l/min
300	4972	400	7679	500	10758
2	5022	2	7737	2	10823
4	5072	4	7795	4	10888
6	5123	6	7853	6	10953
8	5173	8	7912	8	11019
10	5224	10	7971	10	11084
2	5275	2	8029	2	11150
4	5326	4	8088	4	11216
6	5378	6	8147	6	11282
8	5429	8	8207	8	11348
20	5481	20	8266	20	11414
2	5533	2	8326	2	11481
4	5585	4	8385	4	11547
6	5637	6	8445	6	11614
8	5689	8	8505	8	11681
30	5742	30	8565	30	11748
2	5794	2	8626	2	11815
4	5847	4	8686	4	11882
6	5900	6	8747	6	11949
8	5953	8	8807	8	12017
40	6006	40	8868	40	12084
2	6060	2	8929	2	12152
4	6114	4	8985	4	12220
6	6168	6	9051	6	12288
8	6222	8	9113	8	12356
50	6276	50	9174	50	12424
2	6330	2	9236	2	12492
4	6384	4	9298	4	12561
6	6439	6	9360	6	12629
8	6494	8	9422	8	12698
60	6549	60	9484	60	12767
2	6604	2	9547	2	12836
4	6659	4	9609	4	12905
6	6714	6	9672	6	12974
8	6770	8	9735	8	13043
70	6825	70	9797	70	13112
2	6881	2	9860	2	13182
4	6937	4	9924	4	13252
6	6993	6	9987	6	13322
8	7050	8	10050	8	13392
80	7106	80	10114	80	13462
2	7163	2	10178	2	13532
4	7219	4	10242	4	13603
6	7276	6	10306	6	13673
8	7333	8	10370	8	13744
90	7390	90	10434	90	13814
2	7448	2	10499	2	13885
4	7505	4	10563	4	13952
6	7563	6	10628	6	14027
8	7621	8	10692	8	14098

Flödeskurva 3/4-fots parshallränna

h_{max} = 650 mmvp = 15991 l/min



Parshallränna

W = 1 ft = 305 mm Fakt. $h^{1,522}$ · 41424 l/min

mm vp	l/min	mm vp	l/min	mm vp	l/min
		100	1245	200	3576
20	107				
		2	1283	2	3631
30	199	4	1322	4	3686
		6	1361	6	3741
40	308	8	1400	8	3796
		10	1440	10	3852
50	434	2	1480	2	3908
		4	1520	4	3964
		6	1561	6	4021
55	501	8	1602	8	4077
		20	1643	20	4134
60	572	2	1685	2	4192
		4	1728	4	4249
65	646	6	1770	6	4307
		8	1813	8	4365
70	724	30	1856	30	4424
		2	1900	2	4483
75	804	4	1944	4	4541
		6	1988	6	4601
80	887	8	2033	8	4660
		40	2078	40	4720
85	972	2	2123	2	4780
		4	2169	4	4840
90	1061	6	2215	6	4900
		8	2261	8	4961
95	1151	50	2308	50	5022
		2	2355	2	5084
		4	2402	4	5145
		6	2450	6	5207
		8	2498	8	5269
		60	2546	60	5331
		2	2594	2	5393
		4	2644	4	5457
		6	2693	6	5520
		8	2743	8	5583
		70	2792	70	5647
		2	2843	2	5710
		4	2893	4	5774
		6	2943	6	5839
		8	2994	8	5903
		80	3046	80	5968
		2	3098	2	6033
		4	3150	4	6098
		6	3202	6	6163
		8	3255	8	6229
		90	3308	90	6295
		2	3361	2	6362
		4	3414	4	6428
		6	3468	6	6495
		8	3521	8	6562

Kalibrering

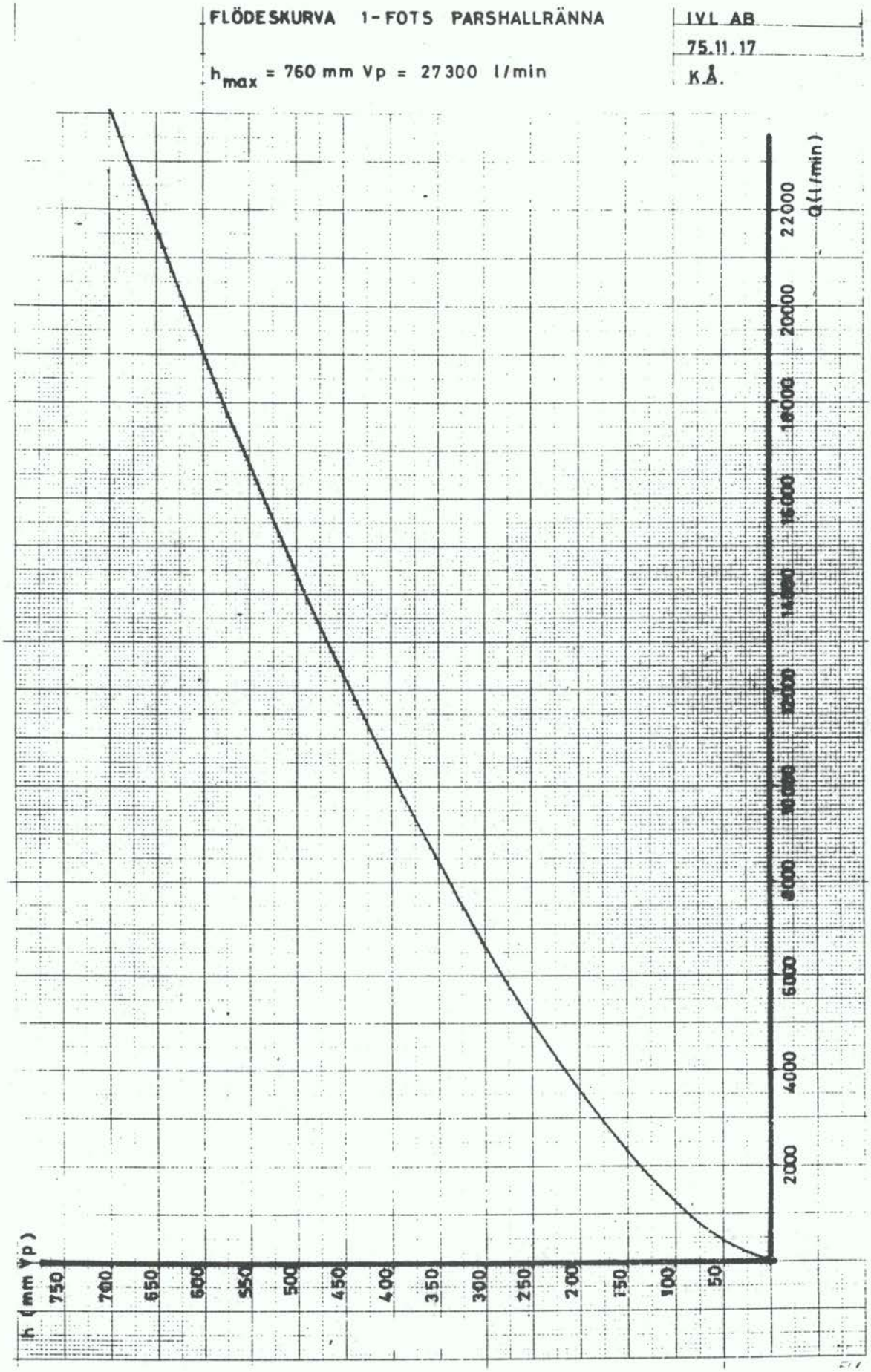
h_{max} = 750 mmvp

25	mm	=	151 l/min
50	"	=	434 "
100	"	=	1245 "
150	"	=	2300 "
200	"	=	3576 "
250	"	=	5022 "
300	"	=	6629 "
350	"	=	8382 "
400	"	=	10270 "
450	"	=	12287 "
500	"	=	14424 "
550	"	=	16676 "
600	"	=	19037 "
650	"	=	21503 "
700	"	=	24071 "
750	"	=	26736 "

Parshallränna

W = 1 ft = 305 mm

mm vp	l/min	mm vp	l/min	mm vp	l/min
300	6629	400	10270	500	14424
2	6696	2	10349	2	14512
4	6764	4	10427	4	14600
6	6832	6	10506	6	14688
8	6900	8	10585	8	14777
10	6968	10	10664	10	14865
2	7036	2	10743	2	14954
4	7105	4	10822	4	15043
6	7174	6	10902	6	15132
8	7243	8	10982	8	15222
20	7312	20	11062	20	15311
2	7383	2	11142	2	15401
4	7452	4	11223	4	15491
6	7523	6	11303	6	15581
8	7593	8	11384	8	15671
30	7664	30	11465	30	15762
2	7734	2	11545	2	15852
4	7805	4	11628	4	15943
6	7877	6	11710	6	16034
8	7948	8	11792	8	16125
40	8019	40	11874	40	16216
2	8091	2	11956	2	16308
4	8164	4	12038	4	16400
6	8236	6	12121	6	16491
8	8309	8	12204	8	16583
50	8382	50	12287	50	16676
2	8455	2	12370	2	16768
4	8528	4	12453	4	16861
6	8601	6	12537	6	16953
8	8675	8	12620	8	17046
60	8749	60	12705	60	17139
2	8823	2	12789	2	17233
4	8897	4	12873	4	17326
6	8972	6	12958	6	17420
8	9046	8	13043	8	17513
70	9121	70	13128	70	17607
2	9196	2	13212	2	17701
4	9272	4	13298	4	17796
6	9347	6	13384	6	17890
8	9423	8	13464	8	17985
80	9499	80	14555	80	18079
2	9575	2	13641	2	18175
4	9651	4	13727	4	18270
6	9728	6	13813	6	18365
8	9805	8	13900	8	18460
90	9882	90	13987	90	18556
2	9959	2	14074	2	18652
4	10036	4	14161	4	18748
6	10114	6	14249	6	18844
8	10192	8	14336	8	18940


FLÖDESKURVA 1-FOTS PARSHALLRÄNNA
h_{max} = 760 mm Vp = 27300 l/min
IVL AB
75.11.17
K.Å.
Q (l/min)
22000
20000
2000
4000
h (mm Vp)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50

Parshallränna

W = 1 1/2 ft = 457 mm Fakt. $h^{1,539}$ · 63369 l/min

mm vp	l/min	mm vp	l/min	mm vp	l/min
		100	1832	200	5323
20	154				
		2	1888	2	5405
30	287	4	1946	4	5488
		6	2003	6	5571
40	447	8	2062	8	5654
		10	2121	10	5738
50	630	2	2181	2	5822
		4	2241	4	5907
		6	2302	6	5992
55	730	8	2363	8	6078
		20	2425	20	6164
60	835	2	2488	2	6250
		4	2551	4	6337
65	944	6	2614	6	6425
		8	2678	8	6512
70	1058	30	2743	30	6600
		2	2808	2	6689
75	1177	4	2874	4	6778
		6	2946	6	6867
80	1299	8	3007	8	6957
		40	3074	40	7047
85	1426	2	3142	2	7138
		4	3211	4	7229
90	1558	6	3280	6	7320
		8	3349	8	7412
95	1693	50	3419	50	7504
		2	3489	2	7597
		4	3560	4	7690
		6	3632	6	7783
		8	3703	8	7877
		60	3776	60	7971
		2	3849	2	8066
		4	3922	4	8161
		6	3996	6	8256
		8	4070	8	8351
		70	4145	70	8447
		2	4220	2	8544
		4	4296	4	8641
		6	4372	6	8738
		8	4449	8	8836
		80	4526	80	8934
		2	4604	2	9032
		4	4682	4	9131
		6	4761	6	9230
		8	4840	8	9330
		90	4919	90	9429
		2	4999	2	9530
		4	5079	4	9631
		6	5160	6	9732
		8	5241	8	9833

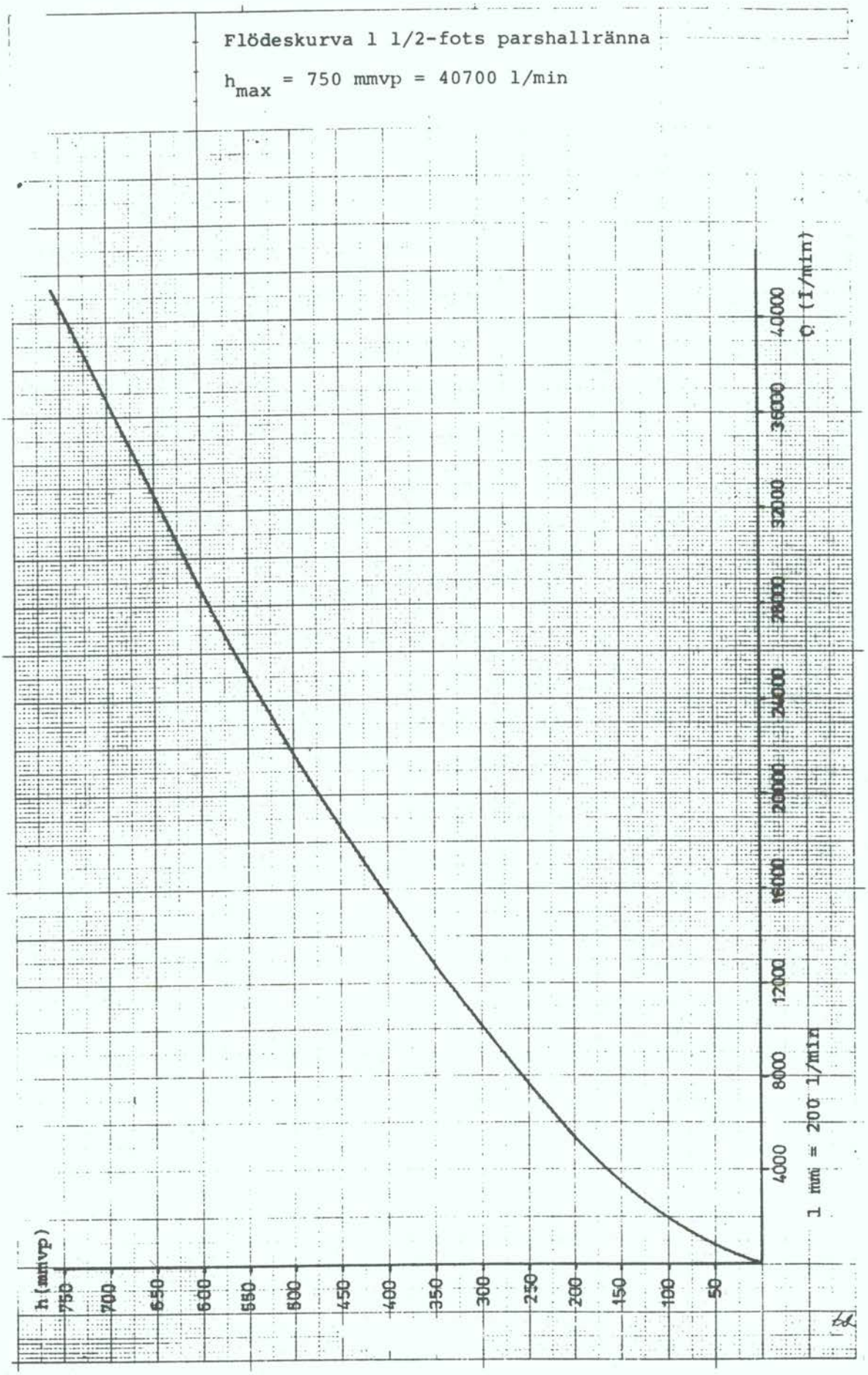
Kalibrering

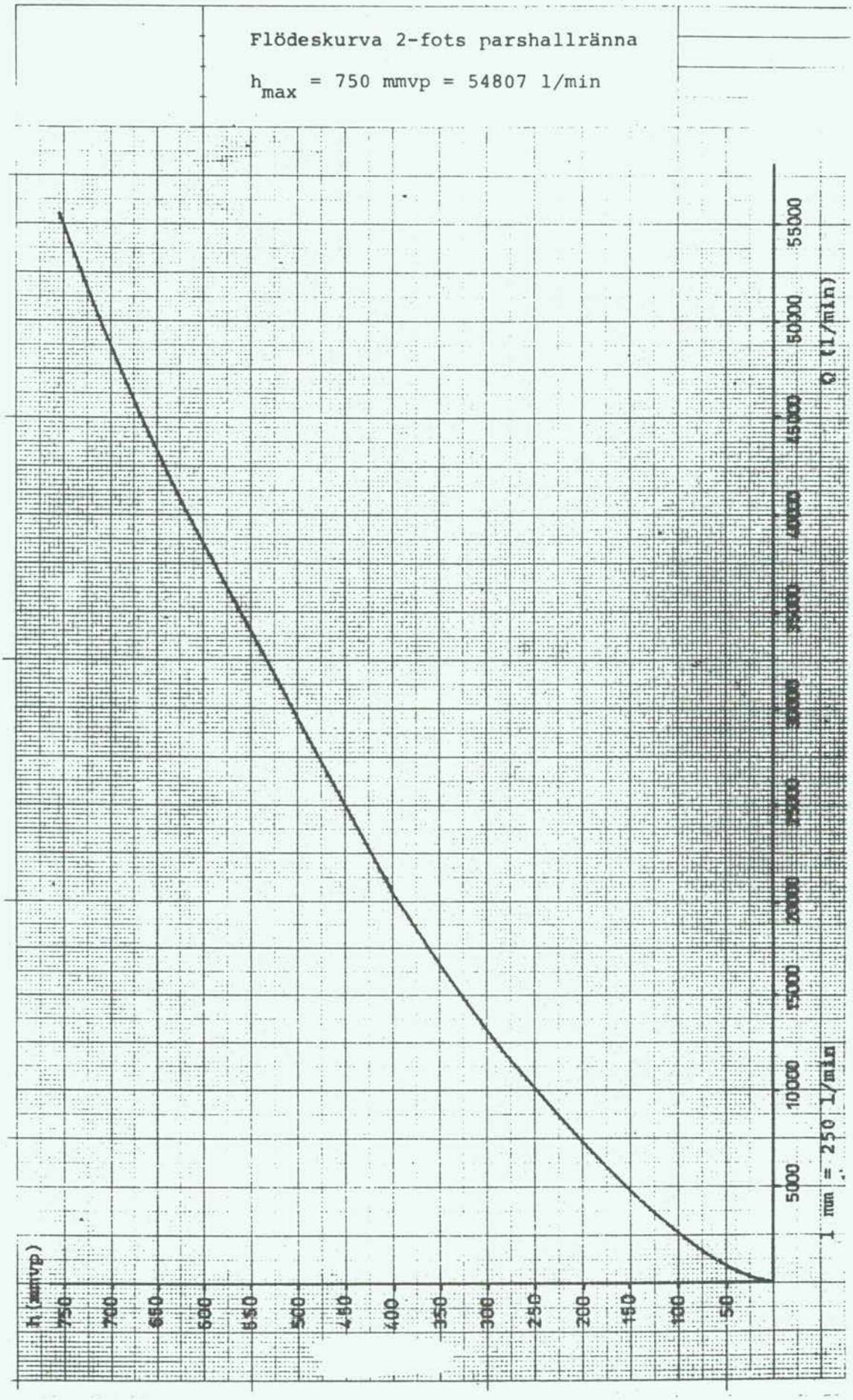
h_{max} = 750 mm

25	mm	=	217 l/min
50	"	=	630 "
100	"	=	1832 "
150	"	=	3419 "
200	"	=	5323 "
250	"	=	7504 "
300	"	=	9935 "
350	"	=	12595 "
400	"	=	15467 "
450	"	=	18543 "
500	"	=	21807 "
550	"	=	25252 "
600	"	=	28870 "
650	"	=	32655 "
700	"	=	36600 "
750	"	=	40700 "

W = 1 1/2 ft = 457 mm

mm vp	l/min	mm vp	l/min	mm vp	l/min
300	9935	400	15468	500	21806
2	10037	2	15588	2	21941
4	10139	4	15707	4	22076
6	10242	6	15827	6	22211
8	10346	8	15947	8	22346
10	10449	10	16068	10	22482
2	10553	2	16188	2	22617
4	10657	4	16309	4	22754
6	10762	6	16431	6	22890
8	10867	8	16553	8	23027
20	10972	20	16675	20	23164
2	11074	2	16797	2	23301
4	11184	4	16920	4	23438
6	11290	6	17043	6	23576
8	11397	8	17166	8	34714
30	11505	30	17290	30	23853
2	11612	2	17414	2	23991
4	11720	4	17538	4	24130
6	11824	6	17662	6	24270
8	11937	8	17787	8	24409
40	12045	40	17912	40	24549
2	12155	2	18038	2	24689
4	12264	4	18163	4	24829
6	12374	6	18290	6	24970
8	12484	8	18416	8	25110
50	12595	50	18543	50	25252
2	12706	2	18670	2	25393
4	12817	4	18797	4	25535
6	12929	6	18924	6	25677
8	13041	8	19052	8	25819
60	13153	60	19181	60	25962
2	13266	2	19309	2	26105
4	13379	4	19438	4	26248
6	13492	6	19567	6	26391
8	13606	8	19696	8	26535
70	13720	70	19826	70	26679
2	13834	2	19956	2	26823
4	13948	4	20086	4	26968
6	14063	6	20217	6	27112
8	14179	8	20348	8	27257
80	14294	80	20479	80	27402
2	14410	2	20610	2	27548
4	14527	4	20742	4	27694
6	14643	6	20874	6	27840
8	14760	8	21006	8	27987
90	14877	90	21139	90	28133
2	14995	2	21272	2	28280
4	15113	4	21405	4	28427
6	15231	6	21539	6	28575
8	15350	8	21673	8	28722
				600	28870


Flödeskurva 1 1/2-fots parshallränna
h_{max} = 750 mmvp = 40700 l/min
h (mmvp)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
4000
8000
12000
16000
20000
24000
28000
32000
36000
40000
Q (l/min)
1 mm = 200 l/min


Flödeskurva 2-fots parshallränna
h_{max} = 750 mmvp = 54807 l/min
h (mmvp)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
5000
10000
55000
Q (l/min)
1 mm = 250 l/min

Parshallränna

W = 2 ft = 610 mm Fakt. $h^{1,549} \cdot 85578$ l/min

mm vp	l/min	mm vp	l/min	mm vp	l/min
		100	2417	200	7074
20	200				
		2	2493	2	7184
30	374	4	2569	4	7294
		6	2646	6	7405
40	585	8	2724	8	7517
		10	2802	10	7629
50	826	2	2881	2	7742
		4	2961	4	7855
		6	3042	6	7970
55	958	8	3124	8	8084
		20	3206	20	8199
60	1096	2	3290	2	8315
		4	3373	4	8431
65	1240	6	3458	6	8548
		8	3543	8	8666
70	1391	30	3630	30	8784
		2	3716	2	8902
75	1548	4	3804	4	9021
		6	3892	6	9141
80	1711	8	3981	8	9261
		40	4071	40	9382
85	1879	2	4162	2	9504
		4	4253	4	9626
90	2053	6	4345	6	9748
		8	4437	8	9871
95	2233	50	4530	50	9995
		2	4624	2	10119
		4	4718	4	10244
		6	4814	6	10369
		8	4910	8	10494
		60	5007	60	10621
		2	5104	2	10748
		4	5202	4	10875
		6	5300	6	11003
		8	5400	8	11131
		70	5500	70	11260
		2	5600	2	11390
		4	5701	4	11520
		6	5803	6	11650
		8	5906	8	11781
		80	6008	80	11913
		2	6112	2	12045
		4	6217	4	12177
		6	6322	6	12310
		8	6427	8	12444
		90	6534	90	12578
		2	6640	2	12713
		4	6748	4	12848
		6	6856	6	12984
		8	6965	8	13120

Kalibrering

h_{max} = 750 mmvp

25 mm	=	282	l/min
50 "	=	826	"
100 "	=	2417	"
150 "	=	4530	"
200 "	=	7074	"
250 "	=	9995	"
300 "	=	13256	"
350 "	=	16832	"
400 "	=	20699	"
450 "	=	24842	"
500 "	=	29246	"
550 "	=	33899	"
600 "	=	38790	"
650 "	=	43910	"
700 "	=	49251	"
750 "	=	54807	"

W = 2 ft = 610 mm

mm vp	l/min	mm vp	l/min	mm vp	l/min
300	13256	400	20699	500	29246
2	13393	2	20860	2	29427
4	13531	4	21021	4	29609
6	13669	6	21182	6	29791
8	13808	8	21344	8	29974
10	13947	10	21506	10	30157
2	14087	2	21669	2	30340
4	14227	4	21832	4	30524
6	14367	6	21996	6	30708
8	14508	8	22160	8	30893
20	14650	20	22324	20	31078
2	14792	2	22489	2	31263
4	14935	4	22654	4	31449
6	15078	6	22820	6	31635
8	15221	8	22986	8	31822
30	15365	30	23153	30	32009
2	15510	2	23320	2	32195
4	15655	4	23488	4	32383
6	15800	6	23655	6	32572
8	15946	8	23824	8	32760
40	16092	40	23992	40	32949
2	16239	2	24161	2	33138
4	16387	4	24331	4	33328
6	16535	6	24500	6	33518
8	16683	8	24671	8	33708
50	16832	50	24842	50	33899
2	16981	2	25013	2	34090
4	17130	4	25185	4	34281
6	17281	6	25357	6	34473
8	17431	8	25530	8	34666
60	17582	60	25702	60	34858
2	17734	2	25878	2	35051
4	17886	4	26049	4	35245
6	18038	6	26224	6	35438
8	18191	8	26398	8	35633
70	18345	70	26573	70	35827
2	18498	2	26748	2	36022
4	18653	4	26924	4	36217
6	18807	6	27100	6	36413
8	18963	8	27277	8	36609
80	19118	80	27454	80	36805
2	19274	2	27631	2	37002
4	19431	4	27809	4	37199
6	19588	6	27987	6	37397
8	19745	8	28166	8	37595
90	19903	90	28345	90	37793
2	20061	2	28524	2	37992
4	20220	4	28704	4	38191
6	20379	6	28884	6	38390
8	20539	8	29065	8	38590
				600	38790

Parshallränna

W = 3 ft = 914 mm

Fakt. $h^{1,566} \cdot 130957$ l/min

mm vp	l/min	mm vp	l/min	mm vp	l/min
		100	3557	200	10532
20	286				
		2	3669	2	10698
30	540	4	3782	4	10865
		6	3897	6	11032
40	848	8	4013	8	11200
		10	4131	10	11369
50	1201	2	4248	2	11539
		4	4368	4	11710
		6	4488	6	11882
55	1395	8	4610	8	12055
		20	4733	20	12228
60	1599	2	4857	2	12403
		4	4982	4	12578
65	1812	6	5109	6	12754
		8	5236	8	12932
70	2035	30	5365	30	13110
		2	5495	2	13289
75	2267	4	5626	4	13469
		6	5758	6	13649
80	2508	8	5891	8	13831
		40	6025	40	14013
85	2758	2	6160	2	14197
		4	6297	4	14381
90	3016	6	6434	6	14566
		8	6573	8	14752
95	3283	50	6713	50	14938
		2	6853	2	15126
		4	6995	4	15314
		6	7138	6	15504
		8	7282	8	15694
		60	7426	60	15885
		2	7572	2	16076
		4	7719	4	16269
		6	7867	6	16462
		8	8016	8	16657
		70	8166	70	16852
		2	8317	2	17048
		4	8469	4	17244
		6	8622	6	17442
		8	8776	8	17640
		80	8931	80	17849
		2	9087	2	18039
		4	9243	4	18240
		6	9401	6	18442
		8	9560	8	18644
		90	9720	90	18847
		2	9880	2	19051
		4	10042	4	19256
		6	10205	6	19461
		8	10368	8	19668

Kalibrering

h_{max} = 750 mmvp

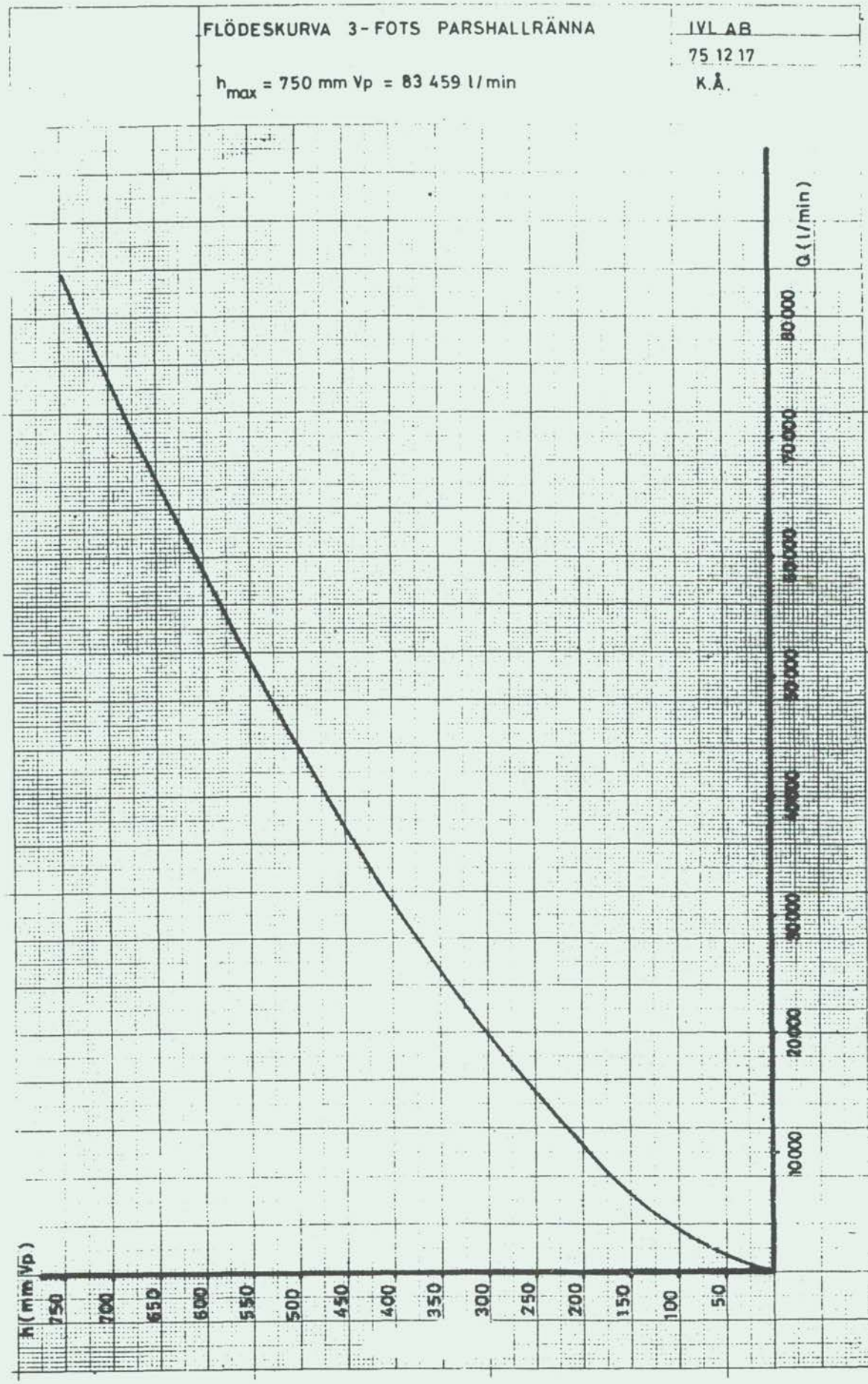
25 mm	= 406	l/min
50 "	= 1210	"
100 "	= 3557	"
150 "	= 6713	"
200 "	= 10532	"
250 "	= 14938	"
300 "	= 18975	"
350 "	= 24301	"
400 "	= 31186	"
450 "	= 37502	"
500 "	= 44230	"
550 "	= 51350	"
600 "	= 58846	"
650 "	= 66704	"
700 "	= 74912	"
750 "	= 83459	"

W = 3 ft = 914 mm

mm vp	l/min	mm vp	l/min	mm vp	l/min
300	19875	400	31186	500	44230
2	20083	2	31430	2	44507
4	20291	4	31675	4	44785
6	20501	6	31921	6	45064
8	20711	8	32168	8	45343
10	20922	10	32415	10	45623
2	21134	2	32663	2	45903
4	21346	4	32912	4	46185
6	21560	6	33161	6	46466
8	21774	8	33411	8	46749
20	21988	20	33661	20	47032
2	22204	2	33913	2	47315
4	22420	4	34165	4	47599
6	22637	6	34418	6	47884
8	22855	8	34671	8	48170
30	23074	30	34925	30	48456
2	23293	2	35180	2	48742
4	23513	4	35435	4	49030
6	23734	6	35691	6	49317
8	23956	8	35948	8	49606
40	24178	40	36206	40	49895
2	24401	2	36463	2	50185
4	24625	4	36722	4	50475
6	24850	6	36982	6	50766
8	25075	8	37242	8	51057
50	25301	50	37502	50	51350
2	25528	2	37764	2	51642
4	25755	4	38026	4	51936
6	25984	6	38288	6	52230
8	26212	8	38552	8	52524
60	26442	60	38816	60	52819
2	26673	2	39080	2	53115
4	26904	4	39346	4	53411
6	27136	6	39611	6	53708
8	27368	8	39878	8	54006
70	27602	70	40145	70	54304
2	27836	2	40413	2	54602
4	28070	4	40682	4	54902
6	28306	6	40951	6	55201
8	28542	8	41220	8	55502
80	28779	80	41491	80	55803
2	29016	2	41762	2	56105
4	29254	4	42034	4	56407
6	29493	6	42305	6	56710
8	29733	8	42579	8	57013
90	29973	90	42852	90	57317
2	30214	2	43127	2	57621
4	30456	4	43402	4	57927
6	30699	6	43677	6	58232
8	30942	8	43953	8	58539
				600	58846

W = 3 ft = 914 mm

mm vp	l/min
610	60389
20	61946
30	63518
40	65104
50	66704
60	68318
70	69946
80	71588
90	73243
700	74912
10	76595
20	78291
30	80000
40	81723
50	83459
60	85208
70	86771
80	88746
90	90534
800	92335


FLÖDESKURVA 3-FOTS PARSHALLRÄNNA
IVL AB
75 12 17
K.Å.
h_{max} = 750 mm Vp = 83 459 l/min
Q (l/min)
80 000
70 000
60 000
50 000
40 000
30 000
20 000
10 000
h (mm Vp)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50

SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

SCAN-C 30:73

Accepted – October 1

DENMARK · FINLAND · NORWAY · SWEDEN · DENMARK · FINLAND · NORWAY · SWEDEN · DENMARK · FINLAND · NORWAY · SWEDEN · DENMARK · FINLAND · NORWAY · SW

SODIUM CONTENT OF WET PULP

Definition

The sodium content of wet pulp is defined as the amount of sodium that can be extracted from a sample of the pulp with hydrochloric acid under specified conditions.

Scope

The method is intended for use in determining the amount of cooking chemicals left in the pulp after various operations. It is recommended for determining the loss of cooking base metal from one section of the mill to another or to the environment.

It is designed primarily for the determination of sodium in pulps produced by the sulphate process but it is also applicable to pulps produced by other processes in which sodium is the base. With relevant modifications, it can be employed in the case of pulps produced by processes in which magnesium is the base metal.

Recommendations for sampling are given in the Appendix. They are intended for use in process control, especially for the purpose of reports to various authorities, but do not form a part of the standardized test procedure.

Principle

The pulp sample is diluted to a pulp concentration of about 2 % and acidified with hydrochloric acid. The sodium content of a sample of the liquid phase is determined by atomic absorption spectrophotometry or flame photometry. The dry matter content of the pulp is determined gravimetrically and the sodium content is calculated; it is expressed in kilograms of sodium sulphate per metric ton of oven-dry pulp.

Apparatus

Flame photometer or atomic absorption spectrophotometer, equipped for the determination of sodium.

Because small amounts of alkali may lead to appreciable errors in the result, all vessels and glass equipment must be thoroughly cleaned with hydrochloric acid and distilled water.

Reagents and chemicals

1. Distilled water
2. Hydrochloric acid, 5 mol/l
3. Sodium sulphate, Na_2SO_4, dried to constant weight

Calibration

Prepare a stock sodium sulphate solution in a 100 ml volumetric flask by dissolving an accurately weighed amount of the sodium sulphate (not less than 500 mg) in distilled water. Make up to the mark and mix well.

Prepare calibration solutions by diluting the stock solution with distilled water. Use pipettes of not less than 10 ml volume and measuring flasks of not less than 100 ml capacity. Use at least 4 concentrations of sodium sulphate, selected to cover the working range of the instrument. Store the calibration solutions in stoppered polyethene bottles.

Prepare a calibration graph by plotting the instrument reading against the sodium sulphate concentration.

Sampling

Recommended sampling techniques, including sample sizes and sampling frequencies, for use in mills with various pulp-washing systems, are given in the Appendix.

Procedure

The amount of sample, especially a gross sample, received in the laboratory is often so large that a smaller test sample must be taken. Before doing so, dilute the sample with distilled water to a pulp concentration of 2 %, preferably in a plastic bucket. Mix the diluted sample by intense stirring. When necessary, disintegrate the pulp in a kitchen mixer or, if the sample is large, in a laboratory mill. Remove large shives before the analysis. While mixing, take the test sample, quickly and in one stroke, using a scoop with a capacity of about half a litre. Transfer the test sample to a glass beaker.

