



Decisions and Procedures to Cleaner Production Concerning on Liquid Effluents Assessment

A. J. G. Santos ^a, M. B. Nisti ^b

a. Universidade Anhembí Morumbi, São Paulo, godoyaj@hotmail.com

b. Instituto de Pesquisas Energéticas e Nucleares, São Paulo, mbnisti@ipen.br

Abstract

This paper describes a study for cleaner production liquid effluent assessment. The radioisotope Tritium (³H), generated in the routine operation plant was stored in a 300m³ capacity tank. The tank flow rate exit was estimated as 10.9 ± 0.9 m³.h⁻¹ for liquid controlled dispenser. The Tritium, potential pollutant was used as radiotracer for estimate the dilution factor liquid effluent. A planned release for stored effluent tank was carried-out. Simultaneously it was made sampling upstream of the storage tank discharge point, monitoring the tritium concentration in the mix sewerage system point. The initial concentration of the ³H was determined as 56881±3255 Bq L⁻¹. The estimated dilution factor for the aqueous effluent, in the discharge point E1 was of 4.3 and 7.4 respectively relative to two consecutive days of planned release and diluted effluents sampling. The developed methodology was rapid and without additional environmental or monetary costs, being able to use in industry, mining, milling, agriculture and others human production field. As the used radiotracer Tritium is already existent routinely in the effluent, doesn't increment radioisotope concentrations into sewage and environment, the goal of cleaner production practices and procedures.

Keywords: *liquid effluent, environmental assessment, radiotracer, tracer, cleaner production.*

1 Introduction

In the XX century 90 decade and beginning of the century XXI the quality systems and the environmental managing were improved, with the objective of reaching the integrated administration. This requires the administration of all the parameters which could influence in the economical components and in the company public image, including in the administration the social and environmental responsibility. The cleaner production practices were primarily used as a tool for saving inputs and reducing further treatment costs. Actually, is being viewed as a much broader perspective. Thus, more environmentally friendly companies and products are now the basic conditions for competitiveness and market survival.

The environmental management legal instruments evolution, for liquid effluents, gaseous effluents, solid residue and waste reach an integration of social inclusion and economical factors, mainly to cycling and reuse of materials, which are the bases for cleaner production technologies.

The presence of chemical species in solid residues and wastes, their redistribution in environmental compartments has been well known. Among industrial wastes containing metallic chemical forms the decisions to environmental assessment must consider dissolved organic matter (DOM), particulate organic matter (POM), residual species, interstitial aqueous and partitioning of traces in several solid phases, which are responsible by chemical disposable to biotic components (Santos, 2005, Santos et al., 2006).

The **Fig.1** presents the evolution of the environmental administration and management in Brazil, being considered the social and economical component, in the last decades.

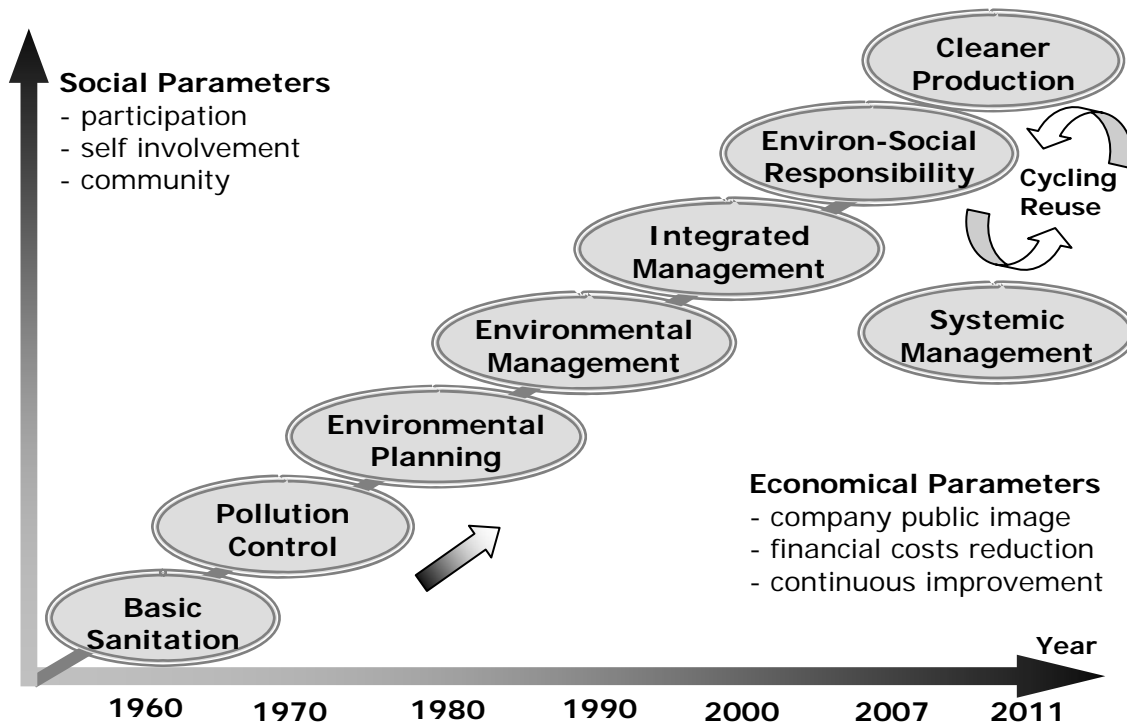


Fig. 1. Environmental management evolution in the Brazil.

The demand for establishment of cleaner procedures for environmental assessment of liquid and gaseous effluents, as well solid residue and waste, requires the implantation of industrial technologies that not include news pollutants to environmental compartments (Nisti, 2009, Nisti et al., 2009).

The current Brazilian regulation foresees that the operational management concerning to liquid effluents release considers the characteristics of the discharged liquid, the knowledge of the dispersion conditions after discharge into the system receptor (sewage and environment), the characteristics description of the effluent receiving system environment and the estimate of the human dose (Nisti et al., 2009).

According to Brazilian environmental rules, regarding liquid effluents releases, all material generated at industrial facilities or laboratories are generated, stored and monitored for their respective quantification of potential pollutants. Are used retention tanks or flasks and treatment station submission. Each batch of the effluents generated must be representatively sampled and analyzed prior to discharge to environment or sewerage system. Within this programme, liquid effluents are analyzed on a regular basis for great regulations (CONAMA, 2005, DOE-SP, 1976).

Considerable attention has been paid to cleaner production (CP) in the Brazilian industry, actually. The promotion of CP in the region's country has been significantly boosted by the establishment of various nucleus studies in academy. In the São Paulo State, the Federação das Indústrias do Estado de São Paulo (FIESP) has supported incentives and development of CP concepts and projects in universities for industrial field improvement. Initiatives such as study cases publication, annual prizes for undergraduate student projects in CP, workshops and discussion forums had contributed to advances and accomplished of CP practices.

Several technological centres, universities and other organizations have incorporated the approach into their training programmes in their endeavor to create a more sustainable Brazilian industry. Among the main factors responsible for this interest in CP, are the Brazilian economic stabilization and the need to maintain their industries' competitiveness in both the local and foreign markets.

In countries that have a strong pollution control structure, this structure functions as an additional incentive to CP. On the other hand, in countries that recognize their shortcomings in relation to the enforcement of the environmental police law, CP is strategic to industries as an alternative for environmental quality preservation outside the formal legal framework. Reach such purpose in the enterprise, it is necessary to manage the environmental parameters under regulation and police into local and federal bases.

2 Methodology

Tritium is produced naturally in the upper atmosphere when cosmic rays strike nitrogen molecules in the air. Tritium is also produced during nuclear weapons explosions, as a byproduct in reactors producing electricity, and in special production reactors, where the isotope lithium-6 is bombarded to produce tritium.

In research reactor operation is also generated Tritium in the radioactive liquid effluent. It is a routinely monitored radioisotope. This measurement is performed after a representative sample is taken of the effluent to be discharged; it determines whether the effluent may be discharged into the receptor sewerage system and sets discharge conditions.

Radioactive wastewater generated at the plant, via a sewer network, to the Barueri Treatment Plant (ETE-Barueri), which is owned and operated by Companhia de Saneamento Básico do Estado de São Paulo, SABESP (Nisti & Santos, 2008). The ETE-Barueri provides wastewater treatment for residential, commercial and industrial customers in the southwest place of the São Paulo Metropolitan Region. It is the main system under the region where the radioactive effluent release study had influence.

These results presents an evaluation and estimative of the dilution factor, considering the recent facilities, the reshaping of the sewerage system and the Tritium concentration in the retention effluent evaluated and comparative with the monitoring data downstream of discharge point.

Dilution of effluents is one parameter that was used for estimating a more realistic radioactive dilution effluent factor. Consideration of dilution factors liquid effluents released from nuclear and radioactive facility in Brazil is a recent rule [CNEN,2005; CNEN 2005a), complementing preliminary regulation (CNEN, 1988).

Then, as the release is strongly dependent on the total amount of the effluent and on the dilution factor, special attention is needed in order to obtain the correct value of that last one (Nisti & Santos, 2008; Nisti, 2009).

2.1 Tritium Radiotracer Use

Liquid effluents from storage tank, with a potential to contain radioactive materials at prescribed threshold levels were measured for specific radionuclides. Quantities of the Tritium with a total $1,08 \cdot 10^{10}$ Bq, 2008 year source-term were determined. However, most radionuclides in effluents at the tank are approaching levels indistinguishable from background concentrations. Tritium was measured by liquid scintillation counting (LSC) technique (Nisti,2009).