Add 10 ml of the hydrochloric acid and mix well for 10 min. Filter the pulp suspension through a Büchner funnel fitted with an «ashless» filter paper, for example Munktell OOR, of known oven-dry weight.

Collect the filtrate in a filter flask and remove as much water from the pulp as possible by suction and by pressing with a thick glass rod having a flat end. Wash the pulp in the funnel three times with 500 ml of distilled water, pressing it each time with the glass rod.

Remove the pressed pulp and the filter paper from the funnel and dry overnight in a drying oven at 105°C. Place them in an desiccator and allow to attain room temperature. Weigh, subtract the weight of the filter paper and note the weight of the oven-dry pulp c to the nearest 0.01 g.

Dilute the combined filtrate and washings so that the sodium content is within the range covered by the calibration solutions; measure the total volume b. Check that the solution is free from fibres and other particulate matter. Determine the sodium content by flame photometry or atomic absorption spectrophotometry, following the instructions given by the manufacturer of the instrument. Check the calibration graph frequently, preferably after each determination.

Calculation and report

From the calibration graph read the sodium sulphate content, a, of the diluted filtrate.

Calculate the sodium content, expressed as the sodium sulphate content of the dry pulp, from the expression:

$$X = \frac{a \cdot b}{c}$$

where

X = the sodium sulphate content of the pulp, kg/ton

a = the sodium concentration in the diluted filtrate, mg of sodium sulphate per litre

b = the volume of the diluted filtrate, l

c = the weight of the oven-dry pulp. g

Express the result in kilograms of sodium sulphate per (metric) ton of oven-dry pulp to the nearest 0.1 kg/ton.

APPENDIX – RECOMMENDATIONS FOR SAMPLING

General

These recommendations relate to sampling and tests performed to determine the washing losses, i.e. the part of the sodium added in the cooking process which is not returned to the recovery system or any similar closed system. The procedures must be modified to suit the local conditions and therefore no precise instructions can be given. This Appendix is not to be considered as part of the standard method SCAN-C 30:73.

It is often difficult to obtain a sample from the point where the pulp leaves the system; this may not be easily accessible or the pulp may not be properly mixed. The sample should then be taken at the first accessible point downstream where the pulp is well mixed and where a minimum of diluting liquor has been added.

Recommendations are given for sampling in various types of pulpwashing systems and for calculating of the washing losses.

In the calculation of the washing losses, the amount of sodium returned to the system from a later stage should be subtracted from the amount of sodium found; on the other hand no correction should be made for sodium added to the system from an earlier stage or from the spent liquor evaporation system. The precision required when determining the parameters for calculating the corrections depends on the relative magnitude of the correction itself. The amount of sodium returned should be measured by a technique corresponding to that described in the standard method.

The sampling frequencies and the sample sizes recommended below are intended for continuous mill control for the purpose of internal and external accounting.

The composite samples obtained from a certain sampling point within a certain time interval may be combined to form a gross sample.

The recommendations do not cover tests for measuring the efficiency of a washing system, for example in an acceptance test; in this case a somewhat different technique should be used.

Sampling in different pulp-washing systems

Continuous digester with hi-heat washing

The washed pulp is blown to a blow-tank.

Recommended sampling point	First accessible point where the pulp is properly mixed, for example, on the pressure side of the pump after the blow-tank. In sampling from closed pipelines the pulp concentration should be less than 4 %; the sample should therefore not be taken from the blow-line.
Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.

Sample size	A random sample of pulp suspension should contain not less than 25 g of dry pulp and should weigh at least 1 kg.
Corrections in calculating the washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with washing or dilution liquor.

Radial washer

Recommended sampling point	The outlet from the washer.
Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.
Sample size	A random sample should contain not less than 25 g of dry pulp and weigh at least 250 g.
Corrections in calculating the washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with the washing or dilution liquor.

Filter washing system

Recommended sampling point	(a) The screw after the last filter. (b) The point where the pulp leaves the last filter.
Sampling frequency	(a) Five consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample. (b) A series of random samples, taken across the pulp web, are combined to form a composite sample. In order that the composite sample shall be representative of the cross-section of the web the series should comprise one random sample per metre of filter width.
Sample size	(a) A random sample should contain not less than 25 g of dry pulp and weigh at least 250 g. (b) The sample size depends on the number of random samples required. Each random sample should be at least 70 mm by 70 mm.
Corrections for calculating washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with the washing or dilution liquor. The relation between the volume of diluting liquor and the amount of pulp should be known, as should the sodium content of the liquor.
Comments	In a random sample, the top and wire side of the pulp web should be equally represented. It is therefore recommended to remove from the filter a fairly large area of pulp web and to take the random sample carefully from this.

Washing presses

Recommended sampling point	Immediately after the press nip or at the point where the pulp leaves the press, for example, after the screw.
Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.
Sample size	A composite sample weighing not less than 250 g.
Corrections in calculating the washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with washing or dilution liquor. The relation between the volume of diluting liquor and the amount of pulp should be known, as should the sodium content of the liquor.

Batch diffuser

Recommended sampling point	After the diffuser bin. Provided that the stirring in the bin is very efficient the sample may be taken in the bin itself.
Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.
Sample size	A composite sample of pulp suspension should weigh at least 1 kg and contain not less than 25 g of dry pulp. If the samples are taken from a pipe, each random sample should be this size.

Corrections in calculating the washing losses: It should be taken into account whether the washings are recirculated or discharged (to the recipient) and whether recirculated white water is used for final washing or rinsing of the diffuser.

Displacement in discontinuous digesters and/or bins

It is assumed that the pulp is transferred to a bin or a similar container, where it is washed and drained.

Recommended sampling point:
(a) Bin emptied with a conveyor. — Take the sample on the conveyor.
(b) Bin emptied by rinsing. — Take the sample at the first point after the bin where pulp is well mixed.

Sampling frequency:
(a) Five consecutive random samples, taken at intervals of 10 min, are combined to form a composite sample. If water is added to the bin for washing, the intervals must be increased so as to cover the entire emptying period.
(b) Three consecutive random samples, taken at intervals of 5 min, are combined to form a composite sample.

Sample size:
(a) A composite sample of at least 1 kg of wet pulp.
(b) A random sample of pulp suspension should weigh at least 1 kg and contain not less than 25 g of dry pulp.

Corrections in calculating the washing losses: It should be taken into account whether the washings are recirculated or discharged (to the recipient) and whether recirculated white water is used for final washing or rinsing of the diffuser.

Corrections

If the pulp is diluted (for example, with white water) between the washing system and the sampling point, a correction must be made for the sodium content of the diluting liquid. The pulp concentration at the sampling point should be approximately 3 %. Sampling at pulp concentrations below 2 % should be avoided because the corrections will be unreliable, and large errors may be incurred in the final result. Determine the flow of the diluting liquid with a measurement orifice or calculate it from the difference in pulp concentration before and after the point of dilution. At the same time take a sample for determination of the sodium content of the diluting liquid.

Correct also for the sodium added with washing liquid obtained from any point downstream from the sampling point.

Sampling from pipelines

The sampling device used in sampling pulp suspensions in pipelines must be designed to avoid systematic errors in the concentration of the pulp sample. A fairly high rate of pulp flow and a fairly large cross-section area of the pulp stream are required. *Figure 1* shows the main principles of a simple sampling device designed to avoid plugging and systematic errors. In some cases more elaborate sampling devices are required; such devices are commercially available.

Some devices can be used for pulps of high concentration, for example, a type which takes out a pulp plug from the stream passing by. With such devices the risk of loosing liquid phase to the lower part of the pipe must be observed.

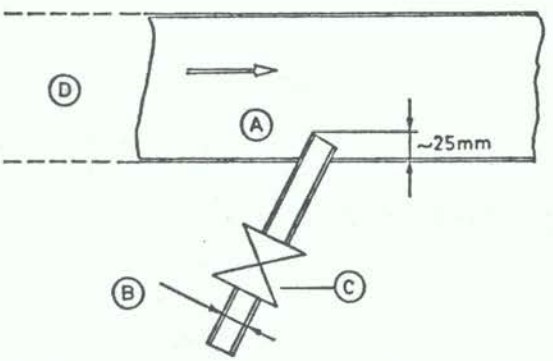


Figure 1. Device for sampling pulp suspensions in pipes.

(A) In order to minimize the hold-up of fibres the sampling tube protrudes at least 25 mm into the pipe and is set at an oblique angle. The opening of the sampling tube is cut off obliquely.
(B) Tube diameter 25 to 40 mm.
(C) A sampling valve with a minimum of constriction is placed in a straight section of the tube.
(D) The sampling device should not be placed immediately after a bend, especially a long, gentle bend, nor after long horizontal straight sections, especially if the pulp flows slowly.

This method has been published in:

Norsk skogindustri 28 (1974):1, 11, 14—16. (English)
Norsk skogindustri 28 (1974):2, 43—46. (Norwegian)
Paperi ja Puu — Papper och Trä 56 (1974):1, 22—23, 26—31. (English, Finnish)
Paperi ja Puu — Papper och Trä 56 (1974):2, 73—76. (Swedish)
Svensk papperstidning 77 (1974):2, 63—70. (Swedish, English)

SCAN testing methods are issued and recommended by the Central Laboratories of the Pulp, Paper and Board Industries in Denmark, Finland, Norway and Sweden. Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-114 86 Stockholm, Sweden.

APPENDIX 4

SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

SCAN-W6:71

Accepted - September 15

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SUSPENDED MATTER IN WASTE WATER

Definition

For the purpose of this method suspended matter in waste water is defined as the matter retained when a sample of the water is filtered through a specified filter. Floating material and supernatant layers of nonaqueous liquids should be removed before the filtration.

Object and scope

The test specified in this method is intended for measuring the amount of suspended matter present in a sample of waste water.

While the test is applicable to most kinds of effluents, special care is required when filtering waters containing suspended matter that builds up a filtering layer having a smaller pore size than the actual filter (Note 1). The method is not intended for the determination of suspended oils.

Principle

The sample is filtered through a filter paper of glass fibres, and the retained dry matter is weighed. Relevant details concerning the filter are presented under «Apparatus».

Apparatus

1. Glass-fibre filters (Note 2), pore size approximately 10 µm (Note 3), 55 mm in diameter (Note 4).
2. Büchner funnels, with an inner diameter to take the filter papers.
3. Filter pump and filter flask, for the Büchner funnels.
4. Drying oven, adjustable to 105°C ± 5°C.

Preparation of sample

Remove floating material and other particulate agglomerates not dispersed on agitating the gross sample. Allow this to attain ambient temperature.

Because some kinds of effluents — for example those from kraft mills — are unstable, the samples should be analysed without delay.

Procedure

Agitate the gross sample vigorously and transfer immediately a suitable volume (generally *ca.* 100 ml) to a measuring cylinder rapidly and in one portion. The volume taken should contain 5 to 100 mg of suspended matter and should be chosen so that the filtering time is less than 1 min. Read off the sample volume on the cylinder scale.

Dry a filter for 1 h at 105°C ± 5°C in the drying oven. Allow it to attain equilibrium with the atmosphere near the balance and weigh to the nearest 0.1 mg. Ensure that during this procedure the filter is not contaminated by dust.

Place the weighed filter in the Büchner funnel and apply suction. Moisten the filter with a few drops of distilled water and check that it fits the funnel tightly.

Transfer the sample quantitatively to the funnel. If the time required for the sample to pass the filter exceeds 1 min, record the time needed. Rinse the cylinder with 20 ml of distilled water and use this for washing the filter. Rinse the sides of the funnel with a few millilitres of distilled water. Remove the filter carefully from the funnel and dry it in the drying oven for 2 h at 105°C ± 5°C. Allow to cool, and weigh as before. Check that the temperature

and relative humidity near the balance have not changed appreciably since the filter was weighed prior to filtration.

Carry out the procedure in duplicate. The results should agree within 10 per cent.

Calculation and report

The suspended-matter content is given by the expression

$$X = 1000(a - b)/c$$

where

a = weight of filter and residue, mg.

b = weight of filter, mg.

c = volume taken for analysis, ml.

X = suspended-matter content, mg/l.

If X is at least 5 mg/l, report to 2 significant figures; otherwise report the result as «less than 5 mg/l».

The report should also state:

(a) The time elapsing between sampling and analysis.

(b) The manufacturer of the filter, its pore size (where known) and other relevant information.

(c) The filtering time, if longer than 1 min.

(d) If relevant, that suspended matter formed a filtering layer having a pore size smaller than that of the filter itself, and that the modification in Note 1 has been used. In this case, the two sample volumes should be reported. State, then, that the results are approximate.

Note 1

Many effluents from pulp, paper or wallboard mills contain minute particles which can block the filter by adhering to the walls of the pores, thus diminishing the pore size. When this happens the filtration time will be prolonged and the results will vary with the sample volume taken for analysis. In this case filter two samples, one twice the size of the other, but both rather small. Report the two results and the sample volumes and state that the results are approximate.

Note 2

Filters made of cellulosic fibres, such as Schleicher and Schüll 589 or Munktell 00R, are in common use in mill control. If such filters have been used, this should be stated specifically. The results shall then not be reported as being obtained in accordance with this standard method.

Note 3

A suitable filter is «Whatman GF/A».

Note 4

If the amount of suspended matter is large, larger filters and funnels may be used.

This method has been published in:

Norsk Skogindustri *25* (1971):12, 389—393. (English, Norwegian)
Paperi ja Puu — Papper och Trä *53* (1971):12, 735—740. (English, Finnish, Swedish)
Svensk Papperstidning *74* (1971):23, 809—810. (English)
Svensk Papperstidning *74* (1971):24, 845—846. (Swedish)

SCAN testing methods are issued and recommended by the Central Laboratories of the Pulp, Paper and Board Industries in Denmark, Finland, Norway and Sweden. Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-114 86 Stockholm, Sweden.

APPENDIX 5

Monthly environmental control form

Mill _____ Submitted by _____

Month _____ Date _____

		Days/Mean value	Remarks of prod	
PRODUKTION				
Number of days				
Unbleached pulp	tonnes			
Bleached pulp	tonnes			
Paper	tonnes			
		Numbers of Determinations	Mean value per day	per t prod
RAW MATERIAL PREPARATION 1				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
COD	kg			
Colour	kg			
FIBRE LINE 2				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
COD	kg			
Colour	kg			
Washing loss	kg			
BLEACHING AND CHEMICAL PREPARATION 3				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
COD	kg			
Colour	kg			

		Numbers of Determinations	Mean value per day	Mean value per t prod
PAPER MAKING 4				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
COD	kg			
CHEMICAL RECOVERY 5				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
COD	kg			
Colour	kg			
UTILITUES 6				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
COMBINED FLOW BEFORE EXTERNAL TREATMENT 7				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
DS	kg			
BOD_5	kg			
COD	kg			

		Numbers of Determinations	Mean value per day	Mean value per t prod
FINAL DISCHARGE 8				
Flow	m^3			
Temperature	C			-
pH				-
SS	kg			
DS	kg			
BOD_5	kg			
COD	kg			
Colour	kg			
Sulfides[1]	kg			
Total Phosphorus	kg			
Kjeldahl Nitrogen	kg			
Mercury	g			
Toxicity[2]				
SAR3				-
Chlorides	kg			-

1) When formed in process

2) Expressed as (LC_{50}-96 hour, i.e. the concentration at which 50% of the individuals in the test fish species are killed after a 96 hour exposure. (Procedure to be finalized.)

3) The SAR value is defined as

$$SAR = \frac{(Na^{+})}{\sqrt{((Ca^{++}) + (Mg^{++}))/2}}$$

where (Na^{+}), (Ca^{++}) and (Mg^{++}) are valued in milliequivalents per litre

APPENDIX 6

Cross Check of Results

1. Raw Material Preparation

SS analysis: Special attention should be paid to the presence of coarse particles in the sample. Filters from SS analysis should be stored for a while so that high SS values can be checked by visual inspection of the filter cake.

2. Fibre Line (unbleached)

SS analysis: See Raw Material Preparation above.

COD analysis: A high COD-emission normally can be related to pore washing efficiency, high accidental spills of spent cooking liqure, discharge of contaminated condensates and finally discharge of porely washed rejects. Check these operations in the operating journal. Determine the washing losses expressed in both base chemical and COD. Compare the ratio base chemical/COD in spent cooking liqure and block check points. Check base chemicals determinations against the make-up.

In most cases a correlation between the COD-value and conductivity can be found. However, observe that the pH will also influence the conductivity. Therefor in situ conductivity measurements are often used as a good indicator on COD-discharges in mill control.

3. Bleaching

SS analysis: Increased SS emissions are normally related to some operating problem, a quick check of the journal will often reveal the cause of the increase. Check filter wires for holes.

Sometimes excess acid from the chlorine dioxide generators may drop the pH in the bleach plant effluent to such a degree that lignans are polymerized, which results in elevated SS values. Check the pH value to determine if this is the case.

COD analysis: The COD emission from a bleaching department is normally relatively constant. If high COD levels appear in the effluent, check the values of the kappa number (unbleached pulp), washing losses and quality of the final pulp in the operating journals. At low pulp viscosities the COD emission will increase.

4. Chemical Recovery

SS analysis: High SS emissions can occur temporarily because of operating disturbances. Check the operating journals to determine if this is the case.

COD analysis: High COD emissions may occur due to accidental losses of spent liqour or discharge of contaminated condensates (see Section 2).

5. Papermaking

Abnormal levels of SS and COD caused by fibres can usually be traced to:

- discharges of fibrous material from overloaded broke systems;

- operating problems in equipment used for internal fibre recovery:

- high washing losses or the presence of substances from processed secondary fibres carried over with the pulp from the pulp mill.

The reasons for increased emissions can normally be found with an internal check of:

- the pulp levels in pulp storage, including broke pulp and untreated white water;

- the SS content in white water from the internal recovery of fibre material;

- the level of washing losses in the pulp mill.

When producing paper grades with filler or coated grades it is often difficult to directly find the cause of increased SS and COD values (besides the conventional causes mentioned above).

High levels of broke due to quality control problems and difficulties with the coating agency are some typical reasons for increased emissions. The only way to determine the cause is to study the operating journals for the paper mill (including the coating kitchen). Keeping suitable journals for the coating stations and the coating kitchen is of critical importance.

Finally, very low or high pH levels in the effluent normally occur when the systems of the paper machine are cleaned since acid and alkaline cleaning agents are normally used. The durations of these periodic shut downs should be noted in the operating journals of the paper mill.

6. Utilities

The utilities normaly will only give a minor contribution to the total discharge and can usually be neglected.

7. Total of Effluent Treatment

Check that the sum of the block discharges equals the total discharge. Check total flow against raw water intake.

The ratio between the COD and BOD_5 values for different effluents is typically as follows:

raw material preparation	2.5-5.0
washing losses	3.5-4.0
bleaching, C stage	4.5-5.0
E stage	less than 4.0
condensate	1.5-2.0
spills of white cooking liquor	infinite
spills of spent cooking liquor	3.5-4.0
paper making	2.0-4.0

The ratio between COD and Na (kraft) for the washing losses is 4-7 (water washing).

The total COD emission exclusive of the bleaching operation, correlates to the make-up requirement. Thus, the ratio between COD and the make up of Na_2SO_4 should be in the range of 0.7-1.5 for kraft pulping.

Appendix 7

Datum / Date	Utgåva / Issue	Order nr Reg nr / Order No Reg No
86-11-21		334035/8318
Kontakta / Prepared by		Telefonnr / Telephone No
G Blidberg/Lgo		08-57 10 00

UNEP-Workshop, Kina

Environmental considerations for non-wood pulping

INTRODUCTION

The raw material for paper in the very beginning of this art in China as well as later in Europe was rag. (Increasing demand for paper through the development of printing created soon a shortage of rags which was accentuated through some technical difficulties with the rag technology at that time.)

In Sweden during the last decades of the nineteenth century increasing quantities of wood and straw were introduced with grinding as the technique for fiberization of wood and mild alkaline cooking in the case of straw. About 100 years ago we had in Sweden a pulp production which was one thousandth of its level today and out of that, 50% was produced from straw.

Later with increasing demand for pulp and with a development of more effective wood pulping processes, wood became the predominant raw material in Scnadinavia for all types of pulps to be used for paper.

In many other countries where wood is more scarce, straw and other non-wood fibers raw materials widely used for the production of paper.

The types of non-wood fibrous raw material used in the pulp and paper industry can be classified into three main groups.

- agriculture residues from sugar, cereal straw crops
- grasses and reeds
- bast and hemp plant fibres

The first group "agriculture residues" is the most important one with the most videspread use and covers raw materials used for paper and board which range from fairly low grades to extremely sophisticated qualities. The most commonly used grasses for pulping are probably bamboo species, but others like esparto are also used and sometimes give

the paper proper properties. Bast fibres are generally used only for speciality grade papers due to their high costs.

The chemical composition does not differ too much between different types of non-wood fibers and the lignin content is largely the same as that for hardwood. The cellulose and hemicellulose contents are also of the same order, but the components are of less molecular mass.

The below given table illustrate this statement. The table is taken from Rydholm. The composition varies a lot but this can be regarded as a grand average.

Raw material	Lignin %	Pentosan %	Ash %	Insoluble ash %
Straw	16	27	8	2.5
Bagasse	19	28	2	1
Bamboo	23	28	2	0.5

When it comes to delignification and the ease by which non-wood fibers are chemically pulped, a marked difference is noticed; non-wood fibers are delignified much faster than wood. The reason for this is said to be the more open structure of the fiber tissue. It is also known that mechanical action has a more pronounced promoting effect on the rate of delignification then is the case for wood.

The chemical pulping processes used today for most non-wood fibers have a fairly short cooking cycle either applied in a continuous or in a batch system using an alkaline cooking liquor. This means that the digester volume can be rather small.

Further processing in the fiber production line like screening, bleaching and drying is largely the same for non-wood fibers as for wood. In the chemical recovery, however, an important difference is experienced. Some non-wood fibers contain up to 3-4% (straw) silica as compared to a few promille for wood. The silica dissolves in the black liquor as silicate, which causes serious scaling during evaporation; an operation necessary to make possible the destruction of the organic substance in the liquor and at the same time recovering energy in the

form of steam. In the recovery of such waste liquors, specific measures have to be taken in order to overcome the scaling problem inherent in such a system.

2. PROCESS AND POLLUTION

I will now go through some of the different steps in the production of non-wood pulp very briefly and comment on the resulting emissions. Most data refer to pulping of bagasse and bamboo but some data are also given for cereal straw.

2.1 Preparation of fibrous raw material

In the manufacture of pulps the preparation of the fibrous raw material is a vital operation for the quality of the pulp and the runnability of the mill. The unit operation involved in the preparation are the following:

- Storage and handling of the raw material
- Separation of inorganic impurities such as stones and sand etc.
- Cutting and screening of the raw material

Bagasse

The storage is dry in bale form or wet, in bulk form. Most of the liquid used in the latter case is reused for slushing or sprinkling the pile. The bagasse depithing, is today normally moist or wet. This in turn leads to discharges to water of both dissolved organic substances and suspended solids from this operation.

The dry preparation of bagasse leads to severe local dust and fire hazard problems. The main part of the dissolved organic substance is then released during the depithing of the bagasse.

In the Ritter process for wet bulk storage the fermentation of residual sugar is prevented by addition of lactic acid bacteria. In a conven-

tional moist bulk storage (e.g. a pile) the lactic acid bacteria normally dominate but formation of acetic acid (and thus more severe degradation) may occur.

The dissolved organic substance is released when the storaged bagasse is washed out on the conveyors or in the depiting operation. The conveyors, the pith presses and depithers are the main sources for the discharges of suspended solids.

Bamboo and straw

The operation used in the preparation of bamboo and straw are normally dry. Water is used for cleaning the bamboo prior to cuting. Nodes are normally separated and rejected in a cyclone in order to decrease the silica input.

A well performed preparation of the fibrous raw material gives the following advantages.

- Decreased silica input to the mill resulting in less scaling problem.
- Decreased chemical consumption in the cook
- Increased pulp quality
- Increased drainage of the pulp, which imply a better washing efficiency

Emissions

The discharges to water from the preparation of bagasse are given in a table below. The figures are based on a very limited number of investigations and should therefore be regarded as indicative only. Available information indicates that the total release of BOD_5 from a well controlled bulk storage is of the order 20 kg BOD_5/ton while a ordinary pile storage system can release up to 60 kg/t bagasse. The yield loss varies conciderably during storage and depithing (5-15%).

The approximate discharge of dissolved and suspended solids from the bagasse preparation operations. Data are given in kg per tonne bagasse pulp

Operation	BOD_5	COD	Susp solids
	---------- kg/t ----------		
Storage dewatering and conveyors and depithing	20-60	30-180	300-400

The discharges to water from handling of straw and bamboo is neglectable.

The air emission problems refer mainly to dust problems in the near surounding of the mill.

2.2 Cooking

The most common processes now used for cooking non-wood fibers is the soda and the kraft process.

The cooking can be performed by either a batch or a continuous process. For at least straw and bagasse pulp the continuous process is the most widely used.

During the cooking procedure most of the lignin, a large amount of the hemicellulose and some of the cellulose are dissolved and the fibres liberated.

Bagasse resembles fairly much hardwoods in chemical composition and this is reflected in the yield which is largely the same as those found for hardwoods but not in cooking time where even less cooking time is required.

Therefor the bagasse cook is very short with low alkali requirements and results in a pulp with fairly low yield. The dominant process used is continous cooking (Defibrator process).

Bamboo cooking is usually carried out in batch digesters and cooking time and alkali charges are of the same magnitude as those encountered for conventionel wood pulping with the exception that cooking temperatur usually is somewhat lower.

The following cooking parameters are averages based upon information from various sources.

Raw material	Cooking time at 170°C, min	Charge of active alkali %	Pulp yield %
Straw	12-15	18.5	47
Bagasse	10-12	13	53
Bamboo	90 (at 160°C)	18	52

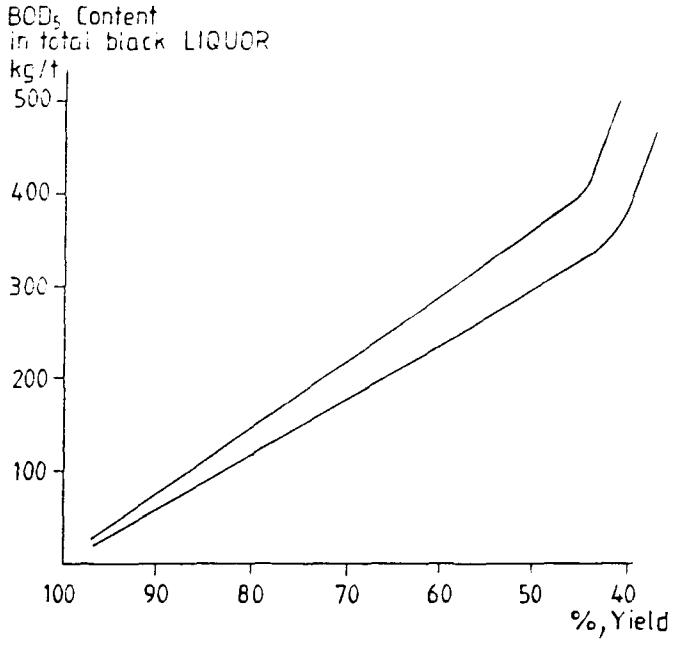
Emissions

The normal output from the cooking process are:

- Pulp
- Spent black liquor
- Blow condensate
- Non condensable gases

Pulp and spent liquor are sent to the washing department. The blow condensate are usually heavily polluted with sulphur compounds (kraft) and alcohols corresponding to a BOD amount of 3-8 kg/ton. The condensate can be stripped and the volitile compounds can then be destructed in a boiler or in the lime kiln together with the non condensable gases.

The main part of the water pollution from a pulping process originates from the spent black liquor or from the wood material dissolved during the cook. This means that the potential amount of pollutants in the black liquor is dependent on the yield as shown in the figure below.



Some typical figures for total black liquor content expressed as BOD_5 are given in table below.

Process	Raw material	Yield	BOD_5
		%	kg/ton pulp
Cold soda	bamboo	85	110
"	straw	60	250
"	"	50	350
"	bagasse	80	150
"	"	54	300
Kraft	bamboo	46	300
"	bagasse	48	350
Alkaline sulphite	wheat straw	48	280
NSSC	bagasse	70	200

The resulting emission from the black liquor is then dependent on the washing efficiency and the amount of black liquor spills.

2.3 Washing

For a cost efficient chemical recovery the spent liquor should be delivered as concentrated as possible and as completely as possible to the recovery system. The aim of the washing operation is to separate the fibres from the spent liquor fullfilling the mentioned criteria. As earlier mentioned any residual spent liquor leaving the washing operation with the pulp will be washed out in a susequent, open process stage (e.g. the screening or bleaching) and contributes to the water pollution.

Thre are also a number of minor pulping units for non-wood that have a production rate too low for chemical recovery. In these cases the whole content of pollutants in the total black liquor will be discharged in washing ad screening departments.

The main factors influencing the results of the washing operation are as follows:

- Type of pulp to be washed
- Type of washing equipment
- Dimensions of the washer
- Number of washing units
- Washing liquid (composition, amount, temperatures)

The washing of non-wood pulp is normally performed on 2-4 drumfilters in series but for straw and bamboo continous digesters with Hi-heat washing are also often used.

The design of the washing equipment has to be more elaborate than for wood pulps due to a slow drainage property of non-wood pulps. This is illustrated in the following table.

Wash filter loadings and dewatering properties of various sulphate and soda pulps.

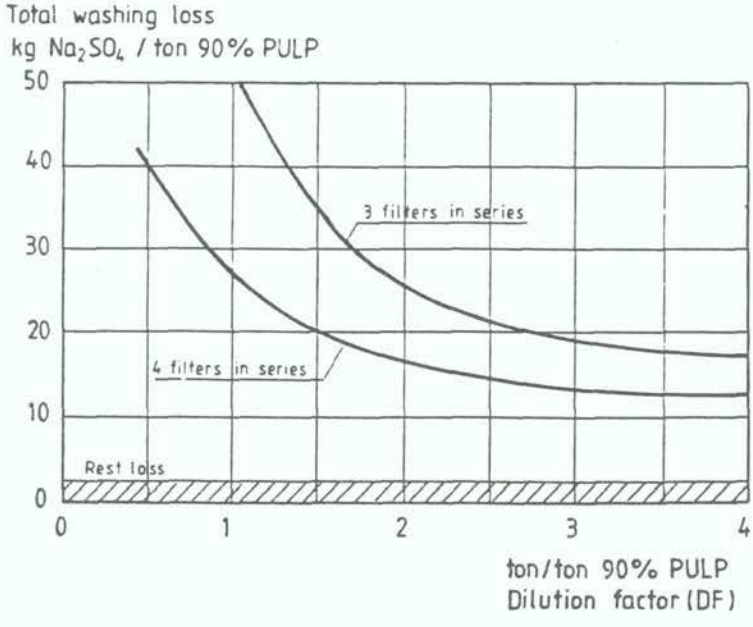
Pulp type	Wash filter loading t_{100}/m^2d	Freeness* °SR
Softwood	5-7	12-13
Hardwood		
birch	4-6	15-16
eucalyptus globulus	6-9	-
Bagasse	2-4	20-25
Bamboo	4	14-16
Rice straw	1.5-2	40
Wheat straw	0.5-2	30

* Assuming chemical pulp yields and no refining

This results in practise in a rather high dilution factor for non-wood pulps e.g. 3-6 m^3/t pulp compared with 1.5-3.0 for wood pulps. Therefore the weak black liquor to evaporation will be low in dry matter.

- Straw and bamboo 8-10% dry matter
- Bagasse 11-13 "
- Wood 15-20 "

The relation between washing efficiency and dilution as well as no of units is illustrated in the below figure.



As a role of thumb the washing loss will be reduced with approximately 50% for each additional unit added.

Emissions

Normally the washing department only discharges spills to the effluent. However, for the total emissions of pollutants to the effluent from non-wood pulping the dominant factor is the total washing efficiency. Normal figures are in range 75-90% e.g. 25-80 kg BOD_5/t pulp.

2.4 Chemical recovery

The chemical recovery systems for non-wood pulping are in most cases simular to the ones used for wood pulping or evaporation, recovery boiler and cooking liquor preparation.

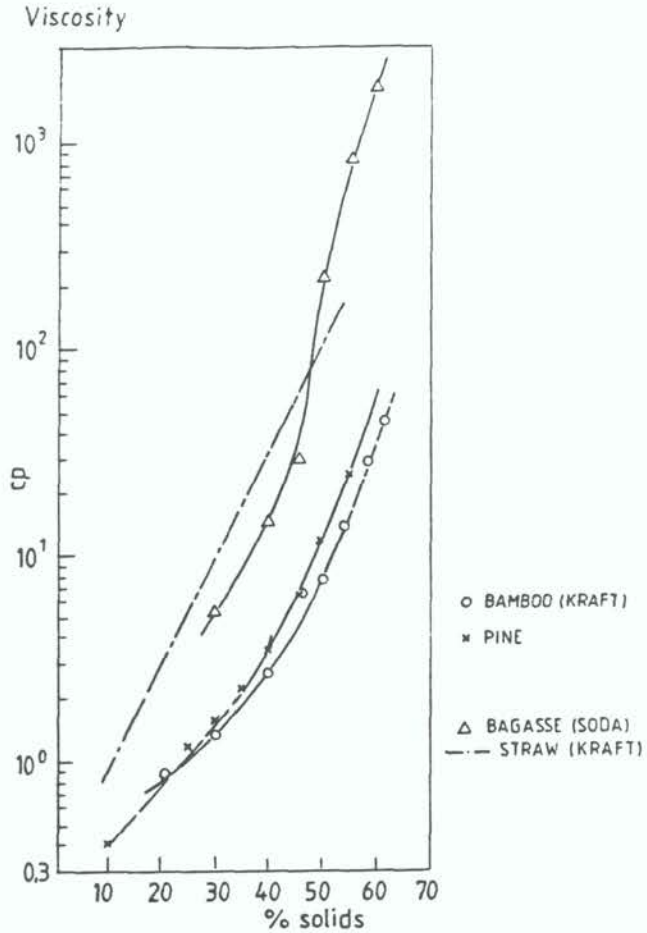
I have chosen to limit this discussion to the main process soda or kraft. Compared with wood pulping, chemical recovery in non-wood pulping have some major drawbacks:

- High content of silica as presented in the following table.

Concentration of silica in spent black liquors as percentage of total dry solids.

Raw material	% of dry solids
Rice straw	16-30
Cereal straw	3-6
Bamboo	2-5
Bagasse	1-3
Softwood	0.01
Eucalyptus	0.01-0.8

- High viscosity, this is shown in the next figure where viscosity v.s. solids content have been plotted for some different liquers. This effect is explained by the higher content of pentosans in the non-wood material.



Viscosity of black liquors at 90°C

- Low heat value due to lower lignin content and higher carbohydrates content resulting in lower carbon content.

Evaporation

Due to the previuously discussed difficulties the evaporation of non-wood black liquors will demand the following prerequisites:

- A relatively high concentration of free alkali in the weak black liquor, at least 8 g/l NaOH. This is normally maintained by adding white liquor before evaporation.

- A short storage time for black liquor.

- A as constant as possible temperature profile throughout the evaporation.

- A low fiber content in the black liquor through installation of a fiberfilter before evaporation.

- A good periodical washing system including a spare unit for final effects.

Normally the evaporation is caried out in four or five effects to a dissolved solids concentration of only 35-45%. Before the recovery boiler the liquor is then further concentrated in a direct contact evaporator to 55-60%. The lower values refer to bagasse, the higher to straw and bamboo.

When the kraft process is used a separate black liquor oxidation unit is advisable to prevent emission of malodorous gases.

Recovery boiler

In the soda process the recovery of heat and chemicals is carried out in several different types of equipment. In all cases the chemicals are recovered as smelt and dust of Na_2CO_3. The simpliest systems have no or minor heat recovery while the refined systems have an efficient high pressure steam production.

In the kraft process a conventional Tomlinson-type boiler is normally used. However, there are a number of specific considerations that must be taken for a sucessful combustion of a non-wood liqure.

- Due to the 10-20% lower heat value compared with wood based liquor an supporting oil firing is normally required.

- To achieve a proper distribution of liquor droplets the liquor pressure at the gun is kept substantially higher than for conventional liquors. In some cases steam shattering have been utilized.

- The thick black liquor pipes have to be kept hot e.g. by means of steam tracing as non-wood black liquor gets stuck very quickly at lower temperatues.

- The black liquor mixing tank should include steam heating, preferably of indirect type to avoid dilution of the liquor.

  In addition a direct steam heater before the gun is required.

- The liquor lines should include ample number of steam connections for cleaning purpose.

- Black liquor pumps should be of rigid design.

- The ash generated at the combustion gives deposits on the tubes in the boiler which are more difficult to remove. Therefore furnace dimensioning, tube pitches, scope of sootblowers, possibility of hand lancing etc. have to be considered.

- To get the smelt properly out of the boiler a high furnace bottom temperature is required and the smelt spouts should be designed short and with good inclination.

- As the risk of building up of deposits on the boiler tubes partly depends on the tube metal temperature it is favorable to select a low boiler pressure and a low superheated steam temperature. The steam temperature should not exceed around 400^{o}C.

Causticizing

The high silica content in non-wood raw materials, normally 1-4%, will result in a high concentration of silica in the black liquor as previously demonstrated. The main part of the silica will be carried

basicly unchanged through evaporation as well as recovery boiler and result in operational difficulties (like scaling) in evaporation. In the caustisation the main part of the silica is transferred to the lime mud and will there build up to very high levels if the lime mud is recirculated through burning in a lime kiln. If this is the case some mud or lime has to be discharged and in this way preventing the silica content from increasing upto too high levels in the lime.

This means that the amount of make-up lime always is high. Therefore it is important to consider that the purchased lime also will give an substantial input of inpurities such as silica, aluminium and phosphorus.

The causticizing will, because of the reasons mentioned above, produce lime mud with a high proportion of contaminating chemicals. The physical properties of the lime mud therefore demand a causticizing designed and operating according to the sedimentation method. It is not possible to utilize modern technique where the lime mud is separated and washed in a filter bag of polypropylen. The high content of fine granular would very soon clogg the filter pores.

Therefore, the causticizing should be performed by the conventional method with white liquor clarifier and lime mud wash thickener and no or partial lime mud recovery.

Summerizing the above discussion it can be concluded that chemical recovery in non-wood pulp production will compared with conventional wood base result in

- lower heat production
- lower degree of reduction (kraft)
- lower degree of causticizing
- lower effectiv alkali (EA)
- higher consumption of make-up chemicals.

Emissions

The emissions from the chemical recovery departments are summarized below.

- Evaporation
  To water: Contaminated condensate and spills
  To atmosphere: Uncondensable gases

- Recovery boiler
  To water: Spills
  To atmosphere: Gases from the combustion

- Causticizing
  To water: Lime mud, grits, dregs and spill
  To atmosphere: Gases from the combustion

The range of the total discharges to water from the recovery departments are exemplified below:

	BOD_5	COD	Susp solids
	---------- kg/t ----------		
Evaporation	10-30	15-80	-
Recovery boiler	1	5	1
Causticizing	-	10	5-250

The range of the total emission to air from the recovery departments are exemplified below:

	TRS[1)]	SO_2
	kg/t S	kg/t
Evaporation	0-2	-
Recovery boiler	0.1-4	0.2-4
Causticizing	0.02-0.2	0.2

1) TRS (total reduced sulphure)

The lower figures refer to soda pulping the higher to kraft pulping.

2.5 Bleaching

Traditionally, non-wood pulps are bleached using a three stage sequence C-E-H or more recently a four stage sequence C/D-E-H-D.

The following factors are of importance for the discharge of pollutants from bleaching plants;

- Lignin content of the unbleached pulp

- Extent to which the unbleached pulp has been washed

- Bleaching conditions such as
  * Bleach sequences and charges used
  * Temperature and pH
  * Final brightness and strength requirement

The extent to which the various systems have been closed and the recirculation pattern of the filtrates are other influential factors.

Emissions

To water:
There is relatively little variation in the BOD and COD values between species while the colour values show an wider range. Besides the traditional effluent characteristics (BOD, COD, colour) the amount of chlorine bound to organic molecules in the bleach plant effluent is significant. The chlorinated organic compounds often show only a slow degradation by biochemical oxidation and some tend to accumulated in organic tissues. By substituting chlorine with chlorine dioxide and by oxygen bleaching the organic chlorine can be reduced subsequently. These modifications, however, require changes in process equipment and will increase the investment and the operating costs.

The same process modifications also reduce the BOD and colour discharges. Most marked is the colour reduction (up to 75%) while the BOD reduction is a less spectacular, 35%. It should be pointed out that

on softwood the delignification in the cook has been extended to kappa number 25 for the bleaching sequences with high amounts of chlorine dioxide.

Below is presented some typical data for bleaching effluents from different types of non-wood pulps.

The BOD_7, COD, colour and TOCl values of the discharge from the bleaching of sulphate and soda pulps at a normal washing loss (for a modern mill).

Fibrous raw material	Pulping process	Kappa number	BOD	COD	Colour	TOCl[1)]
			-------- kg/t pulp ----------			
Bamboo	Sulphate	-	17	90	-	1-2
Straw	Soda	12	16	60	70	
Eucalyptus		20	14	60	70	2.5
Birch	Sulphate	20	14	60	70	2.5
Scots pine	Sulphate	33	15	80	160	5
	Sulphate + O_2	20	12	50	100	3

1) TOCl (total organic chlorine)

To atmosphere

From towers and filters recidual chlorine and chlorine dioxide are vented to atmosphere. The amounts are normally moderate in the range of 0.2-3 kg/t pulp as chlorine.

Annex 2

MANUAL ON RECEIVING WATER QUALITY EVALUATION

PREFACE

This manual is an outcome of the Phase I programme of the Network for Industrial Environmental Management (NIEM). The manual presents, in detail, general agreements reached by the NIEM members concerning the methodology and procedures to be used in conducting water quality evaluations of water bodies receiving discharges from small pulp and paper mills. During NIEM Phase I, Network members, drawn from industry, government and academia, conducted a series of coordinated research projects on water quality evaluation based on the recommendations of this manual in its draft form. The results and experience obtained during the course of the individual evaluations and field applications were used to revise and improve this manual to its present form.

The United Nations Environment Programme gratefully acknowledges the financial contribution by the Swedish International Development Authority that made functioning of the Network possible. Special thanks are extended to Mr. Ti Thiow Hee, Director of the Department of Chemistry, Malaysia, who drafted the text. Suggestions for revisions to the draft were provided by NIEM members.

TO THE USERS OF THIS MANUAL

1) This manual is to be used only as a guide in evaluating the quality of water bodies receiving industrial discharges, particularly from pulp and paper mills.

2) While the main structure of the manual is to be retained, the finer details may be subject to modifications or adaptations according to local conditions and the specific nature of each mill.

3) As the manual will be used by all NIEM countries and the study data obtained will be used for comparison purposes, it is important that any deviation in methodology from what is prescribed in the manual be noted in the final report.

4) Within the framework of flexibility, Network members should attempt to harmonize the various procedures as prescribed in this manual.

Contents

RECEIVING WATER QUALITY EVALUATION

1. Objective

The objective of this manual is to provide guidance to those individuals charged with monitoring the environmental quality of receiving waters. Reasons for monitoring water quality are numerous. The data collected in either long- or short-term efforts can be used:

1) to determine the overall quality of the receiving water and its ability to sustain various beneficial uses;

2) as part of environmental impact assessment studies;

3) to determine the extent to which pollution control measures should be required of the private sector and governments; and

4) for other planning and research activities.

Conducting a monitoring campaign is a complicated task. Because of the high cost of even routine sampling and analysis it is important to carefully plan all aspects of the monitoring programme before the field work begins. This manual is designed to meet this objective by giving a step-by-step approach to conducting a receiving water quality monitoring programme for use by the various NIEM research teams.

The scope of this manual is intended to eventually cover all media but in its present form covers only receiving waters, in particular those receiving discharges from pulp and paper mills.

2. Background Information

2.1 General

The first step for a researcher conducting a NIEM research project is to carry out a general review of existing information and prepare an inventory of all the factors which may influence, either directly or indirectly, the quality of the receiving water body being investigated. This will include cataloguing all discharges or withdrawls occuring along the particular reach of the receiving body. The review should also cover background information on the area, such as geography, topography, climate and weather, hydrology, hydrogeology, hydrobiology, land use, urbanisation, industrialization, and agricultural use. Likely changes which would affect the receiving waters should be examined.

Next, the study team should collect data on the beneficial uses of the receiving body downstream from the point of discharge, their magnitudes, quality requirements and relative importance. It is important to include not only current beneficial uses but also all proposed and

likely changes in use, and consequent requirements in both quality and quantity.

All existing information on the quality of the receiving body should be amassed. Such information may come from previous water quality studies, EIA reports, or research studies. Based on the data collected in this preparatory phase, a site location map illustrating the more important aspects of present and future influences and uses should be prepared.

2.2 Specific

All information available on the general discharge characteristics of the pulp and paper mill being investigated should be collected. The discharge characterization portion of the NIEM study should provide all the necessary information.

2.3 Appraisal of Information

On the basis of the information gathered it should be possible to:

- appraise the relative importance of factors influencing the quality of the receiving water;
- decide what information is needed to meet the appropriate control, planning and baseline requirements of the study;
- select appropriate sampling points for the monitoring programme.

2.4 Dispersion Characteristics of the Receiving Body

Prediction of environmental impact can only be made if the dispersion characteristics of the effluent in the receiving waters are known. There may be appreciable delays in the lateral dispersion of discharges depending upon the velocity, turbulence, and size of the river downstream from the discharge point. Dispersion of pollutants may also be retarded by supressed vertical mixing, particularly when the effluent and receiving water are at a different temperature.

In all cases it is necessary to determine the actual dispersion of the mill effluent in the receiving water.

The actual disperson of the mill effluent in the receiving water can be followed by using specific tracers such as die tracers (eg. Fluorescein, Rhodamine B), salt tracers such as Potassium Chloride (K^+) and Lithium Sulphate (Li^+), radioactive tracers such as Ammonium Dihydrogen Phosphate containing Phosphorus -32, radioactive water containing tritium tracer, and bacteria tracers (species Serratia Indica which can be easily identified by counting the bright red colonies formed on agar plates).

The determination of the theoretical disperson of the mill effluent in the receiving water is extremely complicated and is not required for the present exercise.

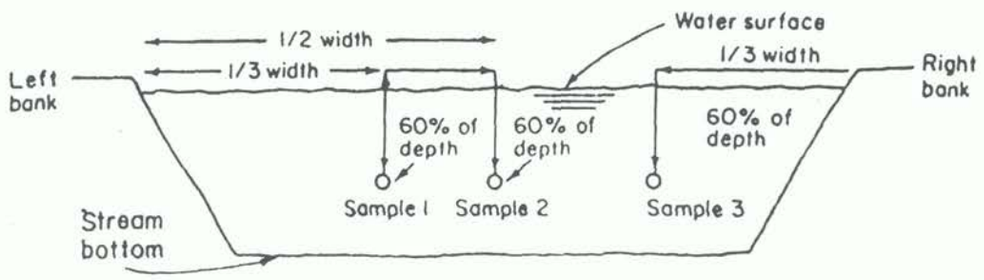
3. Selection of Sampling Points

A preliminary monitoring survey covering the potential network of sampling points should be carried out before the entire programme is initiated. The survey should, if possible, cover a representative period of both river flows and mill operations, and encompass as many potential sampling points as is practically possible. This preliminary monitoring effort will assist in selecting suitable permanent sampling points for the monitoring programme.

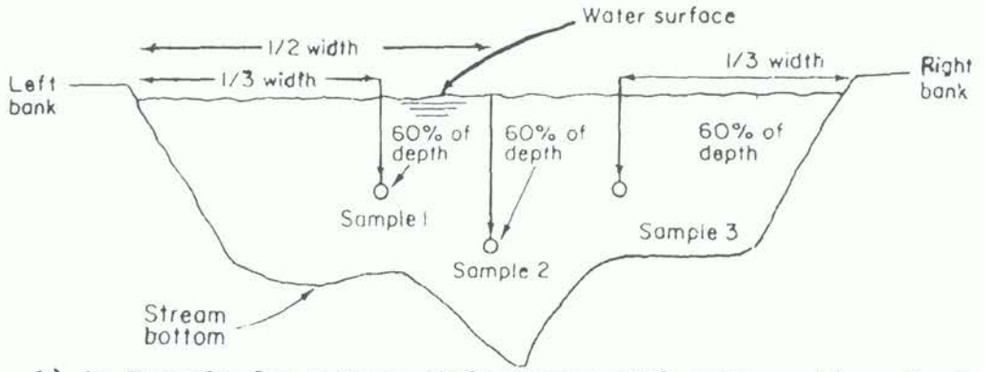
The exact number and position of the sampling points should be determined such that the information from the network gives a clear picture of the receiving water quality at minimum cost. The spatial "net" should be fine enough that it is possible to distinguish the influence of the mill effluents from other sources of pollution.

As a general rule, rivers, which are wide, deep, or non-uniform in flow and waste distribution, must be sampled at different points transversally in the channel, greatly adding to the number of samples required to obtain a reliable mean for the section.

Figure 1: Selection of Sampling Points Transversally in the River



a) An Example for a Deep, Wide Stream with a Uniform Depth



b) An Example for a Deep, Wide Stream with a Non-uniform Depth

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Because of the density differences, currents and the physical peculiarities of certain wastes, multi-depth sampling should be encouraged. Figure 1 shows the selection of sampling points transversally in the river having uniform and non-uniform depth.

In the final monitoring programme, there should:

- be at least one sampling point upstream from the point of discharge of the mill. This sampling point should be representative of the condition of the river free from any influence of the mill discharge;

- be a sufficient number of sampling points downstream from the point of discharge. The number of sampling points selected should indicate the degree of dispersion of the effluent from the mill downstream to the point where complete mixing occurs.

It is worth noting that when the number of samples that can be handled is limited, it is preferable to reduce the number of stations rather than curtail the frequency of sampling.

As a guide, Table 1 shows a typical classification of rivers according to their current velocity and gives the approximate time (based on tests with fluorescein) in which mixing with sewage becomes complete. Though the results were obtained using sewage as the effluent, it can be used, as a rule-of-thumb, for ascertaining the approximate time in which mixing with the mill discharge becomes complete.

Table 1: Classification of Rivers Based on the Current Velocity

Description of river current	Approximate current velocity of river ft/min	Approximate time in which mixing with sewage becomes complete
Very rapid	100 or more	5 - 1 min
Rapid	60 - 100	20 - 10 min
Moderate	40 - 60	90 - 30 min
Slow	20 - 40	3 - 2 h
Sluggish to very sluggish	20 or less	6 - 3 h

Source: 8th Report of the Royal Commission

4. Sampling Frequency

If automatic monitoring equipment is available, the flow, temperature and pH of both the mill discharge and the receiving water near the discharge point should be measured daily if possible. The measurements can either be taken continuously or at intervals.

It was suggested that for the NIEM Phase I projects a monthly sampling frequency be used for a period of one year, giving a total of 12 samples for most of the constituents. This suggestion was based on the human and financial resources that each country participating in the Network could reasonably provide. The actual sampling day within each month should be representative, reflecting the normal condition of the receiving body and mill operations during that month. For example, samples should not be taken immediately after a thunderstorm if climatic data indicates that a particular month is normally dry. One way to determine whether a day is representative or not is to measure the flow of the river and compare the value with the mean monthly flow (assuming the information is available). A phone call or quick visit can then confirm that the mill is operating normally on that particular day.

For a preliminary river water quality evaluation investigation, all parameters at sampling frequency (as given in Table 2) are expected to be carried out.

However, for the subsequent river water quality evaluation investigation, the number of measurements can be reduced and only those parameters which are found critical need to be analysed.

5. Sampling Procedures

5.1 General Considerations

After suitable sampling sites have been selected, it is important to devise a sampling procedure for each station which will ensure that the samples taken there will be both representative and valid.

The collection and handling of samples is the first and most important step in the analysis of specific chemical, biological, or physical constituents in the receiving water. If done incorrectly, even the most fastidious analytical procedures yield results that are at most meaningless, and at worst misleading. Such critical items as collection of representative samples; use of appropriate clean containers; and proper preservation, identification, and transportation of the samples are often neglected. The person collecting the samples should be properly instructed on the importance and significance of following correct sampling procedures, particularly if another individual will later conduct the analysis.

The sample bottles may be either glass or plastic. As a general rule, glass containers are preferred as they are resistant to strong cleaning compounds, can be easily inspected, have walls which do not roughen with time allowing suspended or other impurities to adhere to the inside, and can be easily sterilized by heat if required. Plastic bottles, on the other hand, are less likely to break if handled roughly in the field.

In some cases, chemical considerations such as transfer of chemical substance from the container to the sample, sorption of chemical substance from the water to the container, or direct reaction of the water with the

Table 2 - Sample Preservation and Analytical Methodology

	Measurement	Volume required	Container[1]	Preservation	Holding time	Sampling frequency	Methodology Brief	Reference[2]
1.	Flow	-	-	in situ	-	Daily if possible; if not, weekly	Current meter/float/ discharge measurement	-
2.	Temperature	-	-	in situ	-	Daily if possible; if not, weekly	temperature probe, thermometer	-
3.	pH	-	-	in situ	-	Daily if possible; if not, weekly	pH meter	SM 423, p. 429
4.	Dissolved oxygen	100 ml	P,G	in situ	-	Daily if possible; if not, weekly	Dissolved oxygen meter	-
5.	Suspended solids	100 ml	P,G	Cool to 4°C	7 days	Monthly	Filter with glass fibre filter, dry, weigh	SM 209C, p. 96 (modified)[3]
6.	Dissolved solids	100 ml	P,G	Cool to 4°C	7 days	Monthly	Filter with glass fibre filter Whatman GF/C or equivalent (1.5 um), dry, weigh	SM 209B, p. 95 (modified)[3]
7.	BOD	1000 ml	P,G	Cool to 4°C	24 hours	Monthly	Three dilutions, incubation at 30°C for 3 days	SM 507, p. 525 (modified)[4]
8.	COD	50 ml	P,G	H_2SO_4 to pH<2	7 days	Monthly	Sulfuric acid/potassium dichromate reflux for 2 hours	SM 508A, p. 533
9.	Colour	50 ml	P,G	Cool to 4°C	24 hours	Monthly	Lovibond Colour Comparator (or equivalent), Hazen Units	SM 204A, p. 67
10.	Chloride	50 ml	P,G	None required	7 days	Monthly	Argentometric method	SM 407A, p. 287
11.	Sodium Absorption Ratio[5]	50 ml	P,G	Filter on site, HNO_3 to pH<2	28 days	Monthly	AAS of Na, Ca, Mg: calculate SAR	SM 303A, p. 157
12.	Phosphorous, total dissolved	50 ml	P,G	Filter on site, Cool to 4°C, H_2SO_4 to pH<2	24 hours	Monthly	Sulfuric acid - nitric acid digestion followed by stannous chloride - ammonium molybdate colorimetric determination	SM 424E, p. 446
13.	Kjeldahl nitrogen	500 ml	P,G	Cool to 4°C H_2SO_4 to pH<2	24 hours	Monthly	Kjeldahl digestion, distillation, visual comparison	SM 420A, p. 408

Table 2, continued

Measurement	Volume required	Container[1]	Preservation	Holding time	Sampling frequency	Methodology Brief	Reference[2]
14. Hg total	100 ml	P,G	HNO_3 to pH<2	38 days (glass) 13 days (plastic)	Monthly	AAS (flameless cold vapour technique) or mercury analyzer	SM 320A, p. 232
15. Coliform	100 ml	G	Cool to 4°C	24 hours	Monthly	Membrane filter technique	SM 909A, p. 887
16. Benthic Macro-invertebrates	-	-	Sieve on site; preserve in 10% formalin or 70% ethonol solution	-	Monthly	Appendix 1, Biological Assessment of water Quality in Three British Rivers; also see SM 1005, p. 1113 for further discussion and background information.	-

Optional Measurements

The following pollutants may be measured on an optional basis.

17. Lignin	100 ml	P,G	None required	7 days	Quarterly	Tanin-lignin reagent, carbonate-lignin reagent/visual or photometric determination	SM 513, p. 590
18. Sulfide	100 ml	P,G	Add 4 drops of 2N zinc acetate per 100 ml; cool to 4°C	28 days	Quarterly	Methylene blue method	SM 427C, p. 475
19. Phenols	500 ml	P,G	Phosphoric acid to pH<4; cool to 4°C	28 days	Quarterly	Gas-Liquid Chromatographic method	SM 510D, p. 561
20. PCB's	1000 ml	G	Cool to 4°C	immediate	Quarterly	Gas chromatographic method	-
21. Cyanides	500 ml	P,G	NaOH to pH>12; cool to 4°C; store in dark	14 days	Quarterly	Titimetric or colorimetric method	SM 412C, p. 336 or 412D, p. 337
22. Zinc	100 ml	P,G	HNO_3 to pH<2	28 days	Quarterly	AAS	SM 303A, p. 157
23. Lead	100 ml	P,G	HNO_3 to pH<2	28 days	Quarterly	AAS	SM 303A, p. 157

24. Toxicity - The method to be used for determining toxicity is outlined in the NIEM manual, "Guide on Determination of the Acute Lethal Toxicity of Pulp and Paper Mill Effluent to Freshwater Fish"

Table 2, continued

Notes

[1] P - polyethylene; G - glass

[2] Standard Methods for the Examination of Water and Wastewater, 16th edition; published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation.

[3] Methodology is identical to SM 209B/SM 209C with the exception that a Whatman GF/C 1.2 micron filter or equivalent is used instead of the grade 934-AH filter.

[4] Participants at the NIEM organizational meeting agreed that the standard BOD incubation time and temperature of 5 days and 20°C should be modified for the NIEM studies. It was felt that test results obtained under 3-day, 30°C condition would give a better indication of the immediate oxygen demand caused by wastes discharged into tropical rivers. Researchers are encouraged to determine BOD under both conditions so that a meaniful comparison can be made. If resources preclude running comparative tests, the 3-day, 30°C conditions should be used.

[5] Also report Na as sodium sulfate.

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container, have to be taken into account when chosing the type of container. For the substances analyzed in the NIEM programme, these chemical considerations will not be of much importance. Still, if in doubt over which type of sample bottle to use, check the detailed analytical procedures in Standard Methods or some other authoritative text.

Recommended sample bottles for measurements of various constituents are given in Table 2.

5.2 Manual Sampling

Manual samples are taken over a very brief time and are referred to as "grab", "catch", or "spot" samples. Although there are many types of manual samplers available commercially, the two types described below are recommended for the NIEM study.

i) Surface sampler - A plastic household bucket or jug on the end of a rope serves as an adequate surface sampler. The water in the bucket should be stirred while it is being poured into the sample bottle to prevent suspended matter from settling out.

ii) Depth sampler - A weighted steel case or container on the end of a rope, and containing a sampling bottle can be used as a depth sampler. The bottle can be opened by a rubber bung stopper controlled by a cord, permitting a sample to be taken at any depth. This type of sampler is illustrated in Figure 2. Another kind of depth sampler is illustrated in Figure 3.

The recommendation of these two manual samplers is based on their applicability, simplicity, and low cost. Network members are certainly encouraged to use any patented manual samplers they have available.

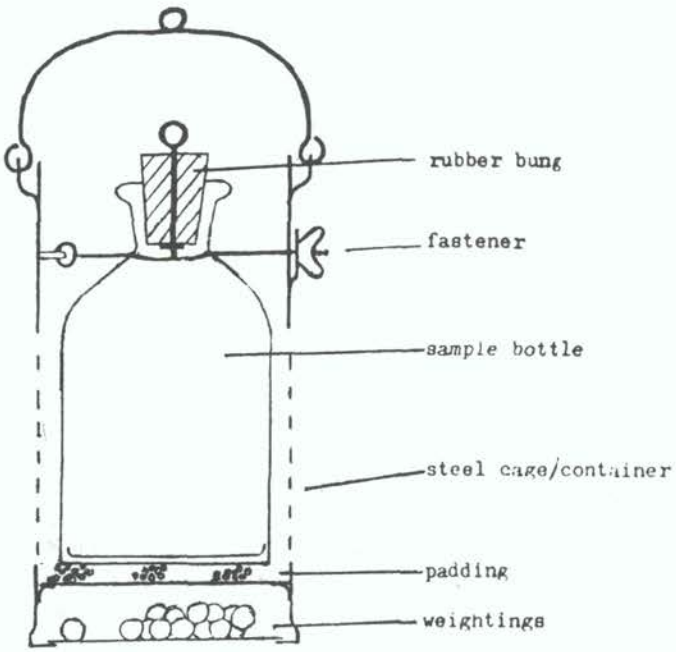
5.3 Automatic Sampling

Automatic samplers are usually quite costly and require regular maintenance. Their purchase is not recommended for the NIEM studies but they may be used if the apparatus is available.

5.4 Composite Sampling

A simple composite sample is usually sufficient for most water quality monitoring programmes. Such a sample is obtained by collecting a series of equal volume grab samples over a period of a day and combining them to form a composite sample. No allowance is made for flow variations that occur over the sampling period, either in the river or in the mill discharge. If either flow variation is significant, a flow based composite sample may be more appropriate.

Composite samples should not be used for measurements of dissolved oxygen, pH, temperature, free cyanide, dissolved metals, or bacteria. Values of these constituents may change with time as a result of chemical reactions, cell die-off or growth, or gas transfer, giving false results.



(Note: Any other sample design is acceptible. The above illustration is given as a guide only.)

Figure 2: One Type of Simple Depth Sampler

With this handy and versatile apparatus, water samples can be taken from any desired depth. The Standard Water Sampler, still open, is lowered by rope into the water. Upon reaching the desired depth, the drop messenger is let down on the rope. When it stikes the Standard Water Sampler, the closing mechanism is released and the lids of the sampling tube close. A thermometer ranging from -2 to +30°C, divided in 0.2°C, indicates the temperature of the sample; the temperature can easily be read through the plastic tube of the sampler. The water sample can be drawn off through the discharge cock in the lower lid for the various analyses.

Figure 3: Standard Water Sampler
(after Ruttner)

5.5 Sample Preservation

Changes in the concentration of the sample constituents will take place from the time the sample is obtained to the time it is analyzed. As a general rule, it is best to analyze the sample as soon as possible after collection.

Various preservation methods are available, but their common general effect is one of retardation rather than fixation, as the complete and unequivocal preservation of samples is a practical impossibility. Preservation is normally accomplished by refrigerating the sample at a temperature of 4°C. If refrigeration is not possible, the bottle containing the sample should be kept on ice in an insulated container.

The other common method of preservation is the addition of chemicals, usually biocides or acids, to the sample. Biocides inhibit or prevent biological action from changing values of constituents. $HgCl_2$, added to the sample such that the final concentration is 20 - 40 mg per litre, is one commonly used biocide. Mineral acids such as nitric acid are often added to collection bottles in sufficient quantities to lower the pH of the sample to about 2 pH units. Doing this will stabilize the concentrations of total and dissolved metals for several weeks. Acidification also inhibits biological activity to a certain extent.

Measurement of constituents falls into the following three groups:

i) those of generally stable constituents, which do not change in concentration or value within a holding time of 24 hours;

ii) those of unstable constituents, whose concentration or values change with time but which can be stabilized for at least 24 hours by appropriate treatment;

iii) those of unstable constituents, whose time varying values cannot be stabilized.

Constituents belonging to the first two groups can be measured by taking representative water samples for subsequent analysis in a laboratory. The third group includes temperature, pH, and dissolved oxygen, which need to be measured in the field.

The recommended method of preservation for the measurement of various constituents is given in Table 2. Other information provided in the table is the volume of the sample required for analysis, the suggested type of container, and the maximum recommended holding times for properly preserved samples.

5.6 Identification of Sample and Sampling Information

To avoid the problem of mis-marking samples, it is preferred that unmarked sampling bottles be taken to the field. Sampling bottles can then be marked immediately after the sample is taken.

The label attached to the sampling bottle should contain the following information:

- station identification;
- date and time the sample was collected;
- preservative added (if any) and;
- collectors name.

The information recorded in the form submitted with the sample bottles should include the following:

- name of water body;
- station identification;
- date and time of collection;
- results of any in situ tests, such as;
  - temperature
  - dissolved oxygen concentration
  - pH
  - flow rate
- appearance of water body and sample;
- weather conditions on the day preceding sampling and on the day of sampling;
- collector's name;
- other miscellaneous information.

6. Analytical Methods

Although several analytical methods can be used to determine concentration or values of most constituents, it was agreed that harmonized procedures would be used by Network members. A brief description of the agreed methodologies is given in Table 2. Detailed descriptions of the analytical methods can be found in the 16th edition of Standard Methods for the Examination of Water and Wastewater, prepared and published jointly by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation.

Portable test equipment is commercially available for in situ analysis of many constituents. Such equipment minimizes the costs and errors associated with sample storage, transport, and handling. Portable test kits and equipment may be used in the NIEM studies provided that the accuracy and precision of the results obtained is comparable to the laboratory methods. It is important that all field instruments be checked and recalibrated in the laboratory at frequent intervals. Records of this should be kept for reference.

7. Reporting of Results

The importance in the expression of results, the precision, accuracy and correctness of analysis has more than often been neglected or overlooked by the analyst.

The analyst's competence may be questioned if ambiguous results are generated and presented. It is, hence, important that the analyst should report such figures as are justified by the accuracy of the work.

For more information on this subject, please refer to Parts 103 and 104 of Standard Methods (16th Edition).

8. Data Processing

Samples collected at the monitoring site will be analysed in situ or in the laboratory, and results of the analysis sent to the Project Coordinator or person responsible for processing the data. Appendix 2 shows the raw data form developed for this purpose.

The results received from the laboratory should be tabulated for each particular station or sampling point for the specific monitoring period. A statistical breakdown of the data should be performed to make the data more manageable.

9. Final Assessment

All information obtained as part of the investigation must be integrated in order to determine the influence of the mill discharge on the receiving water. Of particular importance is the seasonal effect of the effluent and the extent, duration, and types of impacts. A comprehensive final assessment will not only quantify the impact of the mill on the receiving water, but will assess the key factors of any mill control programme that might be undertaken to reduce, prevent or eliminate the adverse impacts.

Appendix 1

Biological Assessment of Water Quality

The following methodology for sampling benthic macro-invertebrates is obtained from a paper written by D. Balloch, C.E. Davies, and F.H. Jones entitled: "Biological Assessment of Water Quality in Three British Rivers," (Water Pollution Control, 1976, pps. 92-114). For brevity, only those sections of the paper dealing with sampling methodology and data analysis are reproduced here. Readers are urged to refer to the full text if they are interested in the background and interpretation of the results of the study.

Materials and Methods

Physico-chemical Sampling

The sampling stations along the lengths of each river and main tributaries were of sufficient number and appropriately distributed to give a clear profile of the prevailing physico-chemical conditions existing in each river, including the effects of known discharges. In general, the selected sampling stations were essentially the same as those sampled routinely by the respective river purification board and river authorities. It was decided not to carry out separate analyses but to use and incorporate data collected by these authorities, thus enabling more time to be allocated for biological assessment methods. Biological sampling timetables were therefore adjusted to coincide with the field collection of water samples by the authorities staff. Official analyses were supplemented by the author's analyses where and when conditions warranted it, for example in relation to additional biological sampling stations.

Two other parameters, i.e. velocity of water flow and nature of the substratum, were considered important environmental factors operating independently of water quality and affecting aquatic biocoenoses. These were determined by either a float or pitot-tube method for water velocity and by a granulometric analyses of substratal material employing a series of sieves

Biological Sampling

The number and distribution of sampling stations, (shown in Fig. 1, 2 and 3) were such that a clear picture of the prevailing biological conditions would be obtained and that the results would yield information commensurate with the labour involved. Benthic macro-invertebrates were chosen, in this study, as the most suitable organisms for assessing water quality for the following reasons; (a) Benthic macro-invertebrates are relatively sessile and their low mobility renders them less capable of avoiding pollution stress; (b) they have relatively long life histories and their presence or absence aids in deducing environmental factors over a long period of time; (c) they are well keyed, easy to identify and enumerate; and (d) qualitative and quantitative benthic sampling techniques are well established and are more reliable than equivalent techniques established for microscopic aquatic organisms. Other aquatic organisms, principally benthic algae and protozoa, although known to be of use in the biological assessment of water quality[3], were not considered in the present paper since they are not suitable for use in routine biological sampling programmes.

The analysis of benthic macro-invertebrate communities demands a quantitative sampling procedure that would enable the collection of samples representative of the total range of species present, irrespective of their irregular and clustered distribution in the chosen substratum to be sampled. The riffle habitat is normally chosen as a result of the large number of micro-habitats and niches offered by the stone surfaces and interstices of this substratum and because most of the macro-invertebrate species sensitive to deteriorations in water quality are located there[4]. In the present study it was proposed to employ two techniques for sampling the invertebrate fauna of riffle reaches. The first technique was the widely used heel-kick and stop net method of Macan[5], which essentially consisted of holding a hand-net (10 meshes/cm) against the river bed whilst the substratum immediately upstream was disturbed by kicking, thus loosening the macro-invertebrates which were swept into the net by the current. Overturned substratal material was also examined for attached species, which were transferred to the net sample. Normally a 60 s sample is adequate to obtain a representative collection of the macro-invertebrate fauna; longer sampling periods do not yield much more information, and the extra results are not commensurate with the labour involved in the subsequent analysis of the samples in the laboratory. The net mesh size of 100 meshes/mm may not adequately sample first and second instars of insect nymphs and a smaller mesh size may be employed[6]. The second sampling technique involved the use of a cylindrical core sampler (Fig. 4), which was a modification of the

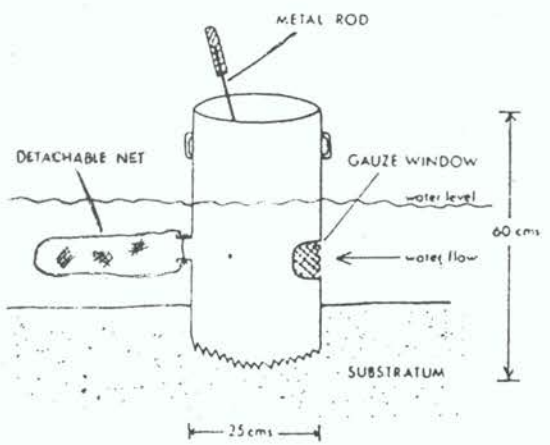


Fig. 4. Neill's Cylindrical Sampler

cylindrical sampler first described by Neill[7]. The apparatus consisted of a metal cylinder with a serrated base which, when screwed into the substratum, enclosed an area of 0·5 m². The sampler was normally screwed into the substratum to a depth of 100 mm, such that both epibenthic and eubenthic macro-invertebrates were sampled. The substratum enclosed within the cylinder was vigorously agitated using a metal rod and dislodged macro-invertebrates were swept into a downstream detachable net (200 meshes/mm) by water flow entering an upstream gauze window.

Rivers in low lying land tend to be slow moving and deep with few riffle reaches. Hence other biotopes, principally marginal emergent macrophytes and the depositing substratum of deep water reaches, were both qualitatively and quantitatively sampled with a view to ascertaining the effect of sampling habitat on the applicability of data processing techniques. Emergent plants, pure stands of *Rorippa nasturtium aquaticum* occurring ubiquitously in the R. Ivel, were chosen as the best substratum. A simple cylindrical sampler was employed in the quantitative sampling of the macro-invertebrates inhabiting the macrophyte stands. A 22-l capacity metal drum 300 mm dia. with its base removed was placed carefully over the plants which were cut at the substratal surface. A fine mesh nylon net (20 meshes/cm) was placed under the drum thus trapping macro-invertebrates dislodged from the plant surfaces during the raising of the sampler. Cut plant material and the collected macro-invertebrates were washed into the nets and transferred to plastic bags for subsequent analysis in the laboratory. Each portion of plant material was examined for attached species which were removed for identification and enumeration. The plant washings were passed through a series of soil sieves of progressively finer mesh size (10, 30, 60, and 90 meshes/cm). Macro-invertebrates collected in the sieves were sorted, identified and enumerated. Plant material was also weighed after draining freely for 5 min. Deep water reaches were sampled qualitatively only, employing a hand-net (20 meshes/cm) to collect plant, macro-invertebrate, and substratal material which was subsequently separated and the macro-invertebrate sorted and identified.

Data Processing Techniques

The qualitative and quantitative benthic macro-invertebrate data arising from the river surveys were subjected to summarization in the form of numerical indexes, and the indexes were

TABLE 1. CLASSIFICATION OF BIOLOGICAL SAMPLES: TRENT BIOTIC INDEX

Clean			Total number of groups present				
			0–1	2–5	6–10	11–15	16+
Organisms in order of tendency to disappear as degree of pollution increases					Biotic Index		
	Plecoptera nymphs present	More than one species	—	VII	VIII	IX	X
		One species only	—	VI	VII	VIII	IX
	Ephemeroptera nymphs present	More than one species*	—	VI	VII	VIII	IX
		One species only*	—	V	VI	VII	VIII
	Trichoptera larvae present	More than one species†	—	V	VI	VII	VIII
		One species only†	IV	IV	V	VI	VII
	Gammarus present	All above species absent	III	IV	V	VI	VII
	Asellus present	All above species absent	II	III	IV	V	VI
	Tubificid worms and/or Red Chironomid larvae present	All above species absent	I	II	III	IV	—
	All above types absent	Some organisms such as Eristalis tenax not requiring dissolved oxygen may be present	0	I	II	—	—
Polluted							

† Bactis rhodani excluded.

* Bactis rhodani (Ephem.) is counted in this section for the purpose of classification

GROUPS

The term 'Group' here denotes the limit of identifiation which can be reached without resorting to lengthy techniques. Thus the Groups are as follows :—

Each known species of Platyhelminthes (flatworms).
Annelida (worms) excluding genus Nais.
Genus Nais (worms).
Each known species of Hirudinae (leeches).
Each known species of Mollusca (snails).
Each known species of Crustacea (log-louse, shrimps).
Each known species of Plecoptera (stone-fly).
Each known genus of Ephemeroptera (may-fly) excluding Baetis rhodani.
Baetis rhodani (may-fly).
Each family of Trichoptera (caddis-fly).
Each species of Neuroptera larvae (alder-fly).
Family Chironomidae (midge larvae) except Chironomus Ch. thummi.
Chironomus Ch. thummi (blood worms).
Family Simulidae (black-fly larvae).
Each known species of other fly larvae.
Each known species of Coleoptera (beetles and beetle larvae).
Each known species of Hydracarina (water-mites).

the subject of assessment and comparison in order to ascertain their value as criteria of water quality.