Tritium may be produced in nuclear reactors by the following five mechanisms: (a) fission product, (b) neutron capture reactions with boron and lithium added to the reactor coolant, (c) neutron capture reactions with boron in control rods, (d) activation of deuterium (hydrogen-2) in water, and (e) high energy neutron capture reactions with structural materials.

A second source of fission-product Tritium in nuclear reactors is due to traces of uranium on the outer side of fuel elements which remain from the fuel fabrication process. This tramp uranium may be only a few micrograms per square inch of fuel surface, but because of the large surface area provided by the many fuel rods in a reactor it can produce detectable fission-product concentrations in the coolant.

The liquid scintillation counting is an analytical technique which is defined by the incorporation of the radionuclide into uniform distribution with a organic liquid chemical medium capable of converting the kinetic energy of nuclear emissions into light energy photons. The scintillation fluid is a mixture of 3 chemicals (solvent, emulsifier, and fluorine) which produces light flashes when it absorbs the energy of the radioactive decay particle.

The interaction of the energies beta for the liquid middle is processed by excitement, and they emit photons of ultraviolet radiation returning to first fundamental state. The photons happen in a tube photomultiplier, where the electrons are multiplied generating a proportional electric sign to the number of incident photons. The sample Tritium concentration was determined by the equation 1.

$$C = \left(\frac{Ca}{Ef_{a,V}} - \frac{Bg}{Ef_{bg,V}} \right) \quad (1)$$

Where:

- C: Tritium sample concentration (Bq L⁻¹)
- C_a: sample counting (cps)
- B_g: background radiation (cps)
- E_{f_a}: sample counting efficiency (cps dps⁻¹)
- E_{f_{bg}}: background counting efficiency (cps.dps⁻¹)
- V: sample volume (L)

Quench is a reduction in system efficiency as a result of energy loss in the liquid scintillation solution. Because of quench, the energy spectrum detected from the radionuclide appears to shift toward a lower energy. The three major types of quench encountered are photon, chemical, and optical quench. Chemical, sometimes called impurity, quenching causes energy losses in the transfer from solvent to solute. Photon quenching occurs with the incomplete transfer of beta particle energy to solvent molecules. Optical or color quenching causes the attenuation of photons produced in solute.

The Quench-indicating Parameter is the Spectral Index of the Sample (QIP) and the external source quench-indicating parameter is the transformed Spectral Index of the External Standard (tSIE). The counting efficiency was certain for the methodology "transformed Spectral Index of the standard External" (tSIE) using a source ^{133}Ba , wherein each radionuclide equation is near linear and is expressed in the form below.

$$y = mx + b \quad (2)$$

Where:

y : QIP value;

m : slope of plot of SIS versus tSIE;

x : tSIE value,

b : intercept on SIS axis of a plot of SIS versus tSIE.

The dilution factor estimated for radioactive sample effluent in the sewerage point was obtained by equation 3.

$$Fd_{E1,i} = \frac{C_{tr1,i}}{C_{E1,i}} \quad (3)$$

Where:

$Fd_{E1,i}$: sewerage point E1 Dilution Factor for radioisotope i .

$C_{tr1,i}$: radiotracer i initial concentration (Bq L^{-1}) for effluent inside storage tank.

$C_{E1,i}$: radiotracer i concentration (Bq L^{-1}) in sewerage effluent sampled (Bq L^{-1})

2.2 Sample Pre-treatment and Measurement

The radioactive liquid effluents samples were homogenized by magnetic plate and an aliquot of 50 mL was transferred with volumetric pipette for a distillation apparatus. The controlled temperature was staying from 96 to 97 °C with heating controller. The distillation process was very slow. The first 10 mL of the distilled was discarded, after was recoiled a distilled volume of about 10 mL.

An aliquot of 1,2 mL was transferred by using micro-pet inside a 20 mL capacity scintillating vial. Scintillator solution Instagel-XF, 18 mL, was increased and gentle mixed for approximately 1 minute, until the total solution homogenization. After the homogenization the cocktail was refrigerated and kept at dark place by a minimum period of two hours before the liquid scintillation counting.

2.3 Calibrations and Methodology Verification

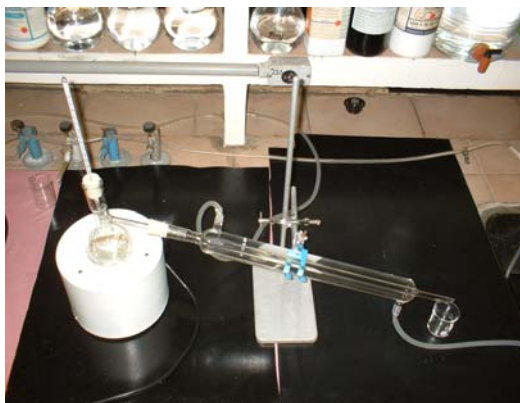
A Tri-Carb model 2100TR Liquid Scintillation Counter composed by two photomultiplier tubes coupled to a discriminator signal pulses was calibrated with the adopted cocktail. The time counting was of 120 minutes. For background radiation detection system determination same scintillating vial kind with deionized water was used, in the same amount and experimental conditions.