Trent biotic index. Woodiwiss[8], working in the former Trent River Authority, developed and proposed his empirical biotic index of river quality using the benthic macro-invertebrates inhabiting riffle reaches of Midland rivers. He devised a scheme in which the number of groups of benthic macro-invertebrates (groups of defined taxa) was related to the presence of six key organisms or groups of organisms namely, plecopteran nymphs, ephemeropteran nymphs, trichopteran larvae, *Gammarus*, *Asellus*, and tubificids and red chironomid larvae. Depending on the number of groups present and the key organisms found in the fauna, the biotic index values ranged from 10 (clean water associated fauna) decreasing with increasing pollution (reciprocal relationship) to 0 (polluted water associated fauna). The index is generally based upon the order in which benthic macro-invertebrate species disappear with deteriorations in water quality. The groups of organisms and classification of biological samples are presented in Table 1.

Graham's biotic index. Graham's Biotic Index[9] was an adaptation of the Trent biotic index and was used in the Lothians River Purification Board area for five years until 1972. Graham's system incorporated a six-point scale in which a clean stream scored an index value of 1, higher values correlating with increasing deterioration in water quality with an upper index value of 6 indicating that no benthic macro-invertebrates were present. Index values possess a direct relationship with increasing pollution. The index is best calculated for each sampling station by averaging the values over a period of a year (usually 6 to 8 samples), and in this way errors of sampling are minimized. Details of the key groups of benthic macro-invertebrates are presented in Table 2.

TABLE 2. GRAHAM'S BIOTIC INDEX

	No. of groups	Index
Stone-flies and non-Baetid may-flies present	10+	1
	0 - 9	2
One or both of the above absent, caddis and shrimps present	10+	2
	0 - 9	3
Stone-flies, non-Baetid may-flies and caddis absent. *Baetis*, shrimps, *Asellus*, snails or leeches present	10+	3
	0 - 9	4
All above groups absent. Fauna restricted to *Tubifex*, *Nais*, midge larva or blood worms	—	5
No macro-invertebrates found	—	6

Chandler's score system. Chandler[10], working on the River North Esk and other rivers in the Lothians River Purification Board's area, developed and proposed his score system. Similar to the Trent and Graham's biotic indices, the score system was based on the order in which benthic macro-invertebrates disappeared with increasing deterioration in water quality. The system incorporates a more detailed list of benthic macro-invertebrates than either of the other British indices. Abundance is taken into account, and the levels of abundance used by Chandler are shown in Table 3

TABLE 3. SAMPLE ABUNDANCE LEVELS

Level	No. of individuals per 5-min sample
Present	1 to 2
Few	3 to 10
Common	11 to 50
Abundant	51 to 100
Very abundant	more than 100

To arrive at an index for a station the fauna are identified and enumerated, and each group present is given a score as set out in Table 4. Sensitive species score high and tolerant species score low, and all species score higher values the more abundant that they are present. The index has no fixed levels (cf. Trent and Graham Biotic Indexes) and possesses a graduation of values between 0 (no macro-invertebrates present), 45–300 (moderate pollution levels), and 300 to over 3000 (mildly polluted to unpolluted conditions).

Community diversity index. Unlike species diversity indexes, community or dominance diversity indices distinguish species of different abundance and thus provide a better numerical measure of community structure. Shannon and Weaver[13], using the Shannon-Wiener function, introduced the following expression:

$$d = -\sum_{i}^{t} = 1\left[(n_i/N).\log_e(n_i/N)\right]$$

where,

d = Diversity Index

t = number of species

n = number of individuals in each species

N = total number of individuals

e = 2·78 or simply 2.

This index, and others of its type, is very useful in pollution studies since it provides a non-biased numerical value for community diversity, and also the technique is generally independent of sample size[14]. To arrive at an index value for a

TABLE 4. CHANDLER'S SCORE SYSTEM

Groups present in sample		Increasing abundance				
		Points scored				
		P	F	C	A	V
Each species of:	Planaria alpina, Taenopterygidae, Perlidae, Perlodidae, Isoperlidae, Chloropedidae	90	94	98	99	100
Each species of:	Leuctridae, Capniidae, Nemouridae (excluding Amphinemura)	84	89	94	97	98
Each species of:	Ephemeroptera (excluding Baetis)	79	84	90	94	97
	Cased caddis, Megaloptera	75	80	86	91	94
	Ancylus	70	75	82	87	91
—	Rhyacophila (Trichoptera)	65	70	77	83	88
Genera of:	Dicranota, Limnophera	60	65	72	78	84
	Simulium	56	61	67	73	75
	Coleoptera, Nematoda	51	55	61	66	72
—	Amphinemura (Plecoptera)	47	50	54	58	63
—	Baetis (Ephemeroptera)	44	46	48	50	52
—	Gammarus	40	40	40	40	40
Each species of:	Uncased caddis (excluding Rhyacophila)	38	36	35	33	31
	Tricladida (excluding P.alpina)	35	33	31	29	25
Genera of:	Hydracarina	32	30	28	25	21
Each species of:	Mollusca (excluding Ancylus)	30	28	25	22	18
—	Chironomids (excluding C.riparius)	28	25	21	18	15
Each species of:	Glossiphonia	26	23	20	16	13
	Asellus	25	22	18	14	10
	Leech (excluding Glossiphonia, Haemopsis)	24	20	16	12	9
—	Haemopsis	23	19	15	10	7
—	Tubifex sp.	22	18	13	12	9
—	Chironomus riparius	21	17	12	7	4
—	Nais	20	16	10	6	2
Each species of:	Air breathing species	19	15	9	5	1
	No. of animal life			0		

sampling station the benthic macro-invertebrates must be both qualitatively and quantitatively sampled, and exact numbers of individuals counted. The taxonomic or group unit employed should preferably be the lowest taxonomic unit (species). However, not all organisms are easily identified to species level, so generic level may be substituted. A mixture of taxonomic groupings may be employed provided the levels chosen and used in the calculation of community diversity indexes are the same for all sampling stations. The latter situation is most likely to be met by river biologists who identify benthic macro-invertebrates to various taxonomic levels depending on their expertise, time and availability of identification keys. Wilhm and Dorris[12] have found 'clean water' areas to have d values greater than 3·0; 'moderate pollution' from 1·0 to 3·0; and 'heavy pollution' in areas where the diversity index is less than 1·0.

Kothé's species deficit. Kothé[11] devoted his attention to the decrease in the number of species under the influence of putrescible wastes and calculated the difference between the number of species (A_1) occurring above the uppermost waste discharge at an undisturbed sampling place (reference station), and the number of species occurring downstream of the discharges (A_x) expressed as a percentage of A_1; the product being the 'species deficit' or Artenfehlbetrag. Calculation is according to the formula:

$$\text{Species deficit} = \left(\frac{A_1 - A_x}{A_1}\right) \times 100 \text{ per cent.}$$

Appendix 2

NIEM Receiving Water Quality Data Form

1. Lab Reference Number _____
2. Station Number _____
3. Date Sample Taken _____
4. Time Sample Taken _____
5. Sample Depth _____ meters
6. Flow Rate _____ m^3/sec
7. Name of Analyst _____
8. Date of Report _____
9. Miscellaneous Comments _____

Measurement	Units	Value			
Flow*	m^3/sec				
Temperature*	^oC				
pH*	pH Units				
Dissolved oxygen*	mg/l				
Suspended solids	mg/l				
Dissolved solids	mg/l				
BOD_3	mg/l				
COD	mg/l				
Colour	Hazen Units				
Chloride	mg/l				

*in situ measurement

Appendix 2, continued

Measurement	Units	Value			
SAR	-				
Phosphorus, total dissolved	mg/l				
Kjeldahl Nitrogen	mg/l				
Mercury, total	mg/l				
Coliform, total per 100 ml	number				
Benthos: name of species number name of species number					

Optional Measurements	Units	Value			

.....

(Signature of Analyst)

Appendix 3

Sodium or Permeability Problem

Mode of Action and Symptoms of Effects

The major problem associated with sodium in irrigation waters is the adverse effects on soil structure and permeability caused by the accumulation of sodium ions in the soil. In addition, sodium has a direct toxic effect on many plants.

When a soil with a high ion exchange capacity has calcium as the predominant adsorbed cation, the soil tends to have a granular structure which is permeable and easily worked. These same soils, however, become dispersed and lose their permeability when the amount of sodium absorped exceeds 10 to 15 percent of the total cation complex. Dispersed soil becomes puddled when wet, reducing aeration and causing low water availability, and forms a hard impermeable crust when dry. In both cases, the net result is a decreased water supply to the crop.

According to Pescod (1973), salinity and sodium hazards of irrigation waters are often interrelated: with low salinity, a higher SAR can be tolerated.

The sodium absorption ratio (SAR) value has been used to estimate the quantity of sodium absorbed into the soil complex:

$$SAR = \frac{[Na^{+}]}{\sqrt{([Ca^{++}] + [Mg^{++}])/2}}$$

Figure A-3.1 illustrates the classification of irrigation waters into the following groups: those containing low, medium, high or very high levels of sodium.

Toxic Ranges of Sodium

Sodium is required in limited amounts for most plant growth. However, high concentration of sodium are not only toxic to plants but deleterious to soil conditions as has been discussed earlier. Fruits like avocado, stonefruits and citrus tolerate up to 5 per cent of exchangeable sodium in the soil (ie. ESP value of 5 per cent) (Bernstein, 1962), while in sprinkler irrigation, sodium concentrations as low as 70 mg/l will cause damage (Bernstein, 1965). Crop tolerance related to the sodium absorption ratio (SAR) of the irrigation water, and to the soils ESP value are given in Table A-3.1.

The FAO (1976) has described the symptoms of sodium toxicity as follows: "The symptoms of sodium toxicity occur first on the oldest leaves since a period of time (days or weeks) is normally required before accumulation reaches toxic levels. Symptoms usually appear as a burn or

drying of tissues at the outer edges of the leaf and as severity increases, progressing inward between the veins towards the leaf centre. Bollard and Butler (1966) indicated that, like lithium, excess sodium causes disruption in cell permeability."

International Recommendations for Safety Levels

Like salinity, investigations have been made on a wide range of crop responses to sodium, and the results combined into general classes. Guidelines for the use of sodium containing irrigation waters are indicated in Figure A-3.1. The method of irrigation also has an effect on the concentrations at which toxic effects are produced by sodium ions. The values quoted below are generally for irrigation methods which do not wet the leaves. Sprinkler irrigation can cause harm even at low sodium concentrations. The FAO (1976) suggested these practices to overcome the permeability problem of soils:

- Using soil or water amendments (gypsum, sulphur, sulphuric acid, etc.) Sulphuric acid is often recommended as a measure to overcome sodium hazards (Gumaa et al., 1976; Miyamoto et. al., 1975; Eyan et al., 1973);
- Changing direction of irrigation to reduce grade or slope of the land;
- With sprinklers, matching rate of water application to soil infiltration rate;
- Blending or changing the irrigation water supply;
- Irrigating more frequently;
- Cultivating and deep tillage;
- Increasing the time allotted duration for an irrigation;
- Collecting and recirculating runoff water;
- Using organic residues.

Although, AWRC (1974) used 5 sodium classes (SAR values of less than 8.5, 8.5 to 18, 18 to 46, 46 to 102, and above 102) to indicate crop tolerance to sodium (Table A-3.1), the FAO (1976) used only 3 classes, viz SAR values less than 3, 3 to 9, and more than 9. The USA (1974) criteria also cover 3 classes, viz SAR values less than 6, 6 to 9, and more than 9.

Criteria for Tropical Countries

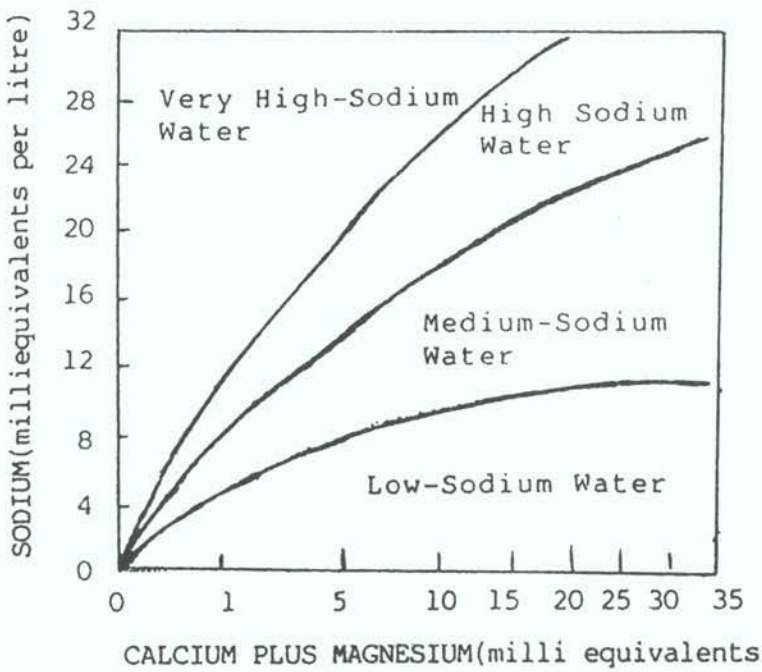
The investigation of sodium effects on crops are numerous and studies made in temperate climates in many cases apply to tropical countries. Evidence indicates that the internationally accepted guidelines that follow are suitable for NIEM countries:

SAR value	Suitability
- less than 3	sensitive crops
- 3 to 9	semi-tolerant crops
- exceeding 9	tolerant crops

Figure A-3.1

Water Quality Criteria for Sodium Containing Water*

(after AWRC'74 and ILACO'81)



Low sodium water (S1) can be used for irrigation on virtually all soils with little danger of the development of a sodium problem, i.e. high ESP levels or soil structure deterioration. Sodium sensitive crops such as stone fruits and avocado may accumulate injurious amounts of sodium in the leaves, however.

Medium sodium water (S2) may present a moderate sodium problem in fine-textured (clay) soils unless the soil contains gypsum and leaching is practised. This water can be used on coarse textured (sandy) or organic soil with good permeability.

High sodium water (S3) may produce troublesome sodium problems in most soils and will require special management, good drainage, high leaching and additions of organic matter. If there is plenty of gypsum in the soil, a serious problem may not develop for some time. Gypsum or a similar material may have to be added if it is not present in sufficient quantities.

Very high sodium water (S4) is generally unsuitable for irrigation except at low or medium salinity levels, where the use of gypsum or some other additive makes it possible to use such waters.

*Sometimes irrigation waters may absorb substantial quantities of calcium from calcereous soils, reducing the sodium hazard.

Annex 3

MANUAL ON RECEIVING LAND QUALITY EVALUATION

Table A-3.1

Tolerance of Various Crops to Exchangeable Sodium (ESP) under Non-Saline Conditions (Pearson 1960)

Tolerance to ESP and range at which crop is affected	Crop	Growth response under field conditions
Extremely sensitive (ESP = 2-10)	Deciduous fruits Nuts Citrus (Citrus spp.) Avocado (Persea americana Mill.)	Sodium toxicity symptoms even at low ESP values
Sensitive (ESP = 10-20)	Beans (Phaseolus vulgaris L.)	Stunted growth at these ESP value even though the physical condition of the soils may be good
Moderately tolerant (ESP = 20-40)	Clover (Trifolium spp.) Oats (Avena sativa L.) Tall fescue (festuca arundinacea Schreb.) Rice (Oryza sativa L.) Dallisgrass (Paspalum dilatum Poir.)	Stunted growth due to both nutritional factors and adverse soil conditions
Tolerant (ESP = 40-60)	Wheat (Triticum aestivum L.) Cotton (Gossypium birsutum L.) Alfalfa (Medicago sativa L.) Barley (Hordeum vulgare L.) Tomatoes (Lycopersicon esc. Mill.) Beets (Beta vulgaris L.)	Stunted growth usually due to adverse physical conditions of soil
Most tolerant (ESP = more than 60)	Crested and Fairway wheatgrass (Agropyron spp.) Tall wheatgrass (Agropyron elongatum (Host) Beau.) Rhodes grass (Chloris gayana Kunth)	Stunted growth usually due to adverse physical conditions of soil

PREFACE

This manual was prepared as part of the Phase I activities of the Network for Industrial Environmental Management (NIEM). Network members, drawn from industry, government and academia, conducted a series of coordinated research projects to evaluate the quality of receiving media which receive wastewater from pulp and paper mills. The manual presents, in detail, methods for sampling and analyzing agricultural soils irrigated with industrial effluents, particularly those from pulp and paper mills, and discusses how the results of this analysis should be interpreted. This manual is a companion to other manuals on the topics of Discharge Characterization and Receiving Water Quality Evaluation, also prepared as part of the NIEM programme.

The United Nations Environment Programme gratefully acknowledges the financial contribution by the Swedish International Development Authority that made functioning of the Network possible. Special thanks are extended to Dr. P.V.R. Subrahmanyam, Prof. P. Khanna, and Dr. A.S. Juwarkar of the National Environmental Engineering Research Institute (India), who drafted the text. Suggestions for revisions to the draft were provided by NIEM members.

Contents

Annexes

MANUAL ON RECEIVING LAND QUALITY

1. Introduction and Objectives

This manual addresses the assessment of land quality on lands irrigated with industrial wastewaters, particularly pulp and paper mill wastewaters.

Its objective is to provide concise information and guidance to environmental scientists and engineers engaged in monitoring the impacts of wastewater application on land. The focus is on assessing and evaluating positive and negative impacts on soils; in other words, of both the enhanced productivity and the deterioration of land or soil which may occur when effluents are used to irrigate crops. Such information is necessary for determining appropriate mitigation measures, when these are required.

The manual presents a step-by-step approach to conducting a soil sampling and evaluation study. Much of the specific information, particularly on the detailed analytical procedures employed, is contained in Annexes.

2. Data Collection

2.1 General Information

The first step in any study should be to assemble as much of the general, or background, information as is readily available, identify gaps, and map out a strategy for collecting the missing data. In most cases, government agencies dealing with agriculture extension, soils, water resources development, weather forecasting, road construction and so on will have already collected much of the data, and a few days visiting their offices will save much time. Obviously the amount of information needed depends on the scale and scope of the study, and the potential risk associated with using mill effluents for irrigation.

Information on the following should be assembled as the preliminary step in the study:

- cropping patterns in the area;
- general cultivation practices of local farmers;
- total area available for irrigation;
- total area currently under irrigation;
- sources of irrigation water;
- types of rocks found in the area;
- origin, depth, and types of soil in the study area;
- ground water potential and depth to the ground water table;
- local climate;
- location of wells and hand pumps around the site; and
- sources and quality of available drinking water.

It is also necessary to obtain one or more large scale maps of the study area.

2.2 Specific Information

The beneficial or harmful effects of using effluents for irrigating crops depend on complex physical, chemical, and biological interactions between the effluent, the soil/subsoil complex, the groundwater, and the crops being grown. Measuring or estimating these interactions would be difficult enough but in most cases the situation is not static. Unlike normal irrigation water, the composition of the effluent may change daily, reflecting the normal process variations that occur in any mill. To some degree, though, treatment systems tend to dampen short term fluctuations. The soil characteristics certainly do not change as rapidly, but they may vary significantly over a small area, meaning that many soil types must be checked for suitability. Cropping patterns also change as farmers make economic decisions about which crops to plant in a given year. Groundwater characteristics, on the other hand, appear more or less stable when compared to the others, but even these can change over time.

This manual is primarily concerned with soil investigations. Sampling methods, sample preservation, sampling frequency, and suggested analytical procedures for mill effluents are presented in detail in the NIEM publication entitled "Manual on Discharge Characterization". A brief summary of the recommended analytical procedures for effluents and groundwaters is provided in Table 1.

The environmental impacts of wastewater irrigation can be quantified only after ascertaining the horizontal and vertical conductivity of the soil. Infiltration of the applied wastewater may be slow or rapid depending upon the topography of the land and hydraulic properties of the soil. It is important, therefore, to estimate both the actual diffusion of wastewater in in situ and the theoretical diffusion under simulated conditions as part of the investigation. The method for determining soil infiltration rates and permeability are found in Annexes 4.1 and 4.2 respectively. The following sections outline in detail how a soil sampling investigation should be planned and conducted.

3. **Planning the Sampling Programme**

3.1 Selection of Sampling Points

For locating sampling points, the investigation team should conduct a preliminary reconnaissance survey covering the entire relevant area. A field sampling diagram should then be prepared based on such information as existing drainage patterns, land elevations, soil texture, soil colour, fertility status (as per crop appearance), location of farm houses and roads, and management practices.

Areas not irrigated with the wastewater should be selected for controls so the impacts of irrigating with wastewater can be determined.

Table 1 - Recommended Analytical Methods for Wastewater and Ground Water

	Measurements	Volume	Type of Sample	Frequency per annum	Methodology	Reference
1.	Colour	50 to 100 ml	Wastewater and ground water	24	Visual Comparison using platinum cobalt standards/ colorimetric method	Standard Methods for the Examination of Water and Wastewater, 16th edn. 1985, APHA, AWWA, WPCF, Washington, D.C. 20005
2.	Suspended solids (SS), mg/l	250 to 1000 ml	Wastewater and ground water	24	Filtration method	-do-
3.	pH	50 to 100 ml	Wastewater and ground water	24	pH measurement	-do-
4.	Electrical conductivity (EC), mmhos/cm at 25°C	50 to 100 ml	Wastewater and ground water	24	Conductivity measurement	-do-
5.	Calcium (Ca), meq/l	50 to 100 ml	Wastewater and ground water	24	EDTA titration/ AAS	-do-
6.	Magnesium (Mg), meq/l	50 to 100 ml	Wastewater and ground water	24	EDTA titration/ AAS	-do-
7.	Sodium (Na) and Potassium (K), meq/l	50 to 100 ml	Wastewater and ground water	24	Flame Photometer method	-do-
8.	Carbonates (CO_3) and bicarbonates (HCO_3), meq/l	50 to 100 ml	Wastewater and ground water	24	Titration method/ potentiometric method	-do-
9.	Chloride (Cl), meq/l	50 to 100 ml	Wastewater and ground water	24	Titration method	-do-
10.	Sulphate (SO_4), meq/l	50 to 100 ml	Wastewater and ground water	24	Photometric/ Gravimetric method	-do-
11.	Nitrate-N (NO_3-N), mg/l	50 to 100 ml	Ground water	24	Colorimetric/ specific ion electrode method	-do-
12.	Boron (B), mg/l	50 to 100 ml	Wastewater and ground water	24	Colorimetric method	-do-
13.	Adjusted sodium adsorption ratio (SAR_{ad})	-	Wastewater and ground water	24	$SAR_{ad} = SAR + (1 + 8.4 - pH_c)$ $SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}}$ $pH_c = p(K_2 - K_c) + p(Ca + Mg) + p(CO_3 + HCO_3)$	Water Quality for Agriculture by Ayers, R.S. and Westcot, D.W., Irrigation Drainage Paper No. 29, 1976, FAO, Rome
14.	Biochemical oxygen demand (BOD), mg/l	1000 ml	Wastewater	24	Dilution, seeding and incubation at 20°C for 5 days	Standard Methods for the Examination of Water and Wastewater, 16th edn. 1985, APHA, AWWA, WPCF, Washington, D.C. 20005
15.	Chemical oxygen demand (COD), mg/l	100 to 200 ml	Wastewater and ground water	24	Dichromate reflex method	-do-
16.	Total organic carbon (TOC)	10 to 20 ml	Wastewater and ground water	24	Combustion, Infrared method	-do-
17.	Lignin, mg/l	50 to 100 ml	Wastewater and ground water	24	Colorimetric method	-do-

Soil obtained near farm houses or buildings, gates, field margins, and highways, and soil from rows applied with manures should not be collected for either controls or samples.

In the case of existing experimental fields, each experimental plot should be considered as an independent sampling unit.

3.2 Sampling Frequency

In an experimental field, soil sampling is carried out before sowing and after harvest of each crop, whether a one, two or three crop cycle is practiced. This frequency is necessary in order to assess nutrient removal by each crop.

In normal fields, soils should be sampled twice per year, prior to and after the monsoon rainy period. This two stage sampling will reveal the effect that rains have on the leaching of accumulated salts and the sodicity hazard of the soil.

3.3 Soil Sampling Apparatus

The apparatus required for soil sampling consists of a spade and a soil auger. Bags made of paper, cloth or polyethylene, and labels for recording information are also required.

A closed cylinder type auger is used in dry soil sampling and a post hole auger for sampling in moist soils (Fig. 1). In addition, a soil sampling tube and spade are used to collect plough layer samples (Fig. 2).

4. **Execution of Sampling**

4.1 General Consideration

After the sampling sites and sampling units are selected, the next step is to devise sampling procedures which will ensure that the collected samples represent the actual soil conditions. It must be emphasized that collection and handling of samples are the most important steps in sample analysis. Materials like weeds, stubble and other unwanted substances must be removed from the sampling point prior to taking the sample. Appropriate collection and mixing of the composite sample - and its proper preservation, labelling and storage - are very important. The person doing the sampling must be properly trained in correct sampling procedures.

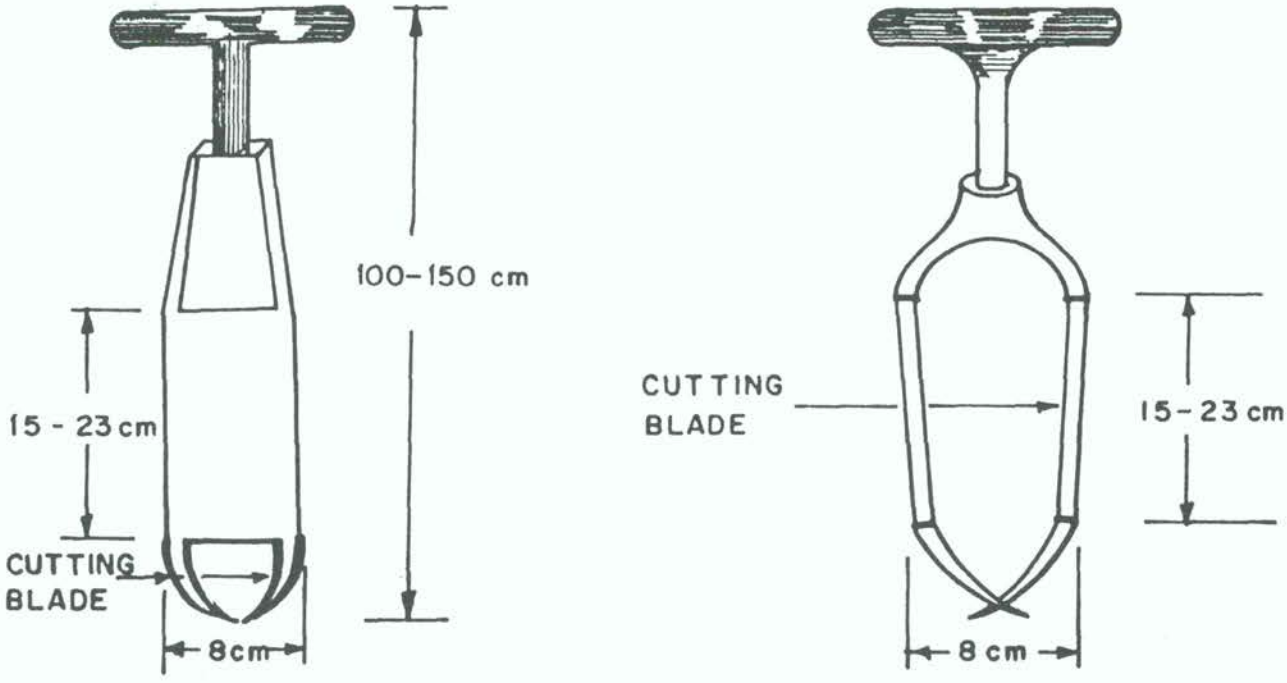


FIG. 1 : AUGERS USED FOR SOIL SAMPLING

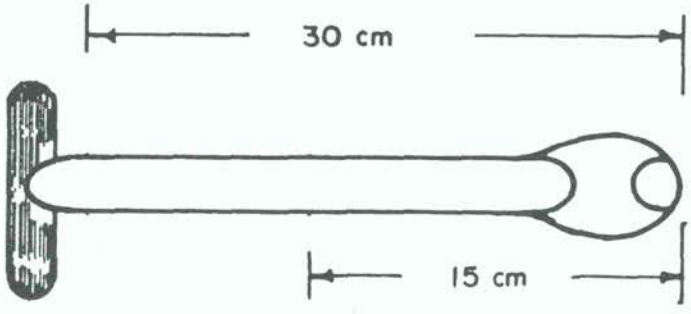


FIG. 2 : SOIL SAMPLING TUBE

4.2 Removal of Samples

In the field or experimental plots to be sampled, soil having the same type, phase and subtype should be considered as one sampling unit. The person collecting the samples should travel across each unit in a zigzag fashion and collect core samples up to the plough layer depth (15-20 cm) every 2-20 steps or so, depending on the size of the unit (Fig. 3). Samples from the border area (about 50 cm) should be avoided. About 10-30 core samples should be collected to make one composite sample from each unit. In moist, friable soil, the roughly 20 individual samples needed for one composite sample can be collected easily within 10-15 minutes using a soil sampling tube.

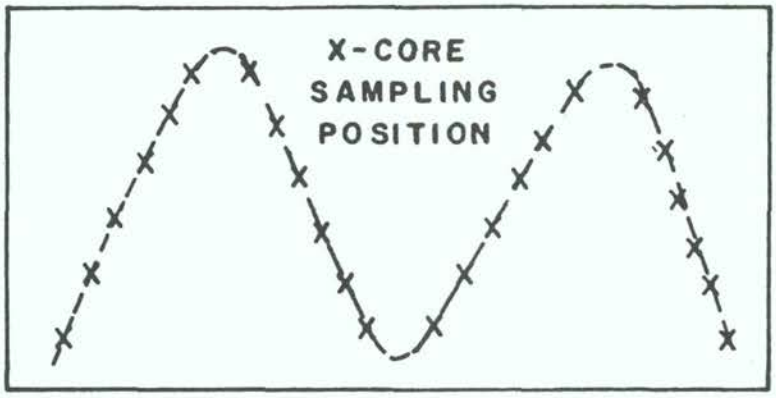


FIG.3: A ZIG-ZAG PATTERN FOR LOCATION OF SAMPLING POINTS

If a soil auger is not available, a spade can be used to collect a soil slice at each sampling point (Fig. 4). A thin slice of soil should be taken at the same 10-30 sampling points in order to obtain one composite sample. About 500-1000 grams of sample is adequate for routine analysis.

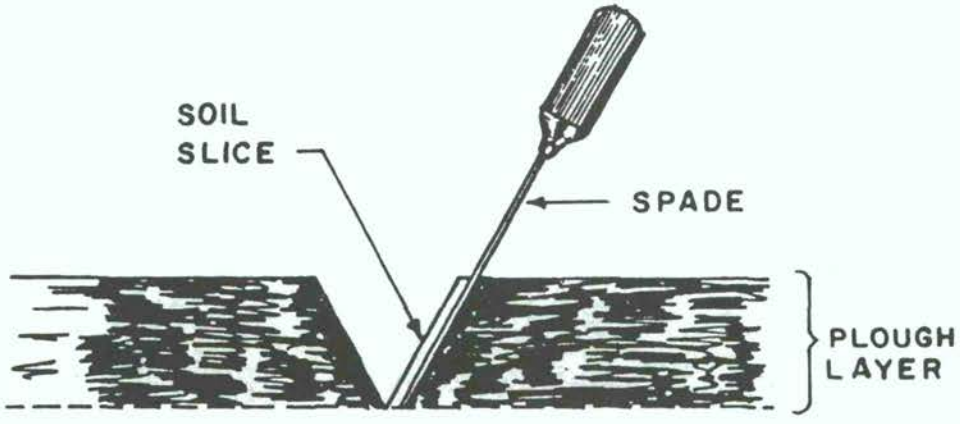


FIG. 4: SOIL SAMPLING USING SPADE

A profile sample should be collected at at least one convenient location within the sampling unit so that the physical-chemical properties of the subsoil can be determined. In order to do this, a profile pit approximately 1 m x 2 m x 1.5 m should be excavated at a convenient location, with the pit oriented in such a way that the profile is uniformly lighted. While sampling, the sample should be collected from the side opposite to the sun (Jackson 1973). In most cases, profile sampling up to 120 cm depth is sufficient. The samples should be collected over the depths 0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm and 90-120 cm, but if natural identifiable soil profiles exist, the sample should be collected at those depths corresponding to the profiles.

A soil auger can also be used to collect the subsoil samples. The collected sample should be kept in the shade to avoid fast drying and associated moisture loss.

4.3 Mixing and Preparation of Composite Samples

Samples collected from the different sampling points within the each separate sampling unit should be mixed by rolling or turning as follows: Opposite corners of the cloth or gunny bag on which the sample is collected are held firmly. One corner is then pulled diagonally across the sample slowly so that soil rolls over the cloth towards the opposite corner. Then the opposite corner of the cloth is pulled back over the soil to roll it back. The process is repeated using the other corners of the cloth, and the entire procedure repeated 5-10 times to ensure a thorough mixture.

The mixed sample is then coned in the centre of the cloth, flattened, and divided into two equal parts with a flat metal sheet or spatula. Each half portion is again divided into half, making a total of four quarters in separate piles. Two diagonally opposite quarters are then discarded quantitatively and the remaining two mixed and preserved as the resulting composite sample.

4.4 Labeling of Samples

To avoid mixing of samples and for accurate record keeping, a label having the following information should be attached to each sample bag:

1. name or number of site/field;
2. depth of sample;
3. date and time of collection;
4. collector's name.

Either on the bag label or in the recording notebook, the following should be noted:

5. name of cultivator or land owner;
6. cropping pattern adopted;
7. times when manure and fertilizer were applied;
8. period during which the land has been irrigated with wastewater;
9. special or advanced management practices adopted, if any.

4.5 Handling and Storage of Samples

Because the ionic species of some elements change when the soil is dried, many analytical tests must be carried out on moist field samples. Examples are tests for exchangeable ferrous iron, and inorganic forms of nitrogen (ammonia, nitrate and nitrite). Soil samples should thus immediately be transported to the laboratory for analysis.

If immediate analysis is impossible, moist soil samples can be preserved in a laboratory freezer for a few days (Gasser, 1958). Before

analysis, moist samples should first be passed through a 6 mm sieve by rubbing the sample with the fingers. Soil samples which will be stored for a protracted period should be air dried.

Air dried soil samples can be ground or pulverized using either a motorized grinder or a mortar and pestle. The ground soil sample should be passed through a 2 mm sieve and stored in a screw-cap covered jar with an appropriate label attached.

5. Methods of Analysis

There are a large number of analytical methods available for determining the various physical-chemical properties of soils. Selection and adoption of the most appropriate methods depends upon the type of soil to be analyzed.

Brief descriptions of the more common analytical methods for some important physical-chemical tests relevant to soil investigations are given in Table 2, while Annex 4 contains descriptions of the analytical methods and procedures recommended for soil studies.

It is also necessary to analyze the crops being irrigated. Annex 1, "Crop Sampling Procedures" and Annex 4.24, "Recommended Analytical Methods for Grains and Consumable Plant Parts" should be consulted if the researcher is unfamiliar with these procedures.

Portable test equipment is commercially available for in situ analysis of many constituents. Such equipment minimizes the costs and errors associated with sample storage, transport, and handling. Portable test kits and equipment may be used in the NIEM studies provided that the accuracy and precision of the results obtained is comparable to the laboratory methods. It is important that all field instruments be checked and recalibrated in the laboratory at frequent intervals. Records should be kept for reference.

As in all investigations of this type, experimental and evaluated results should be presented in a manner that is easy to understand and consistent with good scientific reporting.

In case there are any constraints in measuring all the parameters described in the Tables 1 and 2, and Annex 4, at least some significant parameters should be measured for the evaluation. The most significant parameters for measurement to evaluate soil condition and wastewater, percolate and groundwater quality are given in Table 3.

6. Interpretation of Results and Remedial Action

With the information collected prior to the study and the results of the soil sampling programme in hand, it should be possible to determine the relative significance of those factors affecting the soil or land productivity which are associated with the land application of wastewater. Both Table 4 below, which interprets results of the individual pH, cation exchange capacity, exchangeable sodium percentage,

Table 2 - Recommended Analytical Methods for Soils

	Measurements	Sample Volume/ Weight	Type of Sample	Frequency per annum	Methodology	Reference
I.	**Physical**					
1.	Particle size analysis	20 g	Air dried and sieved	Once	International pipette method	Methods of Soil Analysis C.A. Black, 1965, American Society of Agonomy Inc., Publisher Madison, Wisconsin, USA
2.	Bulk density	-	Undisturbed soil core	Twice	Core or clod method	-do-
3.	Aggregate size distri-bution	50 g	Air dried field sample	Twice	Wet sieving yoder method	Diagnosis and Improvement of Saline and Alkali Soil, 1954, USDA Handbook No. 60
4.	Infiltration rate (Rate of water intake)	-	Undisturbed soil core/ in situ	Twice	Double cylinder infiltro-meter method	Methods of Soil Analysis C.A. Black, 1965, American Society of Agronomy, Inc., Publisher Madison, Wisconsin, USA
5.	Permeability	-	Undisturbed soil core	Twice	Constant head method	-do-
II.	**Chemical**					
1.	pH of saturated soil paste	250 to 1000 g	Air dried and sieved	Twice	pH measurement	Diagnosis and Improvement of Saline and Alkali Soil, 1954, USDA Handbook No. 60
2.	Electrical conductivity of saturation extract (ECe), mmhos/cm at 25°C	250 to 1000 g	Saturation extract	Twice	Conductivity measurement	-do-
3.	Calcium (Ca), meq/l	20 ml	Saturation extract	Twice	EDTA Titration method	-do-
4.	Magnesium (Mg), meq/l	20 ml	Saturation extract	Twice	EDTA Titration method	-do-
5.	Sodium (Na), meq/l	20 ml	Saturation extract	Twice	Flame photo-meter method	-do-
6.	Carbonate (CO_3) and bicarbonate (HCO_3), meq/l	20 ml	Saturation extract	Twice	Titration method/ Potentiometric method	-do-
7.	Chloride (Cl), meq/l	20 ml	Saturation extract	Twice	Titration method	-do-

Table 2 - continued)

	Measurements	Sample Volume/ Weight	Type of Sample	Frequency per annum	Methodology	Reference
8.	Cation exchange capacity (CEC), meq/100 g	5 to 10 g	Air dried and sieved	Twice	(a) Ammonium acetate method (b) Sodium acetate method (c) $BaCl_2$-triethanolamine method	Soil Chemical Analysis, M.L. Jackson, 1973, Prentice Hall of India Pvt. Ltd., New Delhi
9.	Exchangeable Na and K, meq/100 g	25 to 50 g	Air dried and sieved	Twice	Leaching soil with ammonium acetate and Flame photometric measurement	-do-
10.	Exchangeable Ca and Mg, meq/100 g	25 to 50 g	Air dried and sieved	Twice	(a) Non-calcareous soil) Leaching soil with ammonium acetate and titration wiht EDTA (b) Calcareous soil Leaching soil with $BaCl_2$ triethanolamine and titration with permanganate and EDTA	Soil Chemical Analysis, M.L. Jackson, 1973, Pretice Hall of India Pvt. Ltd., New Delhi
11.	Exchangeable Soduim Percent (ESP)	-	-	Twice	$\frac{\text{Exch. Na}}{\text{CEC}} \times 100$	---
12.	Available Nitrogen (N), ppm	20 g	Field moist	Twice	(a) Soil extraction with KCl and estimation of NH_4-N and NO_3-N by distillation (b) Specific ion electrode method	Soil and Plant Testing as a Basis of Fertilizer Recommendations, 1980, FAO Soils Bulletin, 38/2, Rome
13.	Available phosphate, (P_2O_5), ppm	5 to 10 g	Air dried and sieved	Twice	Olson's method	-do-
14.	Available potassium, (K_2O), ppm	5 to 10 g	Field moist	Twice	Ammonium acetate extraction and Flame photometric determination	Soil Chemical Analysis, M.L. Jackson, 1973, Pretice Hall of India Pvt. Ltd., New Delhi
15.	Organic carbon (C), percent	0.5 to 2 g	Air dried 0.2 mm sieved	Twice	Wet digestion, Walkey and Black method	Soil and Plant Testing as a Basis of Fertilizer Recommendations, 1980, FAO Soils Bulletin, 38/2, Rome

and electrical conductivity tests, and Table 5, which draws some interpretations between the tests, can be used in evaluating the results of the investigation. At this point, additional information can be collected in order to plan, monitor, or control the wastewater-land treatment system, or delineate specific farm management practices required to minimize hazards and maximize productivity.

Sometimes a receiving land quality investigation will reveal that the quality of the treated wastewater coming from a particular mill, soil characteristics, and other factors are such that negative effects will occur. Two choices are then possible. First, a less sensitive crop can be grown in the irrigated area. For instance, a switch from beans, which are moderately sensitive to exchangeable sodium, to the more tolerant tomatoes may solve the problem (see Annex 2 for a list of ESP tolerance of crops). Obviously market factors must be taken into consideration in making such decisions.

The second option would be treatment of the soil by applying calcium salts in the form of gypsum or crushed dolomite. Annex 3 discusses the chemical reactions involved and presents a method for calculating the required additions.

Table 3 - Most Significant Parameters for Evaluation of Land Quality

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I. Significant parameters for measurement of regular basis include:

A) Physical Parameters

- Texture
- Infiltration rate
- Permeability

B) Chemical Parameters

- Soil saturation extract, pH and electrical conductivity (EC)
- Cation exchange capacity (CEC)
- Exchangeable sodium per cent (ESP)
- Available N, P_2O_5 and K_2O

II. Other supportive studies for evaluation include:

- Soil and wastewater suitability evaluation
- Percolate and groundwater quality monitoring
- Reclamation of sodic/alkaline soils (Annex 3)

III. Significant parameters for wastewater, percolate and groundwater:

- Colour
- pH
- Electrical conductivity
- SAR
- COD

Table 4 - Interpretation of Soil Chemical Tests

Test Results		Interpretation
1. pH of saturated paste:		
less than	4.2	- too acidic for most crops to do well
	4.2-5.5	- suitable for acid tolerant crops
	5.5-8.4	- suitable for most crops
greater than	8.4	- too alkaline for most crops; indicates a possible sodium hazard
2. Cation Exchange Capacity (CEC), meq/100 g:		
less than	10	- sandy soils (limited adsorbtion)
	12-20	- silt loam (moderate adsorbtion)
greater than	20	- clay and organic soils (high adsorbtion)
3. Exchangeable Sodium per cent (ESP):		
less than	4	- very good
	4-10	- satisfactory
	10-20	- reduced permeability in fine textured soils
greater than	20	- reduced permeability in coarse textured soils
4. Electrical Conductivity of Saturation Extract (ECe), mmhos/cm at 25°C:		
less than	2	- no salinity problem
	2-4	- restricted growth of very salt sensitive crops
	4-8	- restricted growth of many crops
	8-16	- restricted growth of all but salt tolerant crops
greater than	16	- only a few salt tolerant crops experience satisfactory growth

Table 5 - Soil Classification Based on ECe, ESP, and pH

	Soil Tests			Soil Class and Associated Problems
	pH	ECe	ESP	
1.	8.5	4.0	15	saline soil; salt concentration interferes with the growth of most crops; exchangeable sodium does not alter physical soil characteristics; soil generally flocculated
2.	8.5	4.0	15	sodic soil (non-saline alkalie soil); high exchangeable sodium interferes with growth of most crops; drainage and aeration are poor; soils are mostly dark brown in colour and deflocculated
3.	8.5	4.0	15	saline sodic soil; high concentration of soluble salts and exchangeable sodium interferes with crop growth

Annex 1

Crop Sampling Procedure

Identify an area showing minimum variation under each crop in the field for sampling. Place a ring of 1 metere diameter in the field and harvest the crop that comes within the ring. Take at least 10 to 15 such samples from wastewater irrigated as well as canal/well water irrigated field (control) to compare the effect of wastewater on crop yield. Calculate the standard deviation using formula:

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

where σ = Standard deviation

x = Observed yield

$\bar{x}$ = Average yield

n = Number of samples

Annex 2

Tolerance of Various Crops to Exchangeable Sodium (ESP) under Non-saline Conditions (Pearson 1960)

Tolerance to ESP and range at which affected	Crops	Growth response under field conditions
1. Extremely sensitive (ESP = 2-10)	Deciduous fruits Nuts Citrus (*Citrum* spp.) Avocado (*Persea americana* Mill.)	Sodium toxicity symptoms even at low ESP values
2. Sensitive (ESP = 10-20)	Beans (*Phaseolus vulgaris* L.)	Stunted growth at these ESP values even though the physical condition of the soil is good
3. Moderately tolerant (ESP = 20-40)	Clover (*Trifolium* spp.) Oats (*Avena sativa* L.) Tall fescue (*Festuca arundinacea* Shreb.) Rice (*Oryza sativa* L.) Dallis grass (*Paspalum dilatum* Poir.)	Stunted growth due to both nutritional fators and adverse soil conditions
4. Tolerant (ESP = 40-60	Wheat (*Triticum aestivum* L.) Cotton (*Gossypium hirsutum* L.) Alfalfa (*Medicago sativa* L.) Barley (*Hordeum vulgare* L.) Tomatoes (*Lycopersicon esc.* Mill.) Beets (*Beta vulgaris* L.)	Stunted growth usually due to adverse physical conditions of soil
5. Most tolerant (ESP = more than 60)	Crested and Fairway wheat grass (*Agropyron* spp.) Tall wheatgrass (*Agropyron elongatum* Host Beau.) Rhodes grass (*Chloria gayana* Kunth)	Stunted growth usually due to adverse physical conditions of soil

Note: Estimates of the equilibrium ESP can be made from the irrigation water or more preferably from the SAR of the soil saturation extract using the nomogram in Appendix-B. This estimation method is not applicable where soil gypsum is present. Effectiveness of any planned corrective action should be field tested before being applied on a large scale. Soils at ESP = 20 to 40 and above will usually have too poor physical structure for good crop production. The research results given above were obtained with soils whose structure was stabilized with Krilium.

Annex 3

Reclamation of Sodic or Alkaline Soils

Alkaline soils can be reclaimed by the application of calcium salts such as gypsum ($CaSO_4.2H_2O$) and dolomite ($CaCO_3.MgCO_3$). By the use of the above salts the exchangeable sodium per cent (ESP) can be brought down to desired level by the following reaction:

$$\underset{\text{Sodium clay}}{2Nax} + CaSO_4 \text{ -------- } \underset{\text{Calcium clay}}{Cax_2} + Na_2SO_4$$

Sulphur is also recommended whereby it is converted to sulphuric acid by soil bacteria and the exchangeable sodium is replaced by the following reactions:

$$2S + 3O_2 + 2H_2O \text{ -------- } 2H_2SO_4$$

$$H_2SO_4 + CaCO_3 \text{ ---------- } CaSO_4 + CO_2 + H_2O$$

$$CaSO_4 + 2Nax \text{ ---------- } Cax_2 + Na_2SO_4$$

The requirements for calcuim sulphate can be worked out as follows:

To replace 1 meq of sodium from 100 g of soil, 86 meq of gypsum ($CaSO_4.2H_2O$) will be required. Therefore, to place 1 meq of exchangeable sodium from 1 acre-foot of soil (1.82×10^6 kg or 4×10^6 lb), the gypsum requirement will be:

$$\frac{86 \times 1.82 \times 10^6 \times 10^3}{100 \times 10^3 \times 10^3 \times 10^3} \text{ tonnes} = 1.565 \text{ tonnes } CaSO_4.2H_2O \text{ per acre}$$

or

3.867 tonnes per hectare.

Normally 25 percent more than theoretical requirement of the calcium salt is added to achieve the desired reclamation.

Annex 4.1

Determination of Infiltration Rate of Soil

(Double cylinder infiltrometer method)

Principle

Infiltration rate of soil is determined by measuring a constant water level drop using double cylinder infiltrometer.

Apparatus

- Metal cylinders - 25 cm high, Inner cylinder dia. 30-35 cm, Outer cylinder dia. 40-45 cm
- Driving plate, 50 cm dia. and 10 mm thick
- Driving hammer
- Buckets
- Stop watch
- Measuing scale or hook gauge

Procedure

Select ideal site in the field where infiltration rate study is to be carried out. Place the metal inner cylinder (30-35 cm dia), referred to as measuring cylinder, on the soil, cover the cylinder with driving plate and drive the cylinder into the soil to a depth of 10 cm by hammering uniformly on the driving plate. Care should be taken to fix the cylinder vertically. If not, replace the cylinder in other place.

Then fix buffer or outer cylinder (dia. 40-45 cm) around the measuring cylinder in the same way. In the absence of buffer cylinder 8 to 15 cm dike can be prepared keeping a distance of 20 cm away from measuring cylinder.

Place heavy cloth or loosely fitted 5 mm thick board in the measuring cylinder. Then fill water into buffer cylinder or dike to a depth of 10 cm and maintain approximately same water level throughout the study.

Then immediately fill the measuring cylinder to a depth of 10 cm and remove the board/heavy cloth from the measuring cylinder. Record water level in the measuring cylinder and mark on the cylinder. Cylinder edge can conveniently be used as reference point for subsequent measurements.

Record the water level using measuring gauge at intervals of 2, 5, 10, 20, 30, 60, 120, 240, and 360 minutes. When a 50% drop in original water level appears, refill the cylinder with water to the original water level within a short interval. Record the time before refilling and after refilling the cylinder.

Continue the water level drop measurement until a steady state is reached. Drop in water level at steady state indicates infiltration rate and is expressed as mm/hour.

Annex 4.2

Determination of Permeability of Soil

(Constant Head Method)

Principle

Rate of movement of water through the soil media is measured by Constant Head Method using soil permeability test apparatus.

Apparatus

- Soil core sampler
- Funnel
- Beaker
- Wire mesh / muslin cloth
- Constant head device
- Thermometer

Procedure

Remove the undisturbed soil core with the help of core sampler. Cover the lower end of soil core with muslin cloth and keep the sample in water tray to soak the soil for 16 hours or longer period, if not completely saturated.

Connect the empty cylindrical water holder on the top of the sample and secure tightly with coupling and keep the apparatus on a support, just above the conical flask fitted with funnel.

Keep a piece of filter paper on the soil surface and fill water slowly into the water cylinder to 2/3 of its capacity. Connect the apparatus quickly to constant head device and start siphon to maintain a constant head.

Allow the water level on the top of sample to stabilise and then collect the percolate in a beaker. Measure the volume of percolate (Q) that passed through the core sample in a known time 't'. Record the hydraulic head difference (ΔH) and temperature of the percolate.

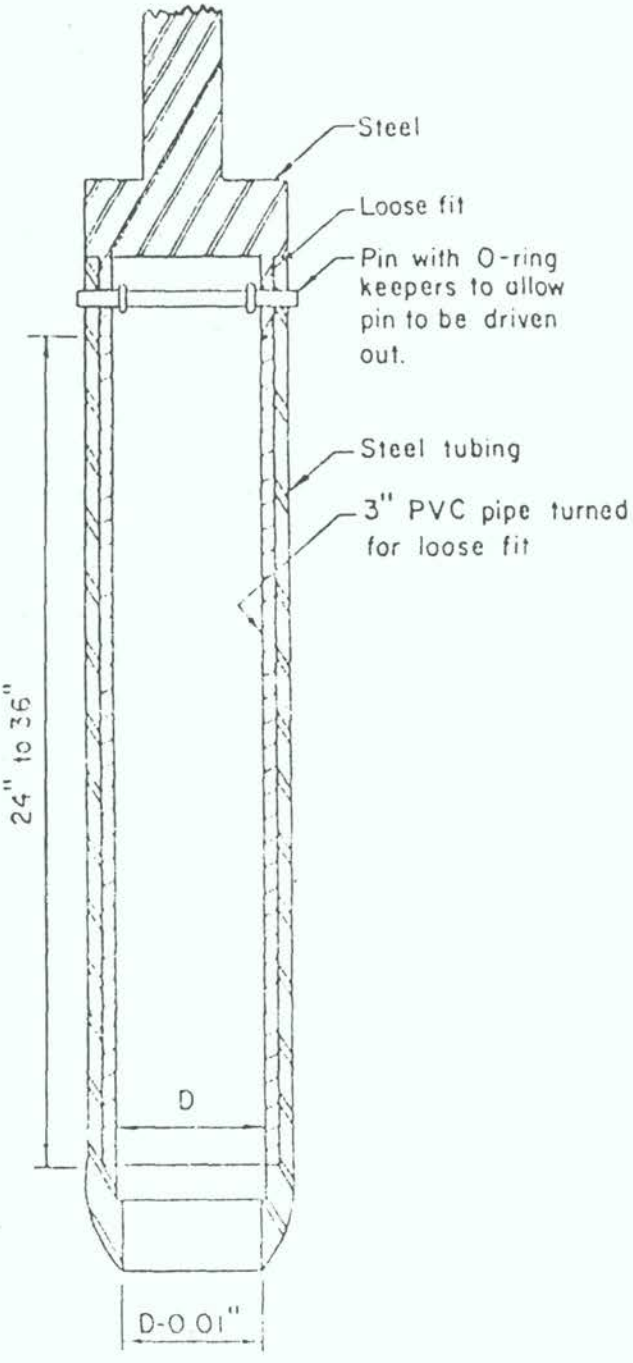
Calculations

$$\text{Hydraulic conductivity, cm/sec, } K = \frac{V}{At} \times \frac{L}{\Delta H}$$

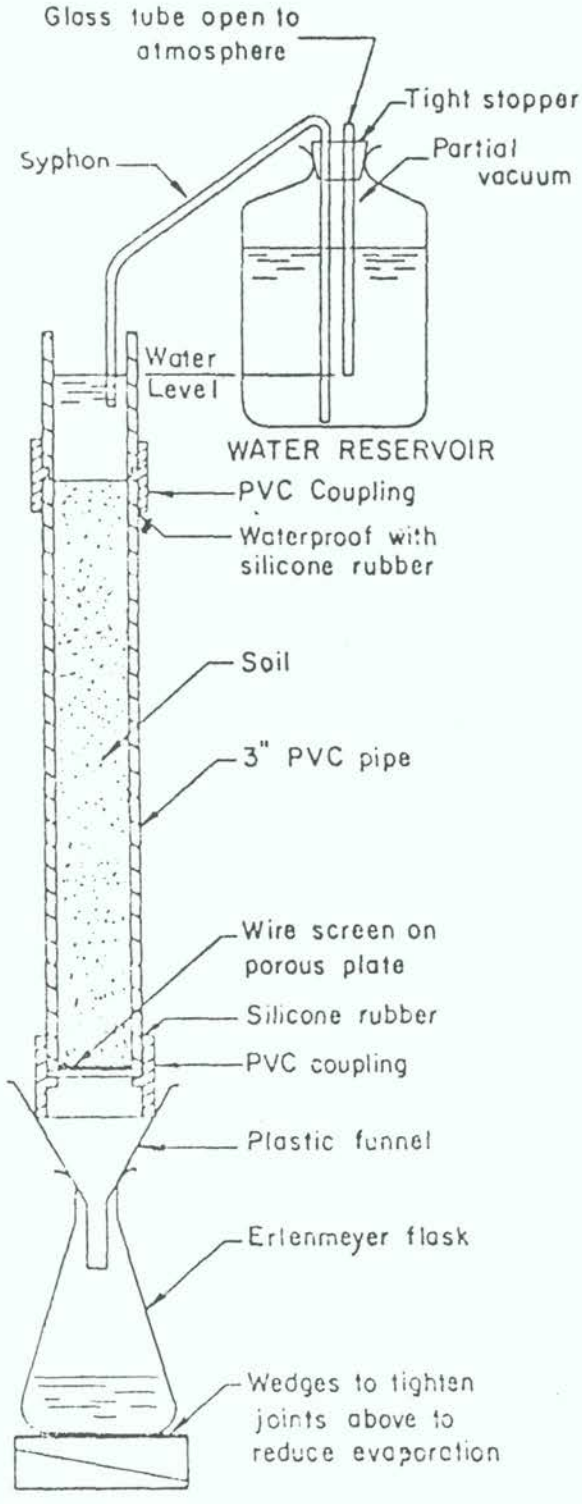
where
- V = Volume (cm^3) of percolate passed through soil at a known time 't'
- L = Length of sample (cm)
- A = Cross sectional area of sample (cm^2)
- ΔH = Hydraulic head difference (cm)

$$\text{Permeability, } cm^2, = \frac{K\,n}{P\,g}$$

where
- K = Hydraulic conductivity (cm/sec)
- n = Fluid viscosity (g/cm sec)
- P = Fluid density (g/cm^3)
- g = Acceleration due to gravity (cm/sec^2)



CORE SAMPLER



SUBMERGED PERMEABILITY TEST APPARATUS

Annex 4.3

Determination of Particle Size in Soil:

Analysis of Sand, Silt and Clay

(International Pipette Method)

Principle

Known amount of soil is dipersed in water in presence of a dispersing agent [Calgon - sodium metaphospha, ($NaPO_4$) or NaOH] and sand, silt and clay are estimated by International Pipette Method using Stoke's Law.

Apparatus

- International pipette
- Brass plunger
- Shaker, horizontal reciprocating type, 2 1/2 inch stroke per minute or Mixer, 1400 rpm: Standard Sieve No. 70
- Beaker, watch glass and policeman
- Porcelain dish or petridish
- Spoutless cylinder, 1000 ml

Reagents

- Calgon solution:
  Dissolve 50 g Calgon ($NaPO_4$) in 1000 ml of distilled water
- Hydrogen peroxide, 30%
- 2N HCl

Procedure

H_2O_2 Treatment: Transfer 20 g air-dried, 2 mm sieved soil to 500 ml beaker, add 50 ml water and 20 ml of 30% H_2O_2 and allow the reaction to proceed for 10 minutes. Stir the contents slowly by swirling to avoid frothing. When the reaction subsides, add additional 20 ml 30% H_2O_2, cover the beaker with watch glass and digest the contents on water bath at 90°C for 60 minutes. Continue the same treatment until organic matter is completely destroyed as indicated by non-effervescence with the addition of H_2O_2.

Acid Treatment: Cool the beaker and clean the sides with policeman. Add 25 ml of 2N HCl and 100 ml of distilled water. Allow the reaction to proceed for 60 minutes. Stir the content by swirling intermittently. Allow the flask to stand as such and decant the clear supernatant slowly. Wash the soil with distilled water 4-5 times and discard the washings.

Dispersion and seperation of particle: Add 10 to 15 ml of Calgon solution to make the contents alkaline (check by adding few drops phenolpthelein). Transfer the contents to 250 ml shaking bottle and make up to mark with distilled water, and shake the contents overnight on horizontal reciprocating shaker (shaking can be completed in a mixer having 1400 RRM speed, in 4-6 minutes).

Take 1000 ml spoutless measuring cylinder and keep funnel and No. 70 sieve on the mouth of cylinder. Pass all the soil and water through sieve to measuring cylinder. Then wash the contents on the sieve with jet of water till no turbid liquid appears (care should be taken that filtrate and washings should not exceed more than 1000 ml).

Transfer the coarse material retained on the sieve to pre-weighed dish and dry at 105°C and then weigh. This fraction represents coarse sand particle (2-0.2 mm dia.).

Separation of silt and clay: Make up the filtrate volume to 1000 ml with distilled water, and record the temperature. Shake the contents thoroughly using plunger for 5 minutes and allow it to stand undisturbed corresponding to the settling time required, in relation to temperature of the suspension, for silt. About 20 seconds before schedule time, lower pipette to a depth of 10 cm in the cylinder slowly and pipette out 25 ml of solution. Transfer the solution to pre-weighed dish and dry at 105°C and weigh. This represents silt plus clay fraction.

Shake the content in measuring cylinder with plunger for 5 minutes and allow to stand as such for a period given for settling clay in relation to temperature of suspension. Pipette out the sample, by lowering the pipette to a depth of 10 cm, dry the contents in oven at 105°C and weigh. This fraction gives clay particle (i.e. 0.002 mm dia).

Separation of fine sand: Decant bulk of the supernatant solution in the flask and transfer the contents to 500 ml beaker. Mark the beaker to 10 cm height and bring the level of solution to 10 cm height. Shake the contents thoroughly and allow to stand for time corresponding to the settling time rate of silt fraction. Decant the supernatant on the lapse of time and refill the beaker. Continue precedure until the liquid is no longer turbid. Then transfer the fine sand fraction to a pre-weighed dish and dry at 105°c in oven and weigh again.

Calculations

1. Coarse Sand

Weight of dish = A_1

Weight of dish + dry sand = A_2

Weight of coarse sand = $A_2 - A_1$

$$\text{Percentage coarse sand} = \frac{(A_2 - A_1) \times 100}{\text{Wt. of soil taken}}$$

2. Silt plus Clay

Weight of dish = A_3

Weight of dish + silt + clay in 25 ml suspension = A_4

Weight of silt + clay = $A_4 - A_3$

$$\text{Percentage silt plus clay} = \frac{(A_4 - A_3) \times 1000 \times 100}{\text{Vol. of suspension taken} \times \text{Wt. of soil}}$$

3. Clay

Weight of dish = A_5

Weight of dish + clay in 25 ml suspension = A_6

Weight of clay = $A_6 - A_5$

$$\text{Percentage of clay} = \frac{(A_6 - A_5) \times 1000 \times 100}{\text{Vol. of suspension taken} \times \text{Wt. of soil}}$$

4. Silt

Percentage of silt = (% silt plus clay) - (% clay)

5. Fine Sand

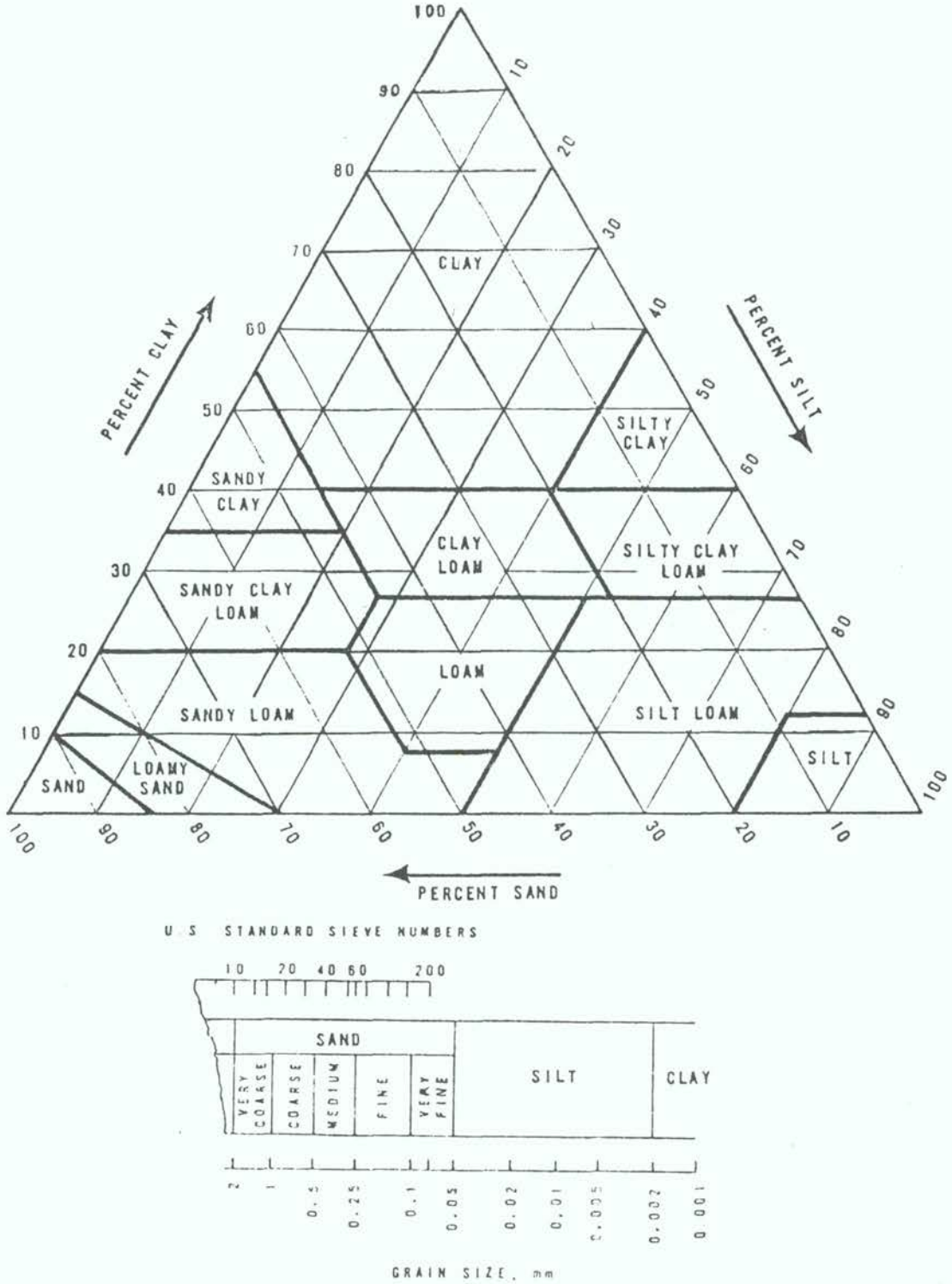
Weight of dish = A_7

Weight of dish + dry fine sand = A_8

Weight of fine sand = $A_8 - A_7$

$$\text{Percentage of fine sand} = \frac{(A_8 - A_7) \times 100}{\text{Wt. of soil taken}}$$

The soil texture is then determined with the help of the triangular diagram (see next page).



TRIANGULAR DIAGRAM FOR SOIL TEXTURAL CLASSIFICATION

Annex 4.4

Determination of Bulk Density of Soil

Principle

Bulk density of soil is estimated by measuring weight per unit volume of soil inclusive of all pore space.

(a) Clod Method

Apparatus

- Measuring cylinder
- Porcelain dish
- Twine thread
- Balance

Reagents

- Paraffin wax

Procedure

Take a clod of soil and after weighing, tie with a twine thread. Immerse the clod in melted paraffin wax contained in a porcelain dish and gently rotate the clod so that it is coated completely with a thin film of paraffin wax. Remove the clod from the dish, allow the wax to dry.

Take water in a measuring cylinder and record the water level. Then suspend the clod in the cylinder and record the rise in water level.

Calculations

$$\text{Bulk density, g/cc} = \frac{W}{B - A}$$

where W = Weight of clod (g)
A = Initial level of water in measuring cylinder (ml)
B = Final level of water in measuring cylinder when the clod is suspended in water (ml)

(b) Core Method

Apparatus

- Core Sampler
- Spatula
- Balance
- Oven
- Dish/container

Procedure

Press the core sampler in the soil by compression of slow hammering to the desired depth. Then remove the sampler along with soil and seperate the inner cylinder from sampler. Trim the excess soil attached to the cylinder and remove the soil core using spatula. Transfer the soil to a container and dry in oven at $105^{o}c$ until constant weight is reached. Measure the diameter (2.2) and height (H) of inner cylinder and calculate volume using formula $\pi r^2 H$. This represents the soil core volume.

Calculations

$$\text{Bulk density, g/cc} = \frac{W}{V}$$

where W = Weight of soil (g)
V = Volume of soil (cc)

Annex 4.5

Determination of Aggregate Size Distribution in Soil

(Wet Sieving Method)

Principle

Known amount of soil is sieved by oscillating vertically under water and amount of soil retained in each sieve is measured. Aggregration is expressed as the mean weight diameter of aggregates (MWD).

Apparatus

- Yoder type wet sieving apparatus
- Sieve holder and 2, 1, 0.5, 0.25, and 0.10 mm sieves
- Sieve, 8 mm
- Oven
- Balance
- Watch glass

Procedure

Collect the sample from moist soil and dry in shade until it is sufficiently friable. Pass the soil through 8 mm sieve, air dry and mix thoroughly and preserve for analysis.

Fix all the sieves (2, 1, 0.5, 0.25, and 0.10 mm size) in sieve holder and install slowly in water container (Yoder apparatus). Adjust the sieve shaker in such a manner that the top sieve coincides with the water surface when the oscillation mechanism is at the top of its stroke. Spread 50 g soil sample on top sieve and allow the sample to wet for 10 minutes by capillary action. Oscillate the sieves at the speed of 30 cycles per minute for 30 minutes, keeping soil submerged all the time.

Remove sieves from water and allow the water to drain. Dry the bottom of all sieves using tissue paper/filter paper and place each sieve on a seperate watch glass. Keep watch glass along with sieve in oven and dry soil at $70^{o}C \pm 2^{o}C$. Transfer all the soil from each sieve to watch glass, dry at $105^{o}C$ and weigh.

In order to determine how much of the soil retained on the individual sieves represents aggregrates and how much is gravel and sand, the oven dried soil taken from the five sieves is dispersed and washed through the sieves with a stream of water. The oven dry weight of primary particle is then determined.

Calculations

The amount of soil remaining on each sieve is expressed as percentage of the total sample:

$$\frac{\text{Wt. of soil retained on each sieve} \times 100}{\text{Wt. of soil taken}}$$

Prepare a graph, plotting the accumulated percentage of soil remaining on each sieve as ordinate against the upper limit of each fraction in millimeters as the abscissa, and measure the area shown by the curve connecting these points and by the ordinate and the abscissa. If 1 mm (sieve size) represents .1 unit of the abscissa and 10 per cent a unit on the ordinate, a square unit will represent 0.1 mm mean weight diameter of the aggregates of the sample. Multiplying the number of square units of the area by 0.1 gives the mean weight diameter of the entire sample, including the material that has been washed through the smallest sieve.

The results from the wet sieving of the dispersed sample are plotted and calculated in the same way. The difference between the mean weight diameter of the original and the dispersed sample gives the aggregation index.

Annex 4.6

Preparation of Soil Saturation Extract

Principle

Soil is brought to the saturation stage with distilled water and extracted under vacuum to get the saturation extract. The extract is used for soluble salts estimation.

Apparatus

- Glass or plastic beaker (1000 ml)
- Spatula
- Buchner funnel
- Conical flask
- Vacuum pump
- Volumetric flask
- Pipette

Reagents

- Sodium hexametaphosphate 0.1% solution:
  Dissolve 0.1 g soduium hexametaphosphate in 100 ml of distilled water.

Procedure

Preparation of soil paste: Take approximately 250 to 600 g of air-dried, sieved soil in beaker and moisten slowly by adding distilled water. Stir contents with spatula adding more water, if required, till it reaches saturation stage. At saturation, soil paste glistens as it reflects light, flows slightly when the container is tipped, and slides freely and cleanly off the spatula (except for clayey soils). Allow the container to stand as such for 60 minutes and recheck the saturation stage. There should be no free flowing water on the soil surface. If paste gets hard and looses its glisten, add more water slowly and continue stirring with spatula till saturation. Allow the paste to stand for 4 to 16 hours (generally 4 hour time is sufficient for coarse textured soil).

Extraction: Transfer the saturated soil paste to buchner funnel fitted with Whatman No. 40 filter paper. Attach the flask to vacuum pump and start extraction. If the extract is turbid, refilter the extract by transferring back to the funnel or discard the extract. Add 1 drop of 0.1% sodium hexametaphosphate per 25 ml to prevent the precipitation of calcium carbonate upon standing. Increase in sodium concentration of the soil extract by the addition of sodium hexametaphosphate will be less than 0.5 ppm.

Annex 4.7

Measurement of Soil pH

Principle

Soil is brought to saturation stage with distilled water and pH is measured with the help of pH meter.

Apparatus

- pH meter
- Beaker
- Spatula

Reagents

- Standard pH buffers, pH 4.0, 7.0, and 9.2.

Procedure

Take 100-200 g of air-dried soil in a beaker and add distilled water till it attains the saturation stage as described under "Preparation of Soil Saturation Extract", Annex 4.6.

Calibrate the pH meter using standard buffers of pH 4.0, 7.0 and 9.2. Then measure the pH of the saturated soil paste. Record the value.

Annex 4.8

Measurement of Electrical Conductivity of Soil Saturation Extract

Principle

Electrical conductivity (EC) of the soil saturation extract indicates ionized constituents of soil solution and is measured using a conductivity meter.

Apparatus

- Conductivity meter
- Beaker
- Thermometer 0-50°C

Reagents

- Standard KCl 0.01N:
  Dissolve 0.7456 g dry KCl in 1 litre of distilled water. This solution has an electrical conductivity of 1.4118 mmhos/cm at 25°C.

Procedure

Transfer 20-50 ml 0.01N KCl solution to 100 ml beaker and bring the temperature to 25°C. Immerse the conductivity cell and read the cell resistance R. Cell constant (K) = EC of standard KCl solution x R. Then take 20 ml of soil saturation extract in 100 ml beaker and record the extract temperature. Immerse conductivity cell in saturation extract and measure conductivity as given in instrument manual. Make necessary correction to get EC at 25°C.

Calculations

Electrical conductivity (EC), mmhos/cm at 25°C = EC of saturation extract, mmhos/cm at 25°C x cell constant (K) at 25°C

Annex 4.9

Determination of Calcium and Magnesium in Soil Saturation Extract

(Versenate Method)

Principle

The method is based on the fact that ethylene diamine tetraacetate (EDTA) forms stable complexes with calcium and magnesium at identical pH conditions. A known volume of extract is titrated with EDTA in presence of murexide using NaOH buffer for calcium whereas magnesium is estimated using eriochromeblack T indicator in presence of NH_4OH-NH_4Cl buffer.