In this study, the efficiency counting was determined by the relative quenching of the sample, by using an external source quench-indicating parameter (QIP) such as the Spectral Index of the External Standard (SIE). This method involves counting the sample with a gamma radiation source (^{133}Ba) external the vial and subsequently in the absence of the gamma radiation source such that the contribution of only the gamma radiation source is studied. The gamma radiation

source generates Compton electrons in the sample solution which behave in a similar manner to decaying nuclear particles.

If quenching is present the pulse-height energy distribution spectra from the gamma radiation generated events will be compressed towards a lower apparent energy. External standard quench-indicating parameters (QIP) include the external standard ratio (ESR), Spectral Index of the External Standard (SIE); H Number, ESP and the transformed Spectral Index of External Standard (tSIE).

The **Fig. 2** shows the distillation apparatus, liquid scintillation counter system and steps in collecting samples of liquid effluents in sewerage point, after controlled discharge from storage tank.



Distillation apparatus for Tritium purification before analysis



Liquid scintillation counter for Tritium measurement in samples



Adjustment of the sampling peristaltic pump in sewerage collecting sample



Cooled sample from sewerage point in controlled

Fig. 2. Distillation apparatus, liquid scintillation counter, sewerage sampling steps in the station monitoring.

2.4 Effluent Dilution Factor Estimative by Tritium Effluent Radiotracer Use

After calibration and verification method the counter was then used to measure tritium levels in effluents samples from tank storage and discharge sewerage point.

The procedure for effluent dilution factor determination in the sewerage discharge point E1 was the following. Three samples of $1.00 \pm 0.10\text{L}$ were collected of the retention tank before of the planned and controlled effluent release. The Tritium, generated as operational unfavorable radioisotope in the studied process, was used as a able radiotracer.

3 Results and Discussion

For the curve quenching construction were used 6 quench cocktail standard with different quenching agents with activity of 327 ± 18 Bq and an standard without quench with activity 4630 ± 68 Bq. The efficiency results and the propagated uncertainties are presented in the Table 1.

Table 1. Calculated counting efficiency by tSIE method for Tritium liquid scintillation counting

Activity (Bq)	QIP	Efficiency (cps dps ⁻¹)
4630	976	0,62 ± 0,02
327	614	0,50 ± 0,03
327	499	0,45 ± 0,03
327	396	0,38 ± 0,03
327	320	0,33 ± 0,02
327	238	0,25 ± 0,02
327	114	0,10 ± 0,01

The **Fig. 3** presents the curve with quenching parameters for ³H calculated for the present study, the ones which were adjusted by shown degree 4 polynomial equation.

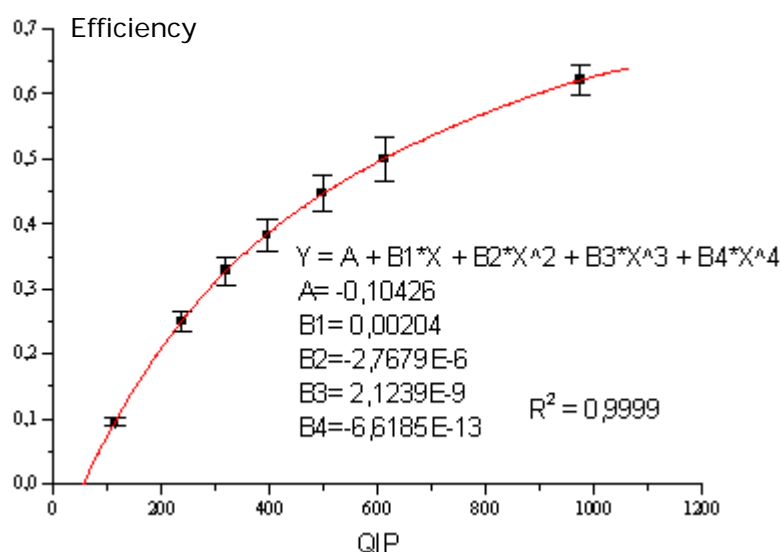


Fig. 3. Quenching curve obtained for Tritium radioisotope by liquid phase scintillation counting

In the Tritium calibration results shown in **Table 1** and **Fig. 2** note the extremes of values for the quenching parameter (tSIE). A maximum efficiency of approximately 62% was achieved with a quench parameter (QIP) of 976. The medium efficiency of about 38% was