Apparatus

- Porcelain casserole (100 ml) or conical flask (150 ml)
- Burette
- Pipette
- Glass rod
- Water bath
- Beaker
- Watch glass

Reagents

- Ethylene diamine tetraacetate solution 0.02N:
  Dissolve 4.0 g of disodium dihydrogen ethylene diamine tetraacetate salt in 1000 ml distilled water. Standardise the solution with 0.02 N calcium chloride solution using Eriochrome black T indicator.
- Eriochrome black T (EBT) indicator:
  Dissolve 0.5 g of EBT and 4.5 g of hydroxylamine hydrochloride salt in 100 ml of 95% ethanol. Preserve the indicator in refrigerator.
- Ammonium purpurate (murexide) indicator:
  Mix 0.5 g murexide with 100 g of powdered K_2SO_4. Grind the mixture in morter and pestle, if required.
- Ammonium chloride - ammonium hydroxide buffer solution pH 10.0:
  Dissolve 67.5 g of ammonium chloride in 575 ml of conc. NH_4OH and dilute the solution to one litre.
- Sodium hydroxide, 4N:
  Dissolve 160 g of sodium hydroxide pellets in 1000 ml of distilled water.
- Carbamate crystals (sodium diethyl dithio carbamate)
- Aqua regia:
  Mix 75 ml conc. HCl with 25 ml conc. HNO_3.
- Standard calcium chloride solution 0.02 N:
  Dissolve 1.0 g of analytical grade $CaCO_3$ in 20 ml of 3 N HCl and dilute to 1000 ml.

Procedure

Pre-treatment: To destroy colour in soil extract, take known volume of soil extract in a beaker and evaporate to nearly dryness on water bath. Then add 10 ml of aqua regia, cover the beaker with watch glass and digest the contents for 15 minutes. Remove the watch glass and evaporate the contents to dryness (repeat the aqua regia treatment if colour persists). Cool the beaker, dissolve the residue in small amount of distilled water and make up the volume equal to original soil extract taken for pre-treatment (for slightly coloured extract, pre-treatment can be omitted).

Calcium estimation: Pipette 5 to 20 ml of soil extract in porcelain dish/conical flask and dilute approximately to 25 ml. Add 1 ml of 4N NaOH a pinch of murexide indicator and a few crystals of carbamate. Titrate the contents with standard EDTA till colour changes from orange-red to purple. Keep blank without sample and follow the same procedure.

Calcium plus magnesium estimation: Take 5 to 20 ml of soil extract in porcelain dish/conical flask and add distilled water to make the total volume to about 25 ml. Then add 1 ml of ammonium chloride - ammonium hydroxide buffer, 10 drops of EBT and a few crystals of carbamate. Titrate the mixture using 0.02 N EDTA till colour changes from purple to blue. Run a blank sample and titrate as above.

Standardisation of EDTA: Pipette 20 ml of standard, 0.02 N calcium chloride solution in porcelain dish, add 1 ml of NH_4OH-NH_4Cl buffer and 10 drops of EBT. Then titrate with 0.02 N EDTA till colour changes from purple to blue.

Calculations

$$\text{Calcium, meq/litre} = \frac{(A-B) \times N \times 1000}{S}$$

where A = ml of EDTA required for sample titration
B = ml of EDTA required for blank titration
N = Normality of EDTA
S = Volume of soil extract taken

$$\text{Calcium + magnesium, meq/litre} = \frac{(A-B) \times N \times 1000}{S}$$

$$\text{Magnesium, meq/litre} = (\text{Ca + Mg meq/litre}) - (\text{Ca meq/litre})$$

Annex 4.10

Determination of Sodium and Potassium in Soil Saturation Extract

(Flame Photometer Method)

Procedure described under "Available Potassium in Soil", Annex 4.17 are to be adopted using the saturation extract. Sodium estimation is similar to potassium and sodium standards using NaCl are to be used and the instrument calibrated with sodium filter.

Annex 4.11

Estimation of Carbonate and Bicarbonate in Soil Saturation Extract

Principle

Carbonate and bicarbonate are estimated by titrating a known amount of soil extract with standard H_2SO_4 in presence of phenolpthelein and methyl orange indicators separately.

Apparatus

- Conical flask, 150 ml or 250 ml
- Pipette and burette

Reagents

- Standard N/50 H_2SO_4

- Phenolpthelein indicator 0.25%:
  Dissolve 250 mg of phenolpthelein powder in 100 ml of 50% ethanol.

- Methyl orange indicator 0.1%:
  Dissolve 100 mg of methyl orange in 100 ml of distilled water.

Procedure

Pipette 5-10 ml of soil extract in 150 ml conical flask and add 2-3 drops of phenolpthelein indicator. If pink colour develops, titrate the content in the flask with standard N/50 H_2SO_4 until colour disappears and record the reading. Continue titration after adding 2-3 drops of methyl orange indicator with N/50 H_2SO_4 until colour changes from orange-yellow to orange-red. Record the burette reading.

Calculations

$$CO_3^{2-} \text{ meq/litre} = \frac{2P \times N \times 1000}{S}$$

$$HCO_3^{-} \text{ meq/litre} = \frac{(T - 2P) \times N \times 1000}{S}$$

where N = Normality of H_2SO_4
P = ml of H_2SO_4 required to phenolphthelein end point
T = ml of H_2SO_4 required to the methyl orange end point
S = ml of soil extract taken

Relationship of titer value and presence of hydroxide, carbonate and bicarbonate alkalinity.

Results of titration	Titration value related to each ion		
	OH	CO_3	HCO_3
P = 0	0	0	T
P < 1/2 T	0	2P	T-2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P-T	2(T-P)	0
P = T	T	0	0

Annex 4.12

Estimation of Chloride in Soil Saturation Extract

Principle

Known amount of soil extract is titrated with standard $AgNO_3$ using K_2CrO_4 indicator. The reaction is as follows:

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White precipitate}}{AgCl} + NaNO_3$$

$$K_2CrO_4 + 2AgNO_3 \longrightarrow \underset{\text{Brick red precipitate}}{Ag_2CrO_4} + 2KNO_3$$

Apparatus

- Conical flask, 150 ml/250 ml
- Burette and pipette

Reagents

- Standard N/50 $AgNO_3$:
  Dissolve 3.3975 g of $AgNO_3$ in 1000 ml of distilled water and standardise against N/50 NaCl.
- Potassium chromate indicator 5%:
  Dissolve 5 g of K_2CrO_4 in 75 ml water and add $AgNO_3$ solution until a red precipitate is formed. Let it stand for 12 hrs., filter and dilute to 100 ml with distilled water.
- Calcium carbonate
- Standard N/50 H_2SO_4

Procedure

Take 5-10 ml of soil extract in 150 ml conical flask, add equal amount of standard N/50 H_2SO_4 required for CO_3^{2-} plus HCO_3^- titration and 2-3 drops of 5% K_2CrO_4 indicator. Titrate the extract with standard N/50 $AgNO_3$ until colour changes from yellow to brick-red. Run a blank without soil extract.

Calculations

$$\text{Cl meq/litre} = \frac{(R - B) \times N \times 1000}{S}$$

where R = ml of standard $AgNO_3$ required for sample
B = ml of standard $AgNO_3$ required for blank
N = Normality of $AgNO_3$
S = Volume of soil extract

Annex 4.13

Determination of Cation Exchange Capacity of Soil

Principle

Soil cation exchange capacity (CEC) is estimated by leaching the soil with either of the following solutions:

(a) 1N, 7.0 pH ammonium acetate, or

(b) 1N, 8.2 pH sodium acetate

(a) Ammonium acetate method: (suitable for non-calcareous soil)

Apparatus

- Buchner Funnel
- Suction flask
- Conical flask (250 ml)
- Distillation assembly
- Vacuum pump
- Burette and pipette

Reagents

- Ammonium acetate 1N:
  Dissolve 77.08 g ammonium acetate (NH_4OAc) in 1 litre of distilled water and adjust to pH 7.0.
- Isopropyl alcohol 99%
- KCl 10%:
  Dissolve 100 g KCl in 900 ml distilled water, adjust the pH to 2.5 with HCl and dilute to 1 litre.
- N/50 H_2SO_4
- Ammonium chloride
- Mixed indicator:
  Dissolve 500 mg bromocresol green and 100 mg methyl red in 100 ml of 95% ethanol. Adjust pH to 4.5 using NaOH/HCl.
- Boric acid 4%:
  Dissolve 40 g H_3BO_3 in 1 litre of distilled water containing 10 ml mixed indicator.
- NaOH 40%:
  Dissolve 400 g NaOH in 1 litre of distilled water.

Procedure

Take 50 g air-dried soil sample in 250 ml conical flask containing 100 ml 1N NH_4OAc and shake for 60 minutes and then allow to stand overnight. Transfer the contents to buchner funnel fitted with Whatman No. 42 filter paper and leach the soil with 400 ml of NH_4OAc, using about 80-100 ml of NH_4OAc at a time. Adjust the leaching rate in such a way that leaching will take at least 1-2 hours. Preserve the leachate for estimation of exchangeable cations.

Add a pinch of ammonium chloride salt to soil and wash the soil with isopropyl alcohol till free of chloride (about 200-250 ml of isopropyl alcohol is required). Care should be taken that at this stage soil should not dry, otherwise ammonia will be lost.

Then leach the soil with 450 ml of 10% KCl solution of pH 2.5 and collect the leachate in a flask. Transfer the extract to volumetric flask and make up to 500 ml.

Transfer 25 to 50 ml of the above extract into a distillation flask, add few drops of phenolpthalein indicator and 40% NaOH till the contents are alkaline. Distill for ammonia and collect the distillate in 4% boric acid. Titrate the absorbed ammonia with N/50 H_2SO_4.

Calculations

$$\text{CEC meq/100 g} = N \times R \times \frac{\text{final vol. of leachate}}{\text{vol. of leachate taken}} \times \frac{100}{\text{wt. of soil}}$$

where N = Normality of H_2SO_4
R = ml of H_2SO_4 required for titration

(b) Sodium acetate method: (suitable for calcareous soil)

Apparatus

- Shaker
- Centrifuge and round bottom centrifuge tubes with narrow neck
- Measuring cylinder
- Flame photometer with sodium filter

Reagents

- Sodium acetate (NaOAc) 1N:
  Dissolve 136.08 g sodium acetate in 900 ml of distilled water and adjust pH to 8.2 using NaOH/acetic acid and make up to 1 litre.
- Isopropyl alcohol 99%
- Ammonium acetate 1N

Procedure

Shake 4-6 g air-dried soil in 50 ml centrifuge tube containing 33 ml of NaOAc of pH 8.2 for 5 minutes. Centrifuge the contents and discard the supernatant. Treat the sample in the same manner with 3 additional 33 ml NaOAc solution and discard the supernatant.

Then add 33 ml of 99% isopropyl alcohol and shake the soil for 5 minutes on shaker. Centrifuge the contents and discard the supernatant. Repeat the procedure twice with 33 ml of isopropyl alcohol and discard the supernatant.

Continue the soil treatment with 33 ml of 1N NH_4OAc 3 times as above and collect the supernatant of each extraction in 100 ml of volumetric flask and make up the volume with NH_4OAc. Estimate sodium in the extract using flame photometer as described earlier and calculate the CEC.

Calculations

$$\text{Sodium, meq/100 g soil} = \text{CEC, meq/100 g soil}$$

$$\text{CEC, meq/100 g soil} = \frac{10}{100} \times R \times \frac{V}{1000} \times \frac{100}{S} \times \frac{1}{23}$$

where
- R = Galvanometer readings for Na
- S = Weight of soil sample
- V = Volume of extracting solution
- $\frac{10}{100}$ = Ten mg/L Na standard adjusted to 100 readings

Annex 4.14

Estimation of Exchangeable Cations in Soil

(Ca, Mg, Na and K)

Principle

Known amount of soil is leached with (a) 1N NH_4OAc of pH 7.0, (b) 1N NaCl of pH 7.0 and (c) 0.2N $BaCl_2$ - triethanolamine and exchangeable cations are estimated.

(a) Ammonium acetate method: (for non-calcareous soil)

Apparatus

- Buchner funnel
- Suction Flask
- Conical flask
- Beaker (250 ml)
- Watch glass and policeman
- Water bath
- Vacuum pump
- Burette and pipette
- Flame photometer with Na & K filters

Reagents

- Ammonium acetate, 1N, pH 7.0
- 6N HNO_3
- 6N NCl
- H_2O_2, 30%
- EDTA 0.02N
- Erichrome black T indicator
- Murexide indicator
- NH_4OH-NH_4Cl buffer pH 10.0
- NaOH 4N buffer pH 12.0
- Diethyl dithiocarbamate
- Sodium and potassium standard solutions of 10 ppm

Procedure

Transfer NH_4OAc extract, preserved for exchangeable cations determination during CEC estimation, to 250 ml beaker and evaporate to dryness on water bath. Wash the sides of beaker with little distilled water and again evaporate. If the residue is dark in colour (usually the case) then add 2 ml of 30% H_2O_2 and 2 ml of 6N HNO_3. Cover the beaker with watch glass and digest the residue on water bath for 30 minutes. Then remove the watch glass from beaker and evaporate the solution to dryness.

Then add 10 ml of 6N HCl and stir the contents with policeman for thorough mixing. Add 15 ml distilled water and filter the contents using Whatman No. 42 filter paper. Collect filtrate and washings in 100 volumetric flask and make up to 100 ml.

Estimate sodium and potassium in the filtrate using flame photometer and calcium and magnesium by EDTA titration method.

Calculations

$$\text{Na, meq/100 g soil} = \frac{10}{100} \times R \times \frac{\text{final vol. of leachate}}{1000} \times \frac{100}{\text{wt. of soil}} \times \frac{1}{23}$$

$$\text{K, meq/100 g soil} = \frac{10}{100} \times R \times \frac{\text{final vol. of leachate}}{1000} \times \frac{100}{\text{wt. of soil}} \times \frac{1}{39}$$

where R = Galvanometer reading for Na and K

$$\text{Ca, meq/100 g soil} = N \times R \times \frac{\text{final vol. of leachate}}{\text{Aliquot taken}} \times \frac{100}{\text{wt. of soil}}$$

$$\text{Ca + Mg meq/100 g soil} = N \times R \times \frac{\text{final vol. of leachate}}{\text{Aliquot taken}} \times \frac{100}{\text{wt. of soil}}$$

$$\text{Mg, meq/100 g soil} = (\text{Ca + Mg meq/100 g}) - (\text{Ca meq/100 g})$$

where N = Normality of EDTA
R = ml of EDTA required for titration

(b) Sodium chloride method: (suitable for Ca and Mg estimation in calcareous soil)

Apparatus

- Buchner funnel
- Suction flask
- Vacuum pump
- Conical flask
- Pipette and burette
- Shaker

Reagents

- NaCl 1N:
  Dissolve 58.45 g NaCl in 1 litre of distilled water and adjust pH 7.0.
- EDTA N/50 solution
- NH_4Cl - NH_4OH buffer pH 10
- NaOH buffer pH 12
- EBT
- Murexide

Procedure

Shake 20 g air-dried soil in 250 ml conical flask containing 100 ml of 1N NaCl of pH 7.0 for 60 minutes and keep the contents as such overnight. Then transfer the soil and extractant to buchner funnel fitted with Whatman No. 40 filter paper and leach the soil with 1N NaCl solution. Give 2 additional washing with 50 ml of 1N NaCl. Collect the leachate and estimate the Ca and Mg by EDTA titration method as described earlier.

Calculations

$$\text{Ca + Mg, meq/100 g} = N \times R \times \frac{\text{final vol. of leachate}}{\text{Aliquot taken}} \times \frac{100}{\text{wt. of soil}}$$

$$\text{Ca, meq/100 g} = N \times R \times \frac{\text{final vol. of leachate}}{\text{Aliquot taken}} \times \frac{100}{\text{wt. of soil}}$$

where N = Normality of EDTA
R = ml of EDTA required for titration

(c) $BaCl_2$ - triethanolame method: (suitable for calcareous soil)

Apparatus

- Crucible with perforated bottom
- Suction flask fitted with crucible holder
- Volumetric flask (100 ml)
- Beaker (150 ml)
- Pipette and burette

Reagents

- $BaCl_2$ - triethanolamine 0.2N:
  Dissolve 48.89 g $BaCl_2$ in 1 litre of distilled water. Take 50 ml of triethanolamine (SG 1.125) and dilute to 500 with distilled water and adjust the pH to 8.1 using 1N HCl and makeup the volume to 1 litre. Mix both the solution and protect for CO_2 of air.

- H_2SO_4 0.1N

- Methyl orange indicator

- Ammonium oxalate $[(NH_4)_2C_2O_4.H_2O]$ 4%:
  Dissolve 40 g of $(NH_4)_2C_2O_4.H_2O$ in 1 litre of distilled water.

- Sodium acetate 20%:
  Dissolve 20 g NaOAc in 1 litre of distilled water.

- Potassium permanganate 0.025N:
  Dissolve 0.790 g $KMnO_4$ in 1000 ml water.

Procedure

Take 1 to 2 g air-dried soil in perforated crucible fitted with moist filter paper and leach the soil with 50 ml of 0.2N $BaCl_2$ - triethanolamine of pH 8.1 slowly. When all the extractant is leached out, add 50 ml of distilled water and collect the percolate in the same flask. Transfer the leachate to 100 ml volumetric flask and makeup to 100 ml mark.

Pipette 25 ml of leachate in 250 ml conical flask add 25 ml of 0.1 N H_2SO_4 and 1 drop of methyl orange indicator. Mix the contents slowly and add 20% NaOAc slowly until rose-orange colour disappears. Heat the content to 70°C on water bath and slowly add 10 ml of 4% $(NH_4)_2C_2O_4H_2O$ with stirring and continue the digestion for 60 minutes. Filter the contents using Whatman No. 42 filter paper and wash with warm distilled water. Preserve the filtrate for magnesium estimation. Dissolve CaC_2O_4 from the precipitate in 50 ml of 1% H_2SO_4 and heat solution to 80° to 90°C. Titrate the contents with 0.025 N $KMnO_4$.

Calculations

$$\text{Ca, meq/100 g} = N \times R \times \frac{\text{final vol. of leachate}}{\text{Aliquot taken}} \times \frac{100}{\text{wt. of soil}}$$

where N = Normality of $KMnO_4$
R = ml of $KMnO_4$ required for titration

Filtrate from the calcium estimation is made to volume and used for Mg determination by EDTA titration method.

Annex 4.15

Available Nitrogen in Soil

Principle

Ammonium salts and nitrate constitute soil available nitrogen. Soil sample is extracted by shaking with KCl and NO_3-N and NH_4-N are estimated after reduction of nitrate to ammonia followed by its measurement by distillation or potentiometric method.

Apparatus

- Steam distillation equipment
- 250 ml conical flask
- Funnel
- Burette and pipette
- Measuring cylinder (100 ml)
- Shaker

Reagents

- 1N KCl:
  Dissolve 74.55 g KCl in 1 litre of distilled water.
- Mixed indicator:
  Dissolve 500 mg bromocresol green and 100 mg methyl red in 100 ml of 95% ethanol. Adjust pH to 4.5 using NaOH/HCl.
- Boric acid 2%:
  Dissolve 20 g H_3BO_3 in 1 litre of distilled water containing 10 ml mixed indicator.
- Devarda alloy powder
- MgO
- N/50 H_2SO_4

Procedure

Extraction: Take 20 g air-dried soil sample in 250 ml conical flask and add 40 ml 1N KCl. Shake the contents for 60 minutes using wrist shaker and filter using Whatman No. 40 filter paper.

Distillation:

(a) NH_4-N: Transfer 20 ml of extract into distillation flask, add 10 ml of distilled water, few drops of phenolpthelein and spoonful of MgO. Distil ammonia and collect the distillate into 50 ml 2% boric acid solution. Titrate the borate solution with N/50 H_2SO_4.

(b) NO_3-N: Add a spoonful of Devarda alloy to the distillation flask and continue distillation. Nitrates are reduced to ammonia. Collect the distillate into 50 ml 2% boric acid solution and determine the ammonia by titration with N/50 H_2SO_4.

Calculation

$$NH_4\text{-N, mg/100 g soil} = \frac{N \times R \times 14 \times 100}{10}$$

$$NO_3\text{-N, mg/100 g soil} = \frac{N \times R \times 14 \times 100}{10}$$

where N = normality of H_2SO_4
R = ml H_2SO_4 required for sample titration

20 cc extract is equal to 10 g soil

Potentiometric Method

Apparatus

- pH meter
- Specific ion electrode - NH_3 & NO_3
- Magnetic stirrer
- Beakers (150 ml)

Reagents

(a) Ammonia nitrogen

- 1N KCl
- 10M NaOH:
  Dissolve 400 g NaOH in 1 litre distilled water.
- NH_4-N: 1000 mg/l stock solution:
  Dissolve 3.8178 g NH_4Cl in 1 litre of 1N KCl, 1 ml = 1 mg NH_4-N.
- Prepare a standard series containing 1, 2.5, 5, 10, and 20 mg-N/l by dilution with 1N KCl.

(b) Nitrate nitrogen

- $KAl(SO_4)_2$ solution 1% in nitrate free water
- NO_3-N standard solution:
  Dissolve 721.80 mg KNO_3 in 100 ml 1% $KAl(SO_4)_2$ solution.
- Prepare a standard solution having 10, 20, 40, 60, 80 and 100 mg-N/l by dilution with 1% $KAl(SO_4)_2$ solution.

Procedure

(a) Ammonia nitrogen: Take 20 g air dry soil in 250 ml conical flask. Add 40 ml 1N KCl and shake for 60 minutes. Filter the sample in a 150 ml beaker using Whatman No. 40. Add 1 ml of 10 M NaOH to bring the pH to 11. Immerse ammonia electrode immediately in the extract and record the potential reading.

(b) Nitrate nitrogen: Shake 30 g air dry soil with 60 ml 1% $KAl(SO_4)_2$ solution in 250 ml conical flask, for 60 minutes. Filter the solution in 150 ml beaker. Immerse NO_3-N electrode into the extract and record the potential difference against $Hg/HgSO_4$ reference electrode.

Calculations

Draw calibration curve on semi-logrithimic graph paper separately for ammonia and nitrate nitrogen. The concentration of N (ammonia/ nitrate) in the sample is read directly from the curve.

$$\text{mg } N(NO_3)/N(NH_4)/\text{kg soil} = \frac{y \times v}{p}$$

where y = mg N per litre
v = volume of extracting solution
p = weight of sample taken

Annex 4.16

Available Phosphorous in Soil

Principle

Soil available phosphorous, which can be correlated with the response of crop to phosphatic fertilizer, is extracted with alkaline $NaHCO_3$ (Olsen method) or dilute solution of NH_4F and HCl (Bray and Kurtz method).

Olsen Method: Suitable for neutral and alkaline soils

Apparatus

- Spectrophotometer
- Analytical balance
- Shaker
- Conical flask (50 ml)
- Volumetric flask (50, 250, and 1000 ml)
- Funnel
- Pipette
- Measuring cylinder (100 ml)

Reagents

- 0.5 M $NaHCO_3$:
  Dissolve 42 g $NaHCO_3$ in 1 litre of distilled water and adjust pH to 8.5 with dilute NaOH.
- Phosphate free activated charcoal
- Chloromolybdic acid 1.5%:
  Dissolve 15 g ammonium molybdate $(NH_4)_6Mo_7O_{24}$ $.4H_2O$ in 300 ml hot distilled water. Cool the solution and add 350 ml 10 N HCl and dilute to 1 litre. This solution is stable for 60 days.
- Chlorostannous acid reductant:
  Dissolve 10 g $SnCl_2.2H_2O$ in 25 ml conc. HCl. Warm if necessary. This concentrated solution can be stored in refrigerator. Dilute 1 ml conc. solution to 132 ml with distilled water and use for estimation. Dilute solution is unstable and thus needs to be prepared freshly.
- 4N NH_4OH
- 4N HCl
- 2,4-dinitrophenol indicator:
  Dissolve 250 mg 2,4-dinitrophenol in 100 distilled water.
- Standard phosphate solution 50 ppm of P:
  Weigh 0.2195 g KH_2PO_4 previously dried at 40°C and dissolve in 400 distilled water. Add 25 ml 7N H_2SO_4 and make the volume to 1 litre.
- Dilute solution (2 ppm):
  Dilute 10 ml of the 50 ppm stock solution to 250 ml.

Procedure

Extraction: Shake 5 g air-dried soil with 100 ml 0.5 M $NaHCO_3$ and 1 teaspoon of activiated charcoal in 250 ml conical flask for 30 minutes. Filter the solution using Whatman No. 40. If filtrate is not clear, add more activated charcoal, shake and filter again.

Estimation: Pipette a 10 ml clear extract into 50 ml volumetric flask. Add 2-3 drops of 2,4-dinitrophenol indicator and adjust pH to 3 with 4N NH_4OH or 4N HCl (indicator turns yellow when pH approaches 3). Add 10 ml chloromolybdic acid to the aliquot and allow the flask to stand quietly for a few minutes and dilute the solution to 40 ml with distilled water. Then add 1 ml dilute stannous chloride solution, mix the contents immediately and dilute to 50 ml. Read the absorbance/transmission at 660 mμ after 10 minutes. Colour stability is for 20 minutes only.

Standard Curve

Take 1.0, 2.5, 5.0, 10.0, 15.0 and 20 ml of 2 ppm stock solution in 50 ml volumetric flask. Add 10 ml 0.5 M $NaHCO_3$ solution, 2-3 drops 2,4-dinitropphenol and adjust the pH to 3.0 using 4H HCl or 4N NH_4OH. Then add 10 ml chloromolybdic acid and allow the flask to stand for a few minutes and dulute the solution to 40 ml. Add 1 ml stannous chloride and dilute the solution to 50 ml. Read the absorbance/transmission after 10 minutes at 660 mμ.

Calculation

$$\text{P, mg/kg soil} = \text{mg P in solution} \times \text{vol. of extracting solution} \times \frac{1000}{\text{wt. of soil}}$$

Bray and Kutrz Method: Suitable for acid and neutral soils

Apparatus

- Conical flask (50 ml)
- Test tubes
- Pipettes (1, 2, 4 and 5 ml)

Reagents

- Ammonium fluoride 2N:
  Take 37 g NH_4F and dissolve in 500 ml distilled water and store in polyethylene bottle.

- Hydrochloric acid 0.5 N:
  Dilute 20.2 ml of conc. HCl to 500 ml with distilled water.

- Extraction solution:
  Mix 200 ml 0.5 N HCl and 15 ml 2N NH_4F and dilute to 1 litre.

- **Sulphomolybdic acid 2.5%:**
  Dissolve 25 g $(NH_4)_6$ $MoO_{24}.4H_2O$ in 100 ml distilled water and warm to 60°C. Prepare 40% sulphuric acid in distilled water. Slowly mix molybdate solution with acid solution, cool and make up the volume to 1 litre. Preserve the solution in dark.

- H_3BO_3 0.8 M:
  Dissolve 49.4 g H_3BO_3 in 1000 ml distilled water.

- Ascorbic acid 1%:
  Dissolve 1 g ascorbic acid in 100 ml water.

- Standard solutions containing 10, 20, 30, 40, and 50 mg/1 P

Procedure

Extraction: Take 2 g air-dried and sieved soil in 50 ml conical flask and add 20 ml extraction solution. Shake the contents for 60 seconds vigorously and filter through Whatman No. 40. If solution is not clear, filter it again.

Estimation: Transfer 1 ml aliquot to dry test tube. Add 4 ml distilled water followed by 5 ml boric acid, 2 ml ascorbic acid and 1 ml sulphomolybdic acid solution.

Mix the content and warm at 35°C on water bath for 10 minutes. Then measure the absorbance at 660 mμ.

Standard curve: Take 1 ml of each standard solution and follow the same procedure.

Calculation

$$\text{P, mg/kg soil} = \text{mg P in solution} \times \text{volume of extracting solution} \times \frac{1000}{\text{wt. of soil taken}}$$

Annex 4.17

Available Potassium in Soil

Principle

Soil available potassium is estimated by leaching the soil with 1N ammonium acetate and determining the potassium using flame photometer.

Apparatus

- Flame photometer with filter for potassium
- Shaker
- 250 ml conical flask
- Funnel

Reagents

- Ammonium acetate 1N:
  Dissolve 77.08 g of ammonium acetate in 1 litre of distilled water.
- Standard K solution 1000 mg/l:
  Take 1.907 g dried KCl and dissolve in 1 litre. Pipette 5 ml and 10 ml of 1000 ppm K solution and dilute to 1 litre for 5 and 10 mg/l K.

Procedure

Extraction: Tansfer 5 g air-dried and sieved soil in 250 ml conical flask and add 100 ml 1 N ammonium acetate. Shake the contents for 30 minutes and filter using Whatman No. 40.

Estimation: Start the flame photometer and adjust 10 mg/l K solution to 100 reading on galvanometer. Feed the extract and record the reading.

Calculations

$$\text{Available } K_2O \text{ mg/kg soil} = \frac{10}{100} \times R \times \frac{100}{1000} \times \frac{1000}{5} \times 1.207$$

where R = galvanometer reading

Factor 1.207 is for conversion of K to K_2O.

Annex 4.18

Organic Carbon in Soil

(Walkey and Black)

Principle

Soil organic carbon is determined by treating the soil with a known amount of $K_2Cr_2O_7$ in presence of conc. H_2SO_4. Oxidation of organic carbon by $K_2Cr_2O_7$ takes place as per the given reaction:

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

$$3C \text{ (organic carbon)} + 6(O) \longrightarrow 3CO_2$$

Excess $K_2Cr_2O_7$ is back titrated with standard $FeSO_4$ solution using diphenylamine indicator.

$$K_2Cr_2O_7 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + 4H_2O$$

Apparatus

- Analytical balance
- Conical flask (500 ml)
- Pipette (10 ml)
- Burette (50 ml)
- Measuring cylinder (50 and 250 ml)

Reagents

- 1N $K_2Cr_2O_7$:
  Dissolve 49.04 g $K_2Cr_2O_7$ in distilled water and make up to 1 litre.
- Concentrated H_2SO_4 (98%)
- H_3PO_4 (85%)
- Diphenylamine indicator:
  Dissolve 500mg diphenylamine indicator in a mixture of 100 ml conc. H_2SO_4 and 20 ml distilled water.
- 1N $FeSO_4$:
  Dissolve 278 g $FeSO_4.7H_2O$ in 1 litre distilled water containing 15 ml conc. H_2SO_4.

Procedure

Take 0.5 to 1.0 g (0.05 g in case of peat soil) of soil sample in 500 ml conical flask. Add 10 ml 1N $K_2Cr_2O_7$ solution and 20 ml conc. H_2SO_4 and mix gently by swirling the flask. Allow the contents in the flask to stand for 30 minutes. Then add 200 ml distilled water, 10 ml H_3PO_4 (85%) and 1 ml diphenylamine indicator. Titrate the solution with 1N $FeSO_4$. To begin with, the colour of the solution is dull green which shifts to turbid blue as the titration preceeds. At the end point, colour turns to brilliant green. Keep a blank titration without soil and follow the same procedure.

Calculations

$$\text{Per cent organic carbon} = 10(1 - T/S) \times 0.7792$$

where S = ml $FeSO_4$ solution used for blank titration
T = ml $FeSO_4$ solution used for sample titration

Factor 0.7792 is calculated as given below taking 0.5 g of soil sample for determination.

$$1N \times \frac{12}{4000} \times \frac{100}{77} \times \frac{100}{0.5} = 0.7792$$

where $\frac{12}{4000}$ = meq. wt. of carbon
$\frac{100}{77}$ = recovery facor
0.5 g = wt. of soil sample

Per cent organic carbon x 1.72 = Per cent organic matter

Annex 4.19

Determination of Total Viable Count in Soil

Principle

Total viable count in soil is estimated by standard plate count method using nutrient agar medium.

Apparatus

- Autoclave
- Sterile petridishes
- Sterile water blanks (90 ml)
- Sterile pipettes
- Incubator

Reagents

Nutrient agar:

Dissolve 3 g beef extract and 5 g peptone in 1000 ml of distilled water. Adjust the pH of the medium to 6.8-7.0 using 0.1N NaOH. Then add 15.0 agar-agar and sterilise the content at 121°C for 30 minutues.

Procedure

Transfer 10 g field moist soil to 90 ml water blank and shake thoroughly for 20-30 minutes. Prepare serial dilutions by pipetting appropriate amount of soil suspension. Pipette 1 ml of aliquot from serial dilutions in sterile petridishes and pour approximately 20 ml of nutrient agar having a temperature of 45°C $\pm$ 1°C. Rotate the plate slowly and carefully clockwise and counter-clockwise at least for 5 times. Maintain three plates for each dilution.

After solidification of agar, incubate the plates at 28-30°C in inverted position for 5 days. Remove the plates after incubation period and select only those plates which show the count between 30 and 300 colonies. Plates showing large spreaders, huge mold colonies, uneven distribution of colonies and evidence of symbiosis and antagonism should be discarded. Record the number of colonies.

Keep part of the soil in oven at 105° C and dry till constant weight to determine the moisture content in original soil.

Calculations

$$\text{Viable count per gram of dry soil} = \frac{A \times D}{W}$$

where A = average count
D = dilution
W = oven dry weight of soil

Reference: Difco Manual of Dehydrated Culture Media and Reagents for Microbiological and Clinical Laboratory Procedures 1977, 9th Edition

Annex 4.20

Determination of Fungi in Soil

Principle

Soil fungi are determined using Martin's Rose Bengal Agar medium by pour plate method.

Apparatus

As described under "Viable Count Estimation", Annex 2.19.

Reagents

Martin's medium:

Solution A - Dissolve 10.0 g dextrose, 5.0 g peptone, 1.0 g KH_2PO_4, and 0.5 g $MgSO_4$ in 1000 ml distilled water and adjust pH to 5 to 5.5 using 0.1N HCl. Then add 33.3 mg Rose Bengal and 15.0 g agar-agar and sterilise the medium at 121°C for 30 minutes.

Solution B - Dissolve 3 g streptomycin in 100 ml distilled water and sterilise through membrane filter.

Cool solution A and add 1 ml of solution B and shake well. This gives 30 µg/ml of streptomycin.

Procedure

Follow the procedure as described under "Viable Count Estimation", Annex 2.19.

Calculations

$$\text{Fungi per gram dry soil} = \frac{A \times D}{W}$$

where A = Average count of fungi
D = Dilution
W = Oven dry weight of soil

Reference: Martin, J.P., Soil Sci., 69, 125, 1950

Annex 4.21

Estimation of Actinomycetes in Soil

Principle

Soil Actinomycetes are estimated by pour plate method using starch casein agar medium.

Apparatus

As described under "Viable Count Estimation", Annex 2.19.

Reagents

Starch casein agar medium:

Dissolve 10.0 g starch, 0.3 g casein, 2.0 g KNO_3, 2.0 g NaCl, 2.0 g K_2HPO_4, 0.05 g $MgSO_4.7H_2O$, 0.02 g $CaCO_3$, 0.01 g $FeSO_4.7H_2O$ in 1000ml distilled water and adjust the pH to 7.2 using 0.1 HCl/0.1N NaOH. Then add 15.0 g agar-agar and sterilise the medium at 121°C for 30 minutes.

Procedure

Follow the procedure as mentioned under "Viable Count Estimation", Annex 2.19.

Calculations

$$\text{Actinomycetes per gram dry soil} = \frac{A \times D}{W}$$

where A = Average actinomycetes count
D = Dilution
W = Oven dry weight of soil

Reference: Jensen, H.L., Soil Sci., 30, 59, 1930

Annex 4.22

Estimation of Azotobacter in Soil

Principle

Soil Azotobacter population is grown on Jenson's medium and estimated by pour plate method.

Apparatus

As described under "Viable Count Estimation", Annex 2.19.

Reagents

Jenson's medium:

Dissolve 20.0 g sucrose, 1.0 g K_2HPO_4, 0.05 g $MgSO_4.7H_2O$, 0.5 g NaCl, 0.01 g $FeSO_4$, 0.005 g Na_2MoO_4, and 2.0 g $CaCO_3$ in 1000ml distilled water and adjust the pH to 7.0-7.2 by 0.1 HCl/0.1N NaOH. Then add 15.0 g agar-agar and sterilise the medium at 121°C for 30 minutes.

Procedure

Adopt the procedure given in "Viable Count Estimation", Annex 2.19.

Calculations

$$\text{Azotobacter per gram dry soil} = \frac{A \times D}{W}$$

where A = Average azotobacter count
D = Dilution
W = Oven dry weight of soil

Reference: Jensen, H.L., Proc. Linn. Soc. (NSW), 66, 98, 1942

Annex 4.23

Determination of Rhizobium in Soil

Principle

Soil Rhizobium is estimated using yeast extract mannitol agar medium and following pour plate method.

Apparatus

As described under "Viable Count Estimation", Annex 2.19.

Reagents

Yeast extract mannitol agar medium:

Dissolve 10.0 g mannitol, 0.5 g K_2HPO_4, 0.2 g $MgSO_4.7H_2O$, 0.1 g NaCl, and 1.0 g yeast extract in 1000 ml distilled water. Adjust the medium pH to 6.8-7.0 and add 15.0 g agar-agar and sterilise the medium at 121°C for 30 minutes.

Congored 1%:

Dissolve 1 g congored in 100 ml of distilled water and sterilise the medium at 121°C for 30 minutes. Then add 2.5 ml of congo-red to 1000 ml yeast extract mannitol agar medium just before pouring the plates.

Procedure

As described under "Viable Count Estimation", Annex 2.19.

Calculations

$$\text{Rhizobium per gram dry soil} = \frac{A \times D}{W}$$

where A = Average Rhizobium count
D = Dilution
W = Oven dry weight of soil

Reference: Fred, E.B., Baldwin, I.L. and McCoy, E., Root Nodule Bacteria and Leumious Plants, Univ. of Wisconsin Press, 1932

Annex 4.24

Recommended Analytical Methods for Grains and Consumable Plant Parts

	Measurement	Type of Sample	Weight/ Volume of Sample	Methodology	References
1.	Total Nitrogen (N), %	Direct	1-2 g	Kjeldahl digestion-distillation Method	Soil and Plant Testing as a Method of Fertilizers Recommendation by Cottenie FAO, Soil Bulletin, Rome, 1980
2.	Total Phosphate (P), %	H_2SO_4-H_2O_2 extract/HNO_3-$HClO_4$-H_2SO_4 extract	10-20 ml extract	Colorimetric method	-do- and Soil Chemical Analysis by M.L. Jackson, Prentice Hall of India Ltd, 1972
3.	Total Potassium (K), %	H_2SO_4-H_2O_2 extract/HNO_3-$HClO_4$-H_2SO_4 extract	10-20 ml extract	Flame Photometric method	-do-
4.	Calcium (Ca), %	H_2SO_4-H_2O_2 extract/HNO_3-$HClO_4$-H_2SO_4 extract	10-20 ml extract	EDTA/AAS/Flame Photometer	-do-
5.	Magnesium (Mg), %	H_2SO_4-H_2O_2 extract/HNO_3-$HClO_4$-H_2SO_4 extract	10-20 ml extract	EDTA/AAS	-do-

For extract preparation 2-5 g of sample to be used.
At least 10 samples for each crop is to be analysed for statistical interpretation.

References

Gosser, J.K.R. (1958). "Use of Deep-Freezing in the Preservation and Preparation of Fresh Soil Samples." Nature 181, 1334-1335.

Pearson, G.A. (1960). "Tolerance of Crops to Exchangeable Sodium." United States Department of Agriculture Information Bulletin 216.

"Process Design Manual for Land Treatment of Municipal Wastewater." (1977), United States Environmental Protection Agency 625/1-77-008.

Annex 4

GUIDE ON DETERMINATION OF THE ACUTE LETHAL TOXICITY OF PULP AND PAPER MILL EFFLUENT TO FRESHWATER FISH

PREFACE

This guide was prepared as part of the Phase I activities of the Network for Industrial Environmental Management (NIEM). It outlines in detail the methods of determining the acute lethal toxicity to fish by pulp and paper mill effluents, and discusses how the results of the analytical analysis should be interpreted. The guide is the slightly modified version of the International Standard ISO 7346/2-1984(E), Water Quality - Determination of the Aquatic Lethal Toxicity of Substances to a Freshwater Fish. The modifications were made based on individual evaluations and experience gained by Network members, who conducted a series of research projects on discharge characterization and receiving media quality evaluation in reference to pulp and paper mill effluents.

The United Nations Environment Programme gratefully acknowledges the financial contribution by the Swedish International Development Authority that made functioning of the Network possible. Special thanks are extended to Dr. Lars Landner, Director of Swedish Environmental Research Group, Sweden, who drafted this text. Suggestions for revisions to the draft were provided by NIEM members.

Contents

GUIDE ON DETERMINATION OF THE ACUTE LETHAL TOXICITY OF PULP AND PAPER MILL EFFLUENT TO FRESHWATER FISH

1. Introduction

The present knowledge of the toxicity of pulp and paper mill effluents to aquatic life is based primarily on bioassay tests performed under controlled laboratory conditions. Findings from acute (short-term) lethal bioassays with fish are used for various purposes, such as:

- intercomparison of toxic loadings and emission rates for various types of pulp and paper mill discharges;
- identification and control of in-plant sources of toxicity and of specific toxic constituents;
- assessment of the efficacy of effluent treatment in removing toxicity;
- routine monitoring of mill discharges for quality control and compliance with respect to governmental regulatory requirements.

In general, the standard laboratory test for evaluating the acute lethal toxicity of pulp and paper mill effluents is the 96-h LC_{50} (median lethal concentration) fish bioassay. This involves placing groups of fish (usually ten per concentration) in a range of concentrations of effluent, diluted with freshwater (to which the fish are acclimated), and observing their survival throughout a 96-h test period. Based on the percentage survival of fish at various effluent concentrations, the median lethal concentration is calculated. Since effluent dilutions are normally on a volume-to-volume basis, LC_{50} values are expressed as percentage effluent by volume (% v/v). The term "LC_{50}" is synonymous with TL_m and TL_{50} (median tolerance limit), used in earlier literature.

The higher the LC_{50} value, the less the toxicity, i.e. the higher the concentration the fish can tolerate. Samples of effluent identified as "non-toxic" are those in which more than half of the test fish exposed to full-strength effluent for 96-h survived.

In addition to the LC_{50} value, it may sometimes be pertinent to express the results in terms of "toxic units" (TU), "toxicity emission rate" (TER) or "toxicity emission factor" (TEF), as illustrated below.

The present Guide is a slightly modified version of the International Standard ISO 7346/2-1984, "Water quality - Determination of the acute lethal toxicity of substances to a freshwater fish - Part 2: Semi-static Method" (Appendix 1). A comprehensive review of aquatic toxicity of pulp and paper mill effluent is given by McLeay et al. (1987).

2. Objective

The objective of determining the acute lethal toxicity of fish of pulp and paper mill effluents is to complement the physical and chemical

characterization of the effluents with a biological test having relevance for a first assessment of the biological effects caused by the discharge. The result of a biological test can also be used as a summary parameter, giving information about the potential harmfulness of the discharge, when specific chemical analysis of types and amounts of toxic components cannot be caried out. Toxicity testing should primarily be applied on the final effluent, but in case an effluent treatment facility exists, the toxicity of both the untreated and treated effluent should be evaluated, so as to obtain an indication of the treatment system's efficacy in reducing the toxicity of mill effluents.

3. Test species

The test procedure recommended (Appendix 1) has been developed for the tropical species Brachydanio rerio, commonly known as the zebra fish. However, the same test procedure can be used for other warm water species, provided small specimens (< 3 g weight) are used. The final choice of species of fish to be used in the test should be left to the investigator. The test species should withstand captivity well, and be common in unpolluted portions of the body of water receiving the waste to be tested. If available, species which are deemed important locally should be given preference. For the NIEM region, suggestions included Puntius spp., Ophicephales striatus, Oryzias latipes, Tilapia nilotica and Cirrhinus mrigala.

4. Test conditions

Water obtained from unpolluted parts of the receiving body should preferentially be used as dilution water in the test, rather than artificial dilution water. The test fish must be acclimated to this dilution water prior to the test. The pH, alkalinity, conductivity, and other standard water quality parameters of the dilution water should be reported.

The temperature at which the test is conducted should reflect ambient conditions in the receiving body, and be maintained throughout the test period, as stipulated in Appendix 1.

Since the aim of the test is to determine the effect of toxic substance in the effluent, and not the (well-known) effect of oxygen depletion, it is recommended to aerate the test solution throughout the test period by applying a slow stream of fine air bubbles. The concentration of dissolved oxygen in the test vessel should be checked (if possible) at least at the beginning of the test and immediately before the renewal of the test solution every 24 h.

5. Expression of results

Results should always be expressed as 48-h LC_{50} and 96-h LC_{50} values, expressed as percentage effluent by volume (% v/v). Since the LC_{50} value is a function of the amount of process water used in the mill (a high water consumption in the mill will cause a dilution of the toxic components, resulting in a higher LC_{50} value), it may be pertinent to

estimate the "amount of toxicity" discharged from a particular mill. For this purpose, the toxicity should first be transformed into "toxic units" (TU), as follows:

$$TU = \frac{100\ \%}{96\text{-h } LC_{50}(\%)}$$

The toxic unit concept can then be used to assess the quantity of toxicity discharged daily by the mill, where the "toxicity emission rate" (TER) is:

$$TER = TU \times \text{daily discharge volume } (m^3/day)$$

TER calculations are useful for comparing the relative quantities of toxic material (toxic loading) discharged daily to the environment at different process conditions in the mill or between mills.

For the process engineer, the quantity of toxicity generated per unit of production is important in evaluating mill operation and/or process design modifications. These data are derived by dividing the TER by the daily tonnage produced to yield a "toxicity emission factor" (TEF).

6. References

McLeay, D. and Associates Ltd. (1987) Aquatic Toxicity of Pulp and Paper Mill Effluent: A Review. Environmental Protection Series Reports, EPS 4/PF/1, Environment Canada, Ottawa, Ontario, Canada.

International Organization for Standardization. (1984) International Standard ISO 7346/2: Water Quality - Determination of the Aquatic Lethal Toxicity of Substances to a Freshwater Fish, Part 2: Semi-static Method, Switzerland.

APPENDIX 1

International Standard ISO 7346/2: Water Quality -

Determination of The Aquatic Lethal Toxicity of

Substances to a Freshwater Fish

Part 2: Semi-static Method

Water quality — Determination of the acute lethal toxicity of substances to a freshwater fish [*Brachydanio rerio* Hamilton-Buchanan (Teleostei, Cyprinidae)] — Part 2: Semi-static method

0 Introduction

The three parts of ISO 7346 describe methods of determining the acute lethal toxicity of substances to the zebra fish (*Brachydanio rerio* Hamilton-Buchanan), but it must be emphasized that the recommended use of the zebra fish does not preclude the use of other species. The methodologies presented here may also be used for other species of freshwater, marine of brackish water fish, with appropriate modifications of, for example, dilution water quality and the temperature conditions of the test.

Within the three parts of ISO 7346, a choice can be made between static, semi-static and flow-through methods. The static test, described in ISO 7346/1, in which the solution is not renewed, has the advantage of requiring simple apparatus although the substance in the test vessel may become depleted during the course of the test and the general quality of the water may deteriorate. The flow-through method, described in ISO 7346/3, in which the test solution is replaced almost continuously, overcomes such problems but requires the use of more complex apparatus. In the semi-static procedure, described in ISO 7346/2, the test solutions are renewed daily, this method being a compromise between the other two.

The flow-through method can be used for most types of substances, including those unstable in water, but the concentrations of the test substance are determined wherever possible. The static method is limited to the study of substances whose tested concentrations remain relatively constant during the test period. The semi-static method can be used for testing those substances whose concentrations can be maintained satisfactorily throughout the test by renewal of the solutions every 24 h.

To assist in the preparation and maintenance of concentrations of substances which may be lethal at concentrations close to that of their aqueous solubility, a small volume of solvent may be used, as specified in the methods.

1 Scope and field of application

This part of ISO 7346 specifies a semi-static method for the determination of the acute lethal toxicity of substances soluble in water under specified conditions to a species of freshwater fish [*Brachydanio rerio* Hamilton-Buchanan (Teleostei, Cyprinidae) — common name, zebra fish] in water of a specified quality.

The method is applicable for assigning, for each test substance, broad categories of acute lethal toxicity to *Brachydanio rerio* under the test conditions.

The results are insufficient by themselves to define water quality standards for environmental protection.

The method is also applicable when using certain other species of freshwater fish as the test organism.[1)]

The method may be adapted for use with other freshwater fish and marine and brackish water fish with appropriate modification of the test conditions, particularly with respect to the quantity and quality of the dilution water and temperature.

1) The following species of freshwater fish can be used, in addition to *Brachydanio rerio*, without modification to this part of ISO 7346:

- *Cichlasoma nigrofasciatum* (Teleostei, Cichlidae)
- *Lepomis macrochirus* (Teleostei, Centrarchidae)
- *Oryzias latipes* (Teleostei, Poeciliidae)
- *Pimephales promelas* (Teleostei, Cyprinidae)
- *Poecilia reticulata* (Teleostei, Poeciliidae)

The results obtained from a test with one species cannot, however, be extrapolated to other species.

2 Principle

Determination, under specified conditions, of the concentrations at which a substance is lethal to 50 % of a test population of *Brachydanio rerio* after exposure periods of 24; 48; 72; and 96 h to that substance in the ambient water. These median lethal concentrations are designated the 24 h LC50; 48 h LC50; 72 h LC50; and 96 h LC50.

The test is carried out in two stages:

a) a preliminary test which gives an approximate indication of the acute median lethal concentrations and serves to determine the range of concentrations for the final test;

b) a final test, the results of which alone are recorded.

Where evidence is available to show that test concentrations remain relatively constant (i.e. within about 20 % of the nominal values) throughout the test then either measured or nominal concentrations may be used in the estimation of the LC50. Where such analyses show that the concentrations present remain relatively constant but are less than about 80 % of the nominal values, then the analytical values shall be used in estimating the LC50. Where evidence is not available to show that the test concentrations remained at an acceptable level throughout the test period or where it is known (or suspected) that the concentrations of the test chemical have declined significantly at any stage during the test then irrespective of whether or not chemical analytical data are available the LC50 cannot be defined, using this test method. In these cases the test is not necessarily invalidated but it can only be stated that the LC50 of the substance is $< x$ mg/l, the value, x, given being estimated from the nominal concentrations used.

3 Test organism and reagents

The reagents shall be of recognized analytical grade. The water used for the preparation of solutions shall be glass-distilled water or deionized water of at least equivalent purity.

3.1 Test organism

The test species shall be *Brachydanio rerio* Hamilton-Buchanan (Teleostei, Cyprinidae), commonly known as the zebra fish. Each test fish shall have a total length of 30 ± 5 mm and a mass of 0,3 ± 0,1 g. They shall be selected from a population of a single stock. This stock should have been acclimated and, in any case, maintained for at least 2 weeks prior to the test in dilution water, continuously aerated (using bubbled air) (see 3.2), under conditions of water quality and illumination similar to those used in the test. They shall be fed as normal up to the 24 h period immediately preceding the test.

Test fish shall be free of overt disease or visible malformation. They shall not receive treatment for disease during the test or in the 2 weeks preceding the test.

Environmental conditions for the maintenance and breeding of zebra fish are given in annex A.

3.2 Standard dilution water

The freshly prepared standard dilution water shall have a pH of 7,8 ± 0,2, and calcium hardness of approximately 250 mg/l, expressed as calcium carbonate, and shall be prepared as follows.

Prepare the following solutions using distilled or deionized water:

a) Calcium chloride solution

Dissolve 11,76 g of calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) in water and dilute to 1 litre.

b) Magnesium sulfate solution

Dissolve 4,93 g of magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) in water and dilute to 1 litre.

c) Sodium hydrogen carbonate solution

Dissolve 2,59 g of sodium hydrogen carbonate ($NaHCO_3$) in water and dilute to 1 litre.

d) Potassium chloride solution

Dissolve 0,23 g of potassium chloride (KCl) in water and dilute to 1 litre.

Mix 25 ml of each of these four solutions and dilute to 1 litre with water.

Aerate the dilution water until the concentration of dissolved oxygen reaches its air saturation value (ASV) and the pH value is constant at 7,8 ± 0,2. If necessary, adjust the pH of the solution by adding sodium hydroxide solution or hydrochloric acid. The dilution water thus prepared shall receive no further forced aeration before use in the tests.

3.3 Stock solutions of test substances

A stock solution of the test substance should be prepared by dissolving a known amount of test substance in a defined volume of dilution water, deionized water or glass-distilled water. The stock solution should be prepared daily except where it is known that the material is stable in solution, in which case sufficient solution for use over 2 days may be prepared. To enable stock solutions to be prepared and to assist in their transfer to the test vessels, substances of low aqueous solubility may be dissolved or dispersed by suitable means, including ultrasonic devices and using organic solvents of low toxicity to fish. If any such organic solvent is used, its concentration in the test solution shall not exceed 0,1 ml/l, and two sets of controls, one containing solvent at the maximum concentration used in any test vessel and one without solvent or test substance, shall be included.

3.4 Test solutions

Test solutions are prepared by adding appropriate amounts of the stock solution of the test substance to the dilution water to give the required concentrations. It is recommended that when a stock solution is prepared in distilled or deionized water, no more than 100 ml of stock solution should be added per 10 l of dilution water.

4 Apparatus

All materials which may come into contact with any liquid into which the fish are to be placed, or with which they may come into contact, shall be inert and should not absorb the test substance significantly.

Usual laboratory equipment [including a dip-net, made of nylon or of another chemically inert material, for the control vessels and another for all the test vessels (4.1)], and

4.1 Test vessels

Test vessels shall have sufficient capacity (which may need to be greater than 10 l) with a large area of interface between the air and the test medium (of about 800 cm^2 for 10 l of medium) and shall be equipped with a securely fixed and close-fitting cover.

Before use, new test vessels shall be carefully washed and then rinsed successively with water and the dilution water. At the end of the test, the vessels shall be emptied, cleaned by appropriate means, rinsed with water to remove all traces of the test substance and cleaning aid, and dried.

Test vessels shall be rinsed with dilution water just before use.

4.2 Temperature control equipment

The temperature of the test solutions and the water in the stock tanks shall be regulated to 23 ± 1 °C by a suitable method.

5 Test environment

The preparation and storage of solutions, the holding of fish, and all the manipulations and tests shall be carried out in premises with an atmosphere free from harmful concentrations of airborne contaminants.

Take care to avoid any unwanted disturbance that may change the behaviour of the fish. All tests should be carried out under normal laboratory illumination with a daily photoperiod of 12 to 16 h.

6 Procedure

6.1 Condition of the fish

Whenever there is a change of stock population, a toxicity test using the method specified in this part of ISO 7346 should be carried out using a suitable reference substance. The results of such tests shall be in reasonable agreement with results obtained previously in the same laboratory.

6.2 Preliminary test

Add at least 2,5 l, preferably 5 l, of standard dilution water (3.2) to each of six vessels and aerate if necessary to restore the concentration of dissolved oxygen to its air saturation value. Prepare test solutions by adding appropriate amounts of stock solution of the test substance (3.3) to five of the vessels in order to obtain an adequate range of concentrations, for example 1 000; 100; 10; 1; and 0,1 mg/l. Nothing is added to the sixth vessel, which serves as a control. The solutions should be adjusted to and maintained at 23 ± 1 °C.

Place five fish in each vessel.

At least twice a day for a suitable period, note the numbers of dead fish and the dissolved oxygen concentration in each vessel. Remove dead fish.

If there are insufficient data for establishing the range of concentrations required for the final test, repeat this preliminary test with alternative ranges of concentrations.

6.3 Final test

Select at least five concentrations, forming an approximately geometric series, for example 8; 4; 2; 1; and 0,5 mg/l, between, but including, the lowest concentration killing all the fish in the preliminary test, and the highest non-lethal concentration in 48 h. This selected series of concentration should provide the possibility of obtaining mortalities of between 20 and 80 % in at least three consecutive concentrations of the geometric series used, for estimation of the LC 50.

In some instances, a narrower range of concentrations may be required to provide the necessary data and for others a wider range may be needed.

Take at least six test vessels and into each pour, for example, 10 l of standard dilution water. Nothing is added to one of these (the control) but to the remainder add the different amounts of stock solution required to give the particular range of concentrations of test substance which has been selected for testing. If an organic solvent has been used to dissolve a substance, prepare a second "control" with the standard dilution water containing sufficient of the organic solvent to give the maximum concentration at which this solvent is present in any of the test solutions. When the test solution has been adjusted to 23 ± 1 °C, place 10 fish in each of the vessels, as follows.

Select the fish at random from the stock and distribute them at random into the test vessels, without delay, using a small mesh dip-net of soft inert material. Discard any fish dropped or otherwise mishandled during the transfer. In a given test, all fish should be added within a period of 30 min.

After 24 h prepare new test solutions in new test vessels and transfer the live fish to them without delay. The renewal of test solutions and transfer of fish shall be repeated every 24 h during the test. In order to avoid significant transfer of test substances between test vessels via the dip-net (see clause 4) the transfer of fish should begin with the lowest concentration and proceed towards the highest concentration.

The solutions shall not be forcibly aerated. Record the number

of dead fish in each vessel at least twice daily over the period of the test. Remove each dead fish from the vessel as soon as possible. Observations can be made more frequently, for example to enable median periods of survival to be calculated for each concentration.

Note any abnormal behaviour of the fish.

If possible, the concentrations of the test substance in the test vessels and the stock solutions should be measured at least at the beginning and end of the test.

Measure the dissolved oxygen concentration, the pH and temperature in each vessel at least at the beginning of the test and immediately before and after the renewal of the test materials.

A suggested form suitable for recording the data is given in annex B.

7 Expression of results

7.1 Validity

The results shall be considered valid if the following requirements were fulfilled:

a) the dissolved oxygen concentration in the test solutions during the test was at least 60 % ASV;

b) the concentrations of the test substance were not known (or suspected) of having declined significantly throughout the test (but see clause 2);

c) the mortality of the control fish did not exceed 10 %;

d) the proportion of control fish showing abnormal behaviour did not exceed 10 %;

e) the 24 h LC50 of the reference chemical for the stock of fish was in reasonable agreement with results obtained previously in the same laboratory.

7.2 Estimation of LC50

Where a simple graphical estimation of the LC50 is considered adequate this can be obtained by plotting mortality (expressed as a percentage of test fish in each test vessel) against concentration of test substance. Using axes with linear scales this will produce a sigmoid relationship from which the LC50 can be derived by interpolating the concentration expected to cause 50 % mortality (see figure 1).

It is more appropriate to plot the data on graph paper having axes with probability and logarithmic scales. Data plotted in this way should produce a linear relationship from which the LC50 can be interpolated as above (see figure 2).

Where estimation of slope and 95 % confidence limits of this and the LC50 are required, the data can be analysed graphically.[2]

Where computing facilities are available probit analysis can be applied.[1]

If insufficient data are available to estimate the LC50 at 24; 48; 72; and 96 h, record the minimum concentration in which 100 % mortality occurred and the maximum concentration giving 0 % mortality at 24; 48; 72; and 96 h. These concentrations will indicate the limits within which the LC50 probably lies.

8 Test report

The test report shall include the following information:

a) the chemical identity and any additional available information about the test substance;

b) the method of preparing the dilution water, stock solutions and test solutions;

c) all chemical, biological and physical data pertaining to the test not otherwise specified in this part of ISO 7346, including details of the acclimation conditions of the test fish, and the mass of fish in grams per litre;

d) the data taken into account when assessing the validity of the test

1) concentration of dissolved oxygen,

2) mortality observed among control fish,

3) proportion of control fish showing abnormal behaviour,

4) LC50 of the reference substance;

e) a tabulated list showing the nominal concentrations tested (with chemical analytical values, where available), and the total percentage mortalities in each, 24; 48; 72; and 96 h after the start of the test;

f) the LC50 values and confidence limits if available at 24; 48; 72; and 96 h, of the substance tested; reference should be given to the method of calculation, and the method of chemical analysis, where applicable;

g) the slope of the concentration-response curve (and its 95 % confidence limit if available);

h) a graphical illustration of the concentration-response relationship;

j) any unusual reactions by the fish under the test conditions and any visible external effects produced by the test substance;

k) any deviation from the procedure specified in this part of ISO 7346, and the reason for it;

m) a reference to this part of ISO 7346.

9 Bibliography

[1] FINNEY, D.J. *Statistical Methods in Biological Assay*. Wycombe, United Kingdom, Griffin, 1978.

[2] LITCHFIELD, J.T. and WILCOXON, F. A simplified method of evaluating dose-effect experiments. *J. Pharmacol. Exp. Ther.* **96** 1949: 99-113.

[3] STEPHAN, C.E. *Measurements for calculating an LC 50. Aquatic Toxicology and Hazard Evaluation*. ASTM (1977), ST. p. 634.

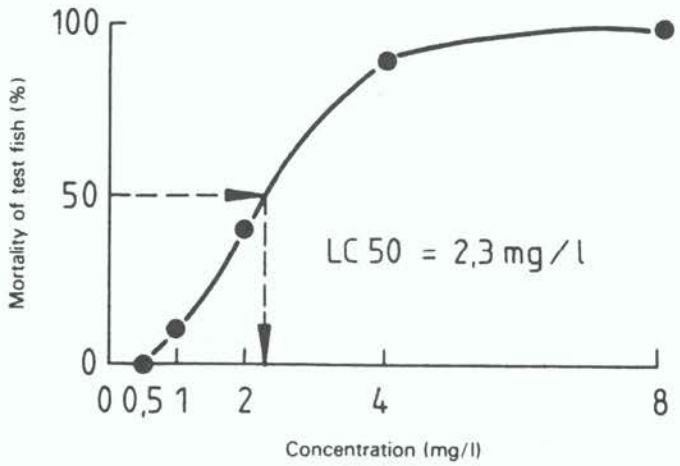


Figure 1 — Graphical interpolation of LC50 (linear scales)

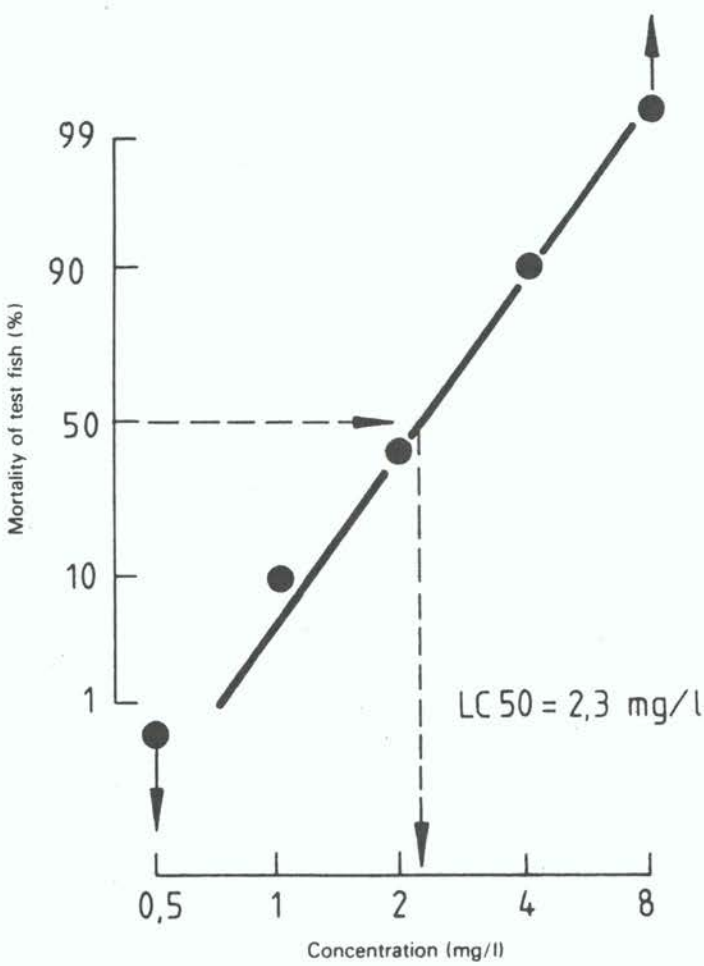


Figure 2 — Graphical interpolation of LC50 (logarithmic and probability scales)

Annex A

Environmental parameters for maintenance and breeding of zebra fish (*Brachydanio rerio* Hamilton-Buchanan)

A.0 Introduction

The species originates from the Coromandel coast of India where it inhabits fast flowing streams. It is a common aquarium fish, so that information about procedures for its care and culture can be found in standard reference books on tropical fish culture. Its biology has recently been reviewed by Laale[A2].

The fish rarely exceeds 45 mm in length. The body is cylindrical with 7 to 9 dark blue horizontal stripes on silver. These stripes run into the caudal and anal fins. The back is olive green. Males are slimmer than females and possess a golden sheen. Females are more silvery and the abdomen is distended particularly prior to spawning.

A.1 Environmental parameters

The fish are capable of withstanding wide ranges of temperature, pH and water hardness. Axelrod[A1] states a temperature range of 15,5 to 43,3 °C and a pH of 6,6 to 7,2. Fish may be bred, reared and maintained in tap water with a total hardness as high as 300 mg/kg (as calcium carbonate) and a pH of 7,7 to 8,2. The temperature is maintained at 26 ± 1 °C and raised to 27 ± 1 °C to induce spawning.

A.2 Material and methods

The fish may readily be spawned in glass tanks of capacity about 70 l. The fry are later transferred to a tank of capacity 200 l.

Since the adult fish are avid egg eaters, a method of protecting newly laid eggs and young fish is necessary. One method, used successfully, is to confine the adult fish in mesh cages in the water so that as the female lays her eggs these fall through the mesh to the bottom of the tank out of reach of the adults.

The mesh cages are made of plastic netting with 3 mm mesh, of dimensions approximately 250 mm x 250 mm x 80 mm. They are clipped to the lips of the tank so that the whole of the upper edge of the cage is above water with the mesh dropping 60 mm into the water. An undergravel filter system should not be used to cleanse the water because it is likely to damage the eggs. The tanks should be illuminated for 8 h per day.

A.3 Conditioning

This period lasts for approximately 2 weeks. Males and females are separated and fed on live food. This consists of white worms (enchytraeids), *Daphnia* and brine shrimp (*Artemia*). The density of stocking during conditioning is kept below 30 fish in tanks of capacity 70 l.

At the end of 2 weeks, the males possess a deep golden sheen and the females are greatly distended with ova.

A.4 Breeding stage

The spawning tank can be set up as follows.

Fill an empty tank with fresh tap water aged at 27 °C for 48 h and place a plastic cage inside the tank under the lip allowing the fish a swimming space of volume about 1 litre. Place six females in the basket in the morning and feed with freeze-dried brine shrimp.

Add nine males to the basket in the evening and feed the fish once more with freeze-dried brine shrimp before the lights are switched off.

Spawning is induced by the morning light and is completed after the lights have been switched on for approximately 4 h. The eggs, which are non-adhesive, fall through the mesh, out of reach of the adults.

When the females are exhausted of eggs, remove the adults and leave the eggs to hatch.

A.5 Development of fry

The eggs hatch in 4 to 5 days, and the fry or alevins adhere tothe side of the tank and remain motionless for 24 to 48 h. When the fry become free-swimming, feed them on suitable proprietary fish food of small particle size. At 3 weeks, the fry can be fed newly hatched brine shrimp and growth then becomes more rapid. After 1 month, they can be transferred to a 200 l tank and fed on a mixture of live and proprietary foods. The fish are sexually mature at 3 months and attain a length of 3,5 cm. It should be noted that spontaneous abnormalities in the developing larvae have been observed in certain strains[A6].

Further studies indicate that a dietary factor is responsible for the deformities and that the zebra fish is especially susceptible to this factor (other species breed normally when fed the same proprietary fish food)[A4].

A.6 Bibliography

[A1] Axelrod, H.P. *Breeding Aquarium Fishes Book 1.* T.F.H. Publication, 1967.

[A2] Laale, H.W. The biology and use of zebra fish (*Brachydanio rerio*) in fisheries research. A literature review. *J. Fish Biol.* **10** (2) 1977: 121-173.

[A3] MERTENS, J. Year-round controlled mass reproduction of the zebra fish. *Aquaculture* **2** 1973: 245-249.

[A4] NEWSOME, C.S. and PIRON, R.D. Aetiology of skeletal deformities in the Zebra Danio fish (*Brachydanio rerio*, Hamilton-Buchanan). *J. Fish Biol.* **21** 1982: 231-237.

[A5] NIIMI, A.J. and LAHAM, Q.N. Influence of breeding time interval on egg number, mortality and hatching of the zebra fish (*Brachydanio rerio*). *Can. J. Zool.* **52** 1974: 515-517.

[A6] PIRON, R.D. Spontaneous skeletal deformities in the zebra fish (*Brachydanio rerio*) bred for fish toxicity tests. *J. Fish Biol.* **13** 1978: 79-84.

Annex 5

GUIDE ON PRELIMINARY ASSESSMENT OF ENVIRONMENTAL EFFECTS OF EXISTING SMALL PULP AND PAPER MILLS

Annex B

Suggested form for recording data

Laboratory				Operator				
Sample No.				Date of start of test				
Substance								
Purity								
Impurities								
If a formulation is being tested, the identity of the components								
Method of preparing the stock solution				Stock solution concentration (mg/l)				
				Maximum concentration of solvent in test vessels, (ml/l)				
Method of chemical analysis								
Control vessels **1 Dilution water only**								
Determinands	Time from start of test (h)							
	0							
Dissolved oxygen concentration (% ASV*) pH Temperature (°C) Number of dead fish								
2 Dilution water and	ml/l	**solvent**						
Determinands	Time from start of test (h)							
	0							
Dissolved oxygen concentration (% ASV*) pH Temperature (°C) Number of dead fish								
Test vessel No. Initial (measured or calculated) concentration of test substance	mg/l							
Determinands	Time from start of test (h)							
	0							
Test substance concentration (mg/l (by analysis)) Dissolved oxygen concentration (% ASV*) pH Temperature (°C) Number of dead fish								

* Air saturation value.

PREFACE

This guide was prepared as part of the Phase I activities of the Network for Industrial Environmental Management (NIEM). This guide serves an important purpose in assisting mill management and agencies responsible for environmental control in improving overall environmental management in pulp and paper mills. It outlines in detail basic procedures for undertaking a rapid and simplified assessment of environmental effects of existing small pulp and paper mills. These procedures were formulated based on the experience gained by Network members, who conducted a series of research projects on discharge characterization and receiving media quality evaluation in reference to pulp and paper mill effluents.

The United Nations Environment Programme gratefully acknowledges the financial contribution by the Swedish International Development Authority that made functioning of the Network possible. Special thanks are extended to Mr. Maheswaran, Environmental Consultant, Malaysia, who drafted this text. Suggestions for revisions to the draft were provided by NIEM members.

Contents

GUIDE ON PRELIMINARY ASSESSMENT OF ENVIRONMENTAL EFFECTS OF EXISTING SMALL PULP AND PAPER MILLS

1. Introduction

Pulp and paper production causes an impact on receiving media, namely water, air and land, to varying degrees. The degree of impact varies with process related factors, such as raw material, pulp production methods, production output, and pollution abatement facilities, as well as with the capacity of the receiving media to sustain pollution. This "tolerance to pollution" is dependent, among other things, on media characteristics and uses of the media by the society, as well as on legal aspects and classification systems set by authorities.

A comprehensive environmental impact assessment is generally cost-prohibitive for small pulp and paper mills. Therefore, there is need to develop and test a relatively rapid and simplified method for assessing the actual environmental effects of these mills. This assessment will assist mill management in deriving full benefit from mill operations, sustain them without causing damage to the environment, and help the national agencies responsible for environmental management to enforce pertinent legislation smoothly and effectively.

Though pulp and paper mills generate wastewater, solid wastes and flue gases, this guide focuses on the wastewater discharges from these mills which are considered the major component causing degradation of receiving water and land quality.

2. Objectives

The objective of this guide is to give an outline of a basic procedure for undertaking a study on assessment of environmental effects of existing small pulp and paper mills. The basic procedures proposed in this guide for assessing the environmental effects are:

- Providing background information on the mill, its discharge characteristics and the surrounding environment;
- Determination of pollution load from the mill;
- Identification and evaluation of the effects of mill discharge on receiving water;
- Determination of permissible discharge levels to maintain acceptable water quality standards in the receiving water;
- Identification and evaluation of the effects of the mill discharge to receiving land;
- Identification of abatement and resource saving measures to achieve stipulated discharge levels.

3. Background Information

The background information to be compiled may vary from case to case, but at least the following major areas should be covered:

(a) Describtion of the mill: Location, size, raw materials, product(s) and processes;
(b) Discharge characteristics;
(c) Characteristics of receiving media; namely, river, land and air;
(d) Water and land use pattern.

4. Determination of Pollution Load from a Small Pulp and Paper Mill

The amount of pollution discharged from a small pulp and paper mill is best determined by measurements on the final effluent carried out in accordance with the NIEM "Manual on Discharge Characterization" using only minimum key parameters. The parameters for this purpose could be confined to the following:

- Flow;
- Chemical Oxygen Demand (COD) and/or Biochemical Oxygen Demand (BOD_5 at 20°C or BOD_3 at 30°C);
- Suspended Solids;
- pH.

It is recommended to calculate the parameters BOD, COD, and SS as kg of BOD, COD or SS per metric ton of product to make the figures comparable with figures from other mills. In addition, these parameters, except pH, should be expressed in mg/l to compare with the effluent standards set by local pollution control agencies.

As an alternative to the determination of the levels of discharged dissolved organic substances through a full discharge characterization program of sampling and analysis, matrices could be prepared and included in the manual where pollution load in terms of COD and BOD are plotted for various processes and raw materials. These matrices would be based on findings from NIEM Phase I and Phase II field studies and other sources. A matrix could be constructed as shown in Appendix 1 and should be based on figures prior to any external treatment.

A more reliable calculation might be obtained if the matrix is further broken down into components; namely, raw material handling and preparation, pulping, and paper making (see Appendix 2). Figures would be given for different raw materials, as well as curves given for various processes where COD or BOD is plotted against the pulp yield (pulp yield is calculated from the amount of raw material consumed and the amount of product received).

The emissions of Suspended Solids (SS) can not, however, be given in a matrix form. This parameter, as well as pH levels, must be measured individually at each mill. Also note, if measurements at the final discharge point are not achieveable, the wastewater flow can be calculated with fairly good approximation from the amount of consumed raw water.

5. Identification and Evaluation of the Effects of Mill Discharge on Receiving Water

In order to determine the effects of the mill discharge, an evaluation of the status of the receiving water in terms of selected key parameters will have to be carried out in accordance with the procedure outlined in the NIEM "Manual on Receiving Water Quality Evaluation" and the "Guide on Determination of Acute Lethal Toxicity of Pulp and Paper Mill Effluent to Freshwater Fish". For this purpose a checklist of minimum selected parameters could be set up as follows:

- Dilution ratio;
- Dissolved Oxygen;
- Chemical Oxygen Demand (COD) and/or Biochemical Oxygen Demand (BOD_5 at 20^oC or BOD_3 at 30^oC);
- Suspended Solids;
- pH;
- Toxicity.

Effects are best identified through the establishment of sampling points upstream and downstream of the discharge point. The extent of the changes in the receiving water are then assessed by preparing maps of the receiving water showing sections that are clean, mildly polluted, moderately polluted and grossly polluted, in terms of Biochemical Oxygen Demand (BOD), Dissolved Oxygen (DO) and Suspended Solids (SS) as shown in Appendix 3A, 3B and 3C, respectively. In addition, curves showing the distribution of the average values of BOD, DO and SS along the main water body at the selected sampling points upstream and downstream of the discharge point are prepared as shown in Appendix 4A, 4B and 4C. The maps and the curves will clearly identify the effects of the mill discharge on the quality of the receiving water in terms of the key parameters selected for the purpose.

Effects of the mill discharges are evaluated in terms of water quality objectives and criteria. Data should be assembled on the beneficial uses of the receiving water and the national quality criteria and standards for these different water uses. For the purpose of this guide, a simplified classification of quality criteria for different water uses covering three general river system quality states is given in Appendix 5 as example. Also, raw water used for potable supplies generally should conform to specific quality criteria limits and the range of standards proposed by the World Health Organisation (WHO).

Interaction matrices are now being prepared on the basis of the results obtained from field studies carried out during the NIEM Phase I and Phase II work for each type of process and the type of raw materials used. By comparison of the data obtained from these field studies with water quality criteria and standards it can be determined whether the impact of the mill discharge on each of the key parameters selected are significant or not. Example of the interaction matrix is given in Appendix 6.

6. Determination of Permissible Discharge Levels to Maintain Acceptable Water Quality Standards in the Receiving Waters

Discharge standards stipulating acceptable levels of the selected parameters in the final effluent should be determined in order to acheive acceptable conditions in the receiving water. The acceptable receiving water conditions or 'pollution tolerance limit' should be calculated on the basis of the type of receiving water uses and standards for this usage as mentioned above. A typical example of calculating the BOD effluent limit for discharge to a river system is given in Appendix 7.

7. Identification and Evaluation of the Effects of Mill Discharge on Receiving Land

Assessment of environmental effects on land receiving wastewater from pulp and paper mills should be carried out in accordance with the NIEM "Manual on Receiving Land Quality Evaluation". From NIEM Phase I studies, no observable adverse effects on crops irrigated with wastewater from small pulp and paper mills was noted. Therefore, the identification and evaluation study should primarily focus on monitoring effects of the mill discharges on soil, and percolate and groundwater quality. For this purpose, a checklist of minimum selected parameters could be set up as follows:

A) Soil

- Physical parameters; texture, infiltration rate and permeability
- Chemical parameters; soil saturation extract, pH and electrical conductivity (EC), cation exchange capacity (CEC), exchangeable sodium per cent (ESP) Available N, P_2O_5 and K_2O

B) Percolate and groundwater; colour, pH, EC, nitrogen

8. Pollution Abatement and Resource Conservation Measures

The environmental effect report should also contain a discussion of the need for pollution control measures. A wide range of measures are available to prevent, reduce and remedy the adverse effects; which include essentially, process modification, in-plant measures, implementation of waste treatment system, monitoring, training of personnel, and development of an appropriate environmental management plan. The best cost-effective measures to achieve acceptable conditions in the receiving media should be assessed and proposed.

APPENDIX 1

Matrix for Final Discharge in Terms of Pollution Load

Parameter: COD or BOD kg/ton of pulp prior to external treatment

RAW MATERIAL / PROCESS	MIXED HARDWOOD	BAMBOO	BAGASSE	GRASS	WHEAT STRAW	RICE STRAW	WASTE PAPER
KRAFT							
SULPHITE							
SODA PROCESS							
WASTE PAPER							

Note: The colums of the matrix can be filled after the field work under NIEM Phase I and II is completed.

APPENDIX 2

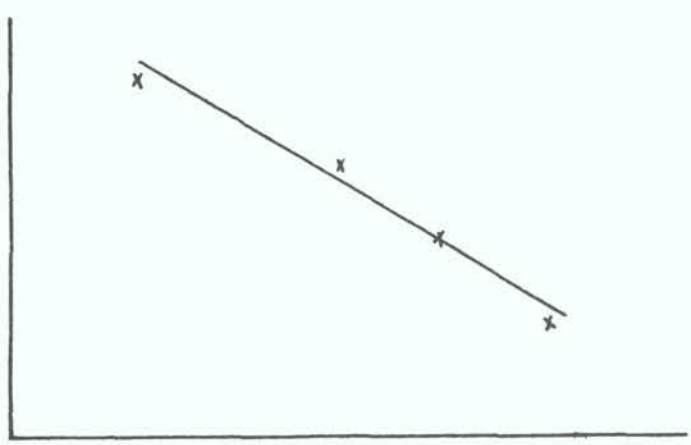
Matrix for Component Discharge in Terms of Pollution Load

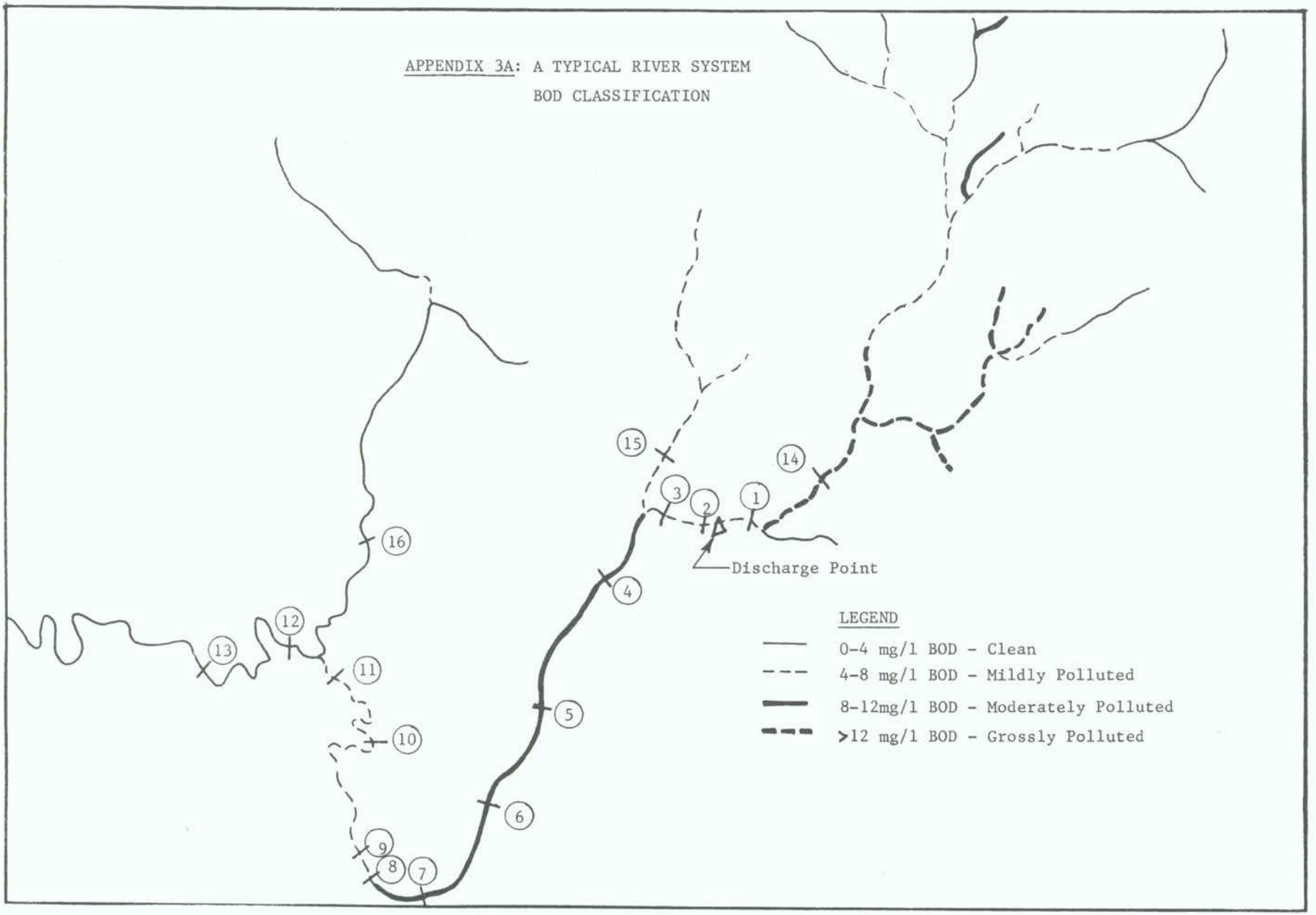
Parameter : COD or BOD kg/ton of pulp prior to external treatment

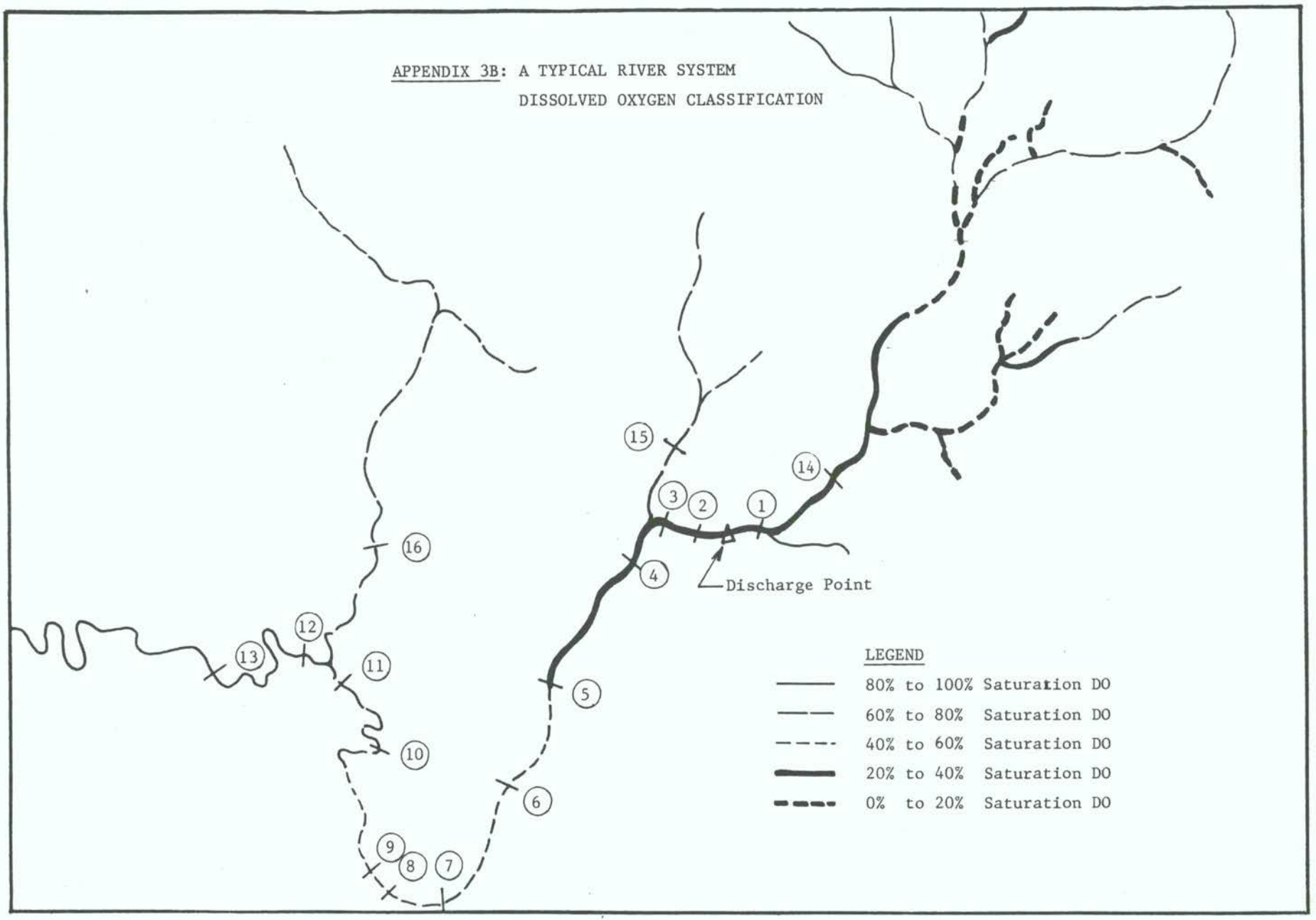
Components: Raw material handling and preparation
Pulping
Paper making

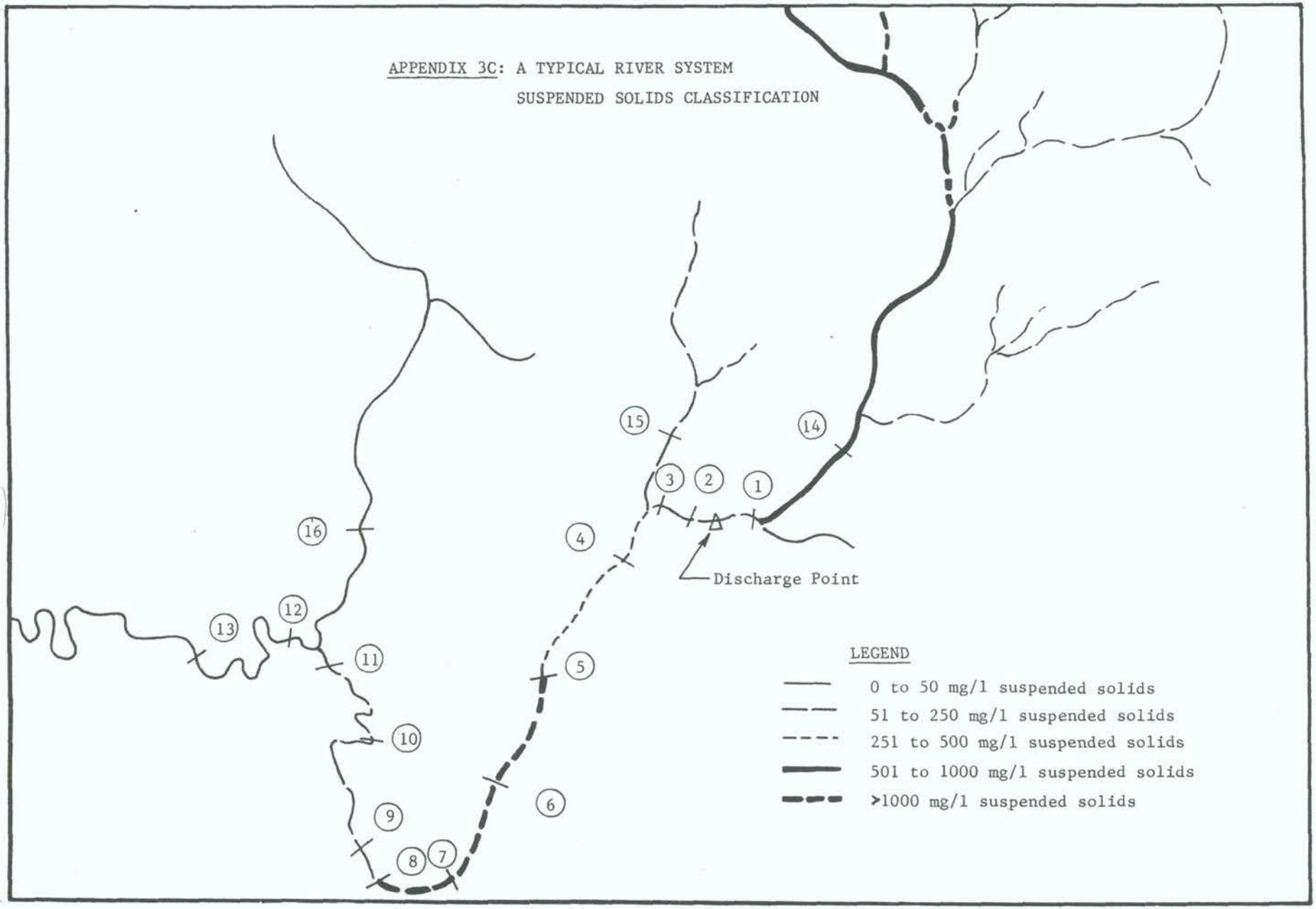
RAW MATERIAL / PROCESS	MIXED HARDWOOD	BAMBOO	BAGASSE	GRASS	WHEAT STRAW	RICE STRAW	WASTE PAPER
KRAFT							
SULPHITE							
SODA PROCESS							
WASTE PAPER							

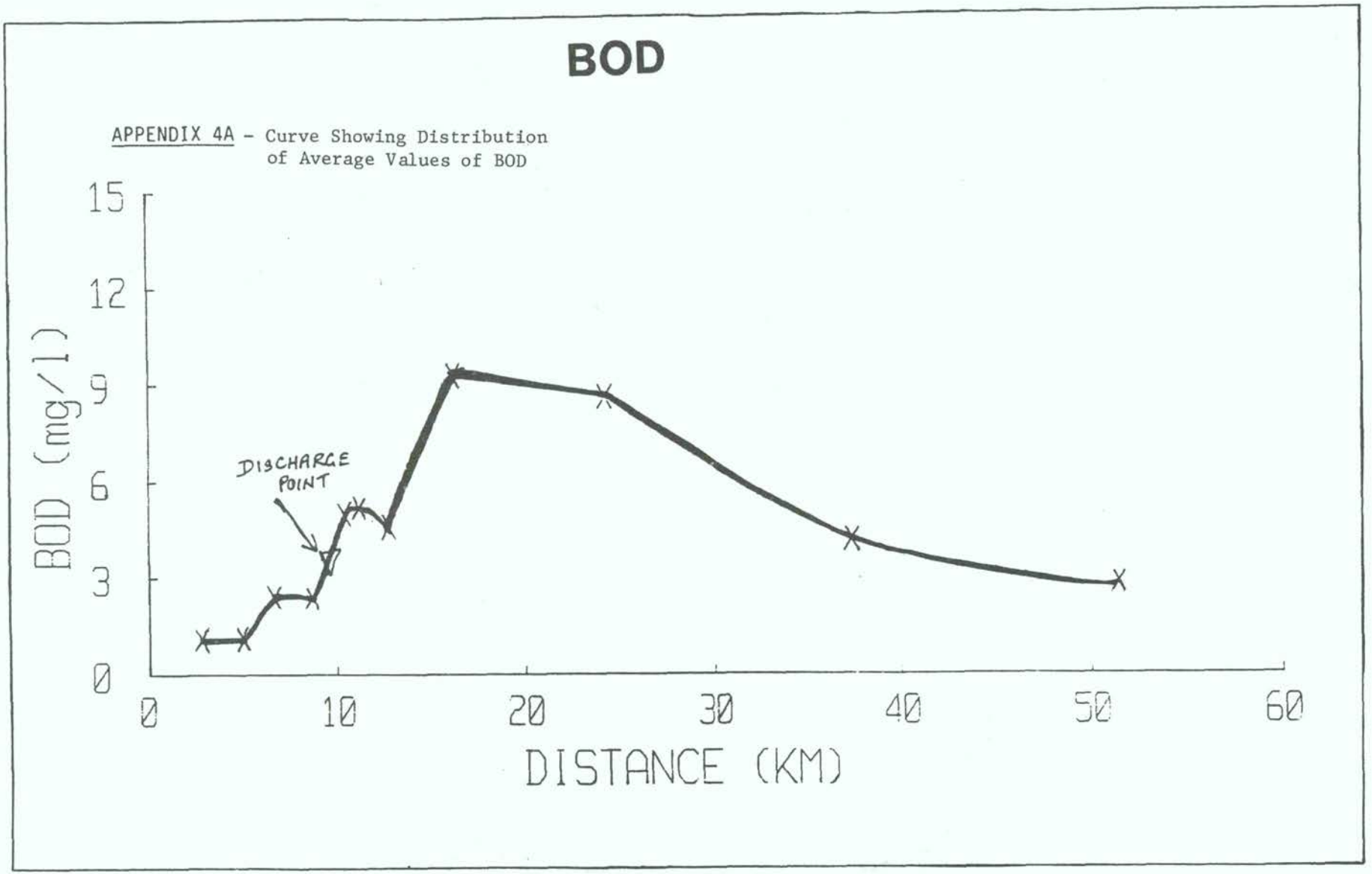
II. Pulp Yield vs COD/ BOD for various processes

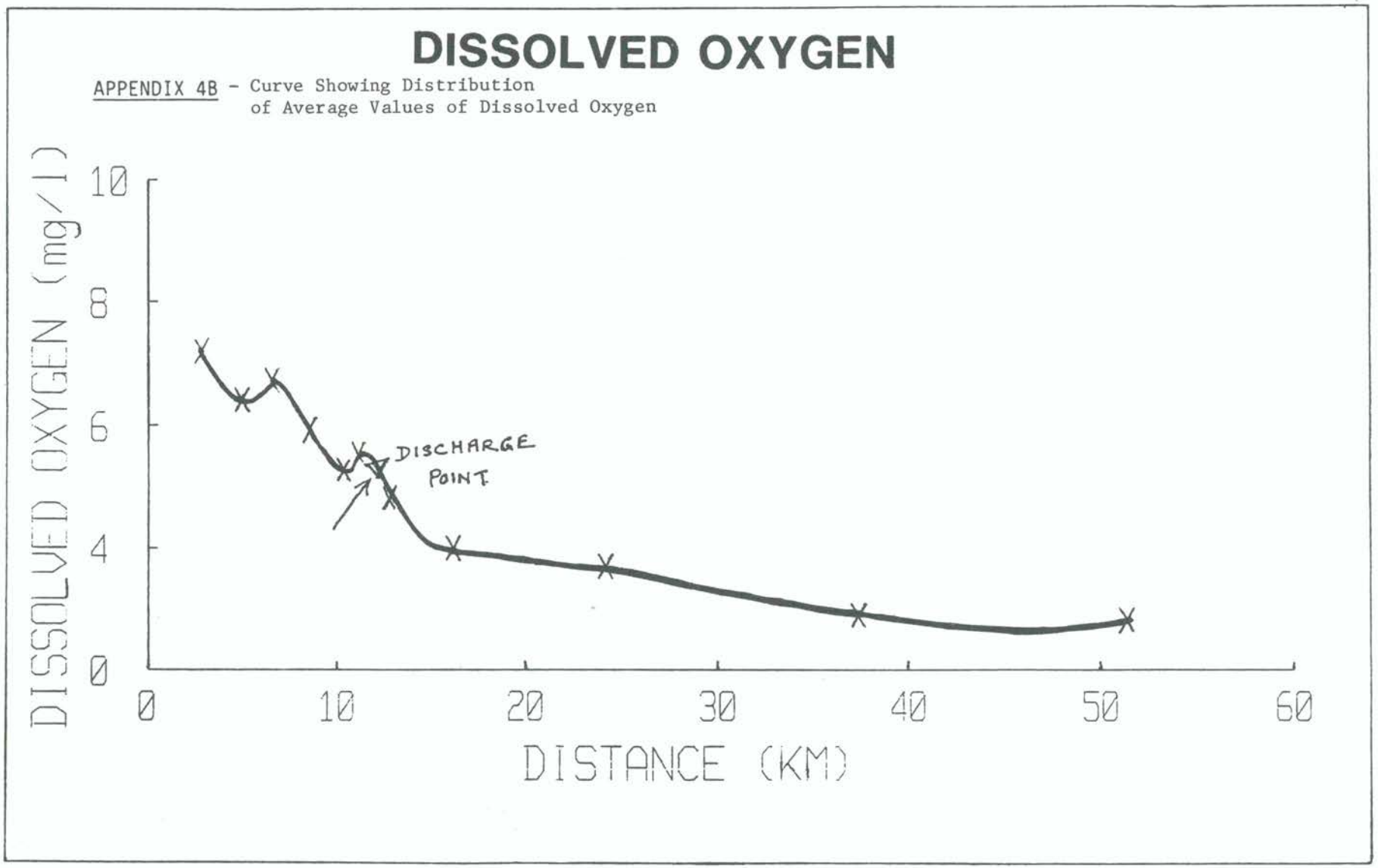



APPENDIX 3A: A TYPICAL RIVER SYSTEM
BOD CLASSIFICATION
Discharge Point
LEGEND
0-4 mg/1 BOD - Clean
4-8 mg/1 BOD - Mildly Polluted
8-12mg/1 BOD - Moderately Polluted
>12 mg/1 BOD - Grossly Polluted


APPENDIX 3B: A TYPICAL RIVER SYSTEM
DISSOLVED OXYGEN CLASSIFICATION
15
14
3
2
1
16
4
Discharge Point
12
13
11
5
10
6
9
8
7
LEGEND
80% to 100% Saturation DO
60% to 80% Saturation DO
40% to 60% Saturation DO
20% to 40% Saturation DO
0% to 20% Saturation DO

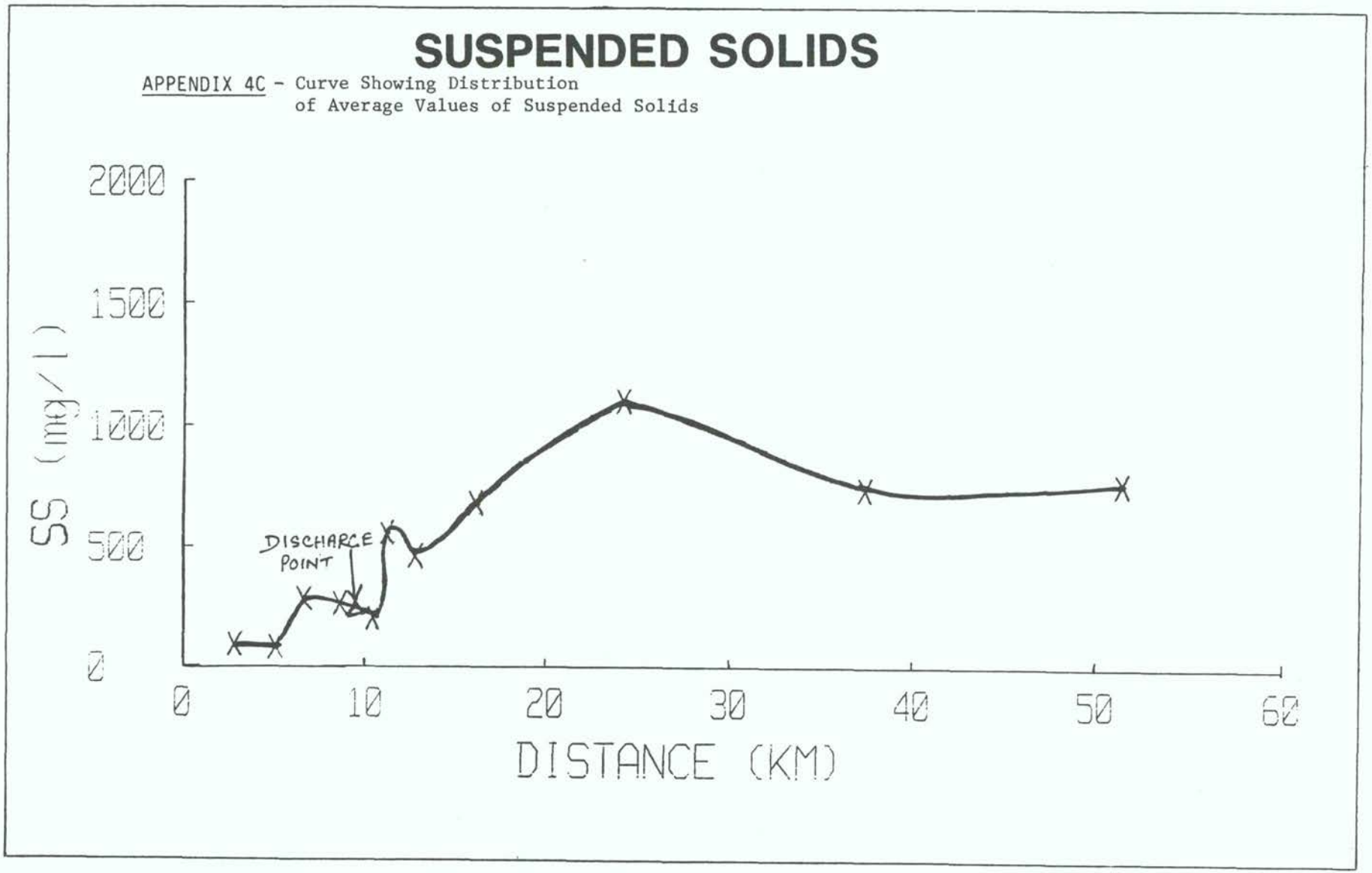

APPENDIX 3C: A TYPICAL RIVER SYSTEM
SUSPENDED SOLIDS CLASSIFICATION
15
14
3
2
1
16
4
Discharge Point
12
13
11
5
10
9
6
8
7
LEGEND
0 to 50 mg/l suspended solids
51 to 250 mg/l suspended solids
251 to 500 mg/l suspended solids
501 to 1000 mg/l suspended solids
>1000 mg/l suspended solids


BOD
APPENDIX 4A - Curve Showing Distribution of Average Values of BOD
BOD (mg/l)
15
12
9
6
3
0
DISCHARGE POINT
0
10
20
30
40
50
60
DISTANCE (KM)


DISSOLVED OXYGEN
APPENDIX 4B - Curve Showing Distribution of Average Values of Dissolved Oxygen
DISSOLVED OXYGEN (mg/l)
10
8
6
4
0
DISCHARGE POINT
0
10
20
30
40
50
60
DISTANCE (KM)

SUSPENDED SOLIDS

APPENDIX 4C - Curve Showing Distribution
of Average Values of Suspended Solids



APPENDIX 5

Water Quality Objectives and River Standards

For the purpose of this manual, a simplified classification for quality criteria for different water uses to give three general quality states would be as follows:

Standard 3: Related to a river system suitable for conveying wastewaters and perhaps, as a source of low grade industrial water after the removal of gross solids. This in fact should be the minimum acceptable standard for a river under any circumstances. It will be necessary to control toxic compounds to acceptable limits to prevent long-term ecological damage.

Standard 2: Relates to a river system suitable for casual fishing, boating, irrigation, limited industrial use after pretreatment, and for conveying effluents which do not materially affect the quality of the river water.

Standard 1: Relates to a river system suitable for bathing and water contact activities in addition to the uses listed for Standard 2. This standard of water could be used as a source of domestic supply provided it received adquate treatment.

Specific quality criteria for the three proposed standards are presented in the table below:

Quality Criteria for the Recommended Standards of River Water

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Standard 3

The water shall:

(a) be free from nuisance, odours, unsightly gross solids, floating matter, oil and grease and large organic solids that would form sludge banks;

(b) have an average dissolved-oxygen concentration of not less than 1 mg/l, but with the instantaneous value never zero;

(c) have a pH value in the range 5.5 to 9;

(d) have a temperature preferably less than 35°C (95°F);

(e) have toxic substances controlled to values of not more than twice those for a Standard 2 water, but excluding radioactive substances and mercury which shall remain the same as in Standard 2.

Standard 2

The water shall:

(a) be as for Standard 3(a) and also be free from colour and tainting compounds;

(b) have an average dissolved-oxygen concentration of not less than 3 mg/l with the instantaneous value never less than 2 mg/l;

(c) have a pH value greater than 5.5 and less than 9. Free CO_2 should preferably be less than 25 mg/l (as CO_2);

(d) have total dissolved solids less than 500 mg/l with the average suspended solids less than 100 mg/l;

(e) not contain toxic substances in concentrations greater than: cynanide 0.1 mg/l; ammonia 1.5 mg/l; boron 1.0 mg/l; detergent 1.0 mg/l; copper 0.2 mg/l; nickel 0.2 mg/l; zinc 0.3 mg/l; mercury 0.01 mg/l; chromium (hexavalent) 0.1 mg/l; lead 0.1 mg/l; cadmium 0.01 mg/l; selenium 0.01 mg/l;

(f) have other toxic subtances e.g. organo-halogenated compounds and PCB's controlled to limits acceptable to local species of fish. Typical values might be:

DDT	0.002 mg/l
Endrin	0.004 mg/l;

(g) gross beta-minus activity should be less than 1,000 picocuries/litre.

Standard 1

The water shall be similar to Standard 2 but should also have a turbidity less than 40 units, a dissolved-oxygen concentration near saturation, i.e. above 6 mg/l, and a BOD_5 always less than 4 mg/l. The MPN of coliform organisms should also be less than 500 per 100 ml.

APPENDIX 6

Evaluate the effects of the discharge from the various processes on each of the parameters given above for the different types of raw materials used through the use of an interaction matrix as given below.

Raw Material: Mixed Hardwood

PARAMETERS / PROCESS	BOD	COD	SS	pH
KRAFT				
SULPHITE				
SODA PROCESS				
WASTE PAPER				

Similar matrices developed for each type of raw material used. The colums for the matrix can be filled after the field work under NIEM Phase I and II is completed.

APPENDIX 7

Calculation of Effluent Standard for BOD for Discharge into a River System

Let x = 5-day/3-day BOD of paper mill effluent (mg/l)
y = 5-day/3-day BOD of river (mg/l) just above effluent discharge point
z = Dilution factor (i.e. proportion of river water to effluent)

Taking 4 mg/l as the maximum safe BOD in the river just below the discharge point (i.e. mixture of effluent and river water) then, by the law of mixtures

$$4(z+1) = (x \times 1) + (y \times z)$$

e.g.

If the dilution factor is 8 and the BOD of river above discharge point is 2 mg/l then the effluent standard for discharge will be

$$4(8+1) = (x \times 1) + (2 \times 8)$$
$$36 = x + 16$$
$$x = 20 \text{ mg/l}$$

Annex 6

GUIDE ON CONDUCTING NATIONAL TRAINING WORKSHOP

PREFACE

This guide was prepared based on the inputs made by members of the Network for Industrial Environmental Management (NIEM) at the first training workshop conducted under the NIEM Phase I programme held in June 1988 in Bangkok. The guide outlines the methods and procedures to be considered in organizing and conducting national and regional training workshops for mill personnel and government officials.

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GUIDE ON CONDUCTING NATIONAL TRAINING WORKSHOP

1. Introduction

Pollution control is commonly considered as an end-of-pipe-line, add-on expensive, non-profitable undertaking and hence reluctantly carried out. It should be noted, though, that waste is a misplaced resource. With this awareness, pollution control technology can be considered as an efficient resource management tool. Adoptation of pollution abatement and control, and resource recovery and recycling technologies are important strategies for providing cost-effective and sustainable industrial development.

However, this approach requires people at various levels (managers, supervisors) that are knowledgeable about pollution control methodology. Such professionals should have knowledge of:

- inputs and discharges from mills;
- sources of discharges;
- internal and external treatment methods;
- cost-benefit analysis.

A key to developing efficient and productive management is to train a large number of industry and government personnel to monitor process discharges, and use this information for process control. This training/continuing education can start through regional training of NIEM members who, in turn, are capable of conducting their own national training programme, thus generating a multiplier effect. These trainings should concentrate on how to monitor/control effluents through knowledge of:

- process;
- discharge characterization;
- receiving media quality;
- input material quality;
- environmental impact assessment.

The success of such a training programme will depend on effective organization of workshops. A structured training framework and training materials must be carefully prepared. NIEM can prepare this basic framework and training materials through an expert group having good pedagogical expertise, and particularly drawing upon the results and experience of the guidelines, handbooks and manuals prepared and used by Network members.

The basic materials should be provided with appropriate local-language audio for dissemination to various training centres throughout the Network. The NIEM Secretariat can then assist in organizing National Workshops using these basic materials through selected experienced national/international experts. The NIEM Secretariat can also co-sponsor national seminars in various member countries. The result of such trainings will be the fostering of a large competent task force capable of meeting challenges in the future.

2. Summary

1) The purpose of training workshops should be to:

- develop monitoring skills through the use of NIEM procedures/manuals;
- build strengths to generate mill data through NIEM harmonized procedures and to utilize this data to identify environmental impact;
- enhance efficient resource utilization;
- improve housekeeping and internal measures;
- develop control technologies;
- encourage process and equipment modification to optimize use of raw materials;
- help create awareness of NIEM activities.

2) Through training workshops, participants should develop skills in planning, executing, and interpreting results of discharge characterization and receiving water quality evaluation using harmonized procedures.

3) The training workshops can be:

- country or region based;
- for different target groups;
- for different areas within a country.

4) Target areas can include:

a) Discharge Characterization
b) Receiving Media (water and land) Quality Evaluation
c) Assessment of Environmental Effects

5) About 15 -20 participants for each workshop is recommended, while the target groups can be:

a) for discharge characterization:
- mill managers/ government officials/ supervisors;
- analysts/sample collectors.

b) for assessment of environmental effects:
- mill managers/ government officials.

6) Training packages should be developed centrally through expert/core group participation and include NIEM manuals, tapes, slides and video cassettes. Studies, problem solving and mill visits should form an integral part of the workshops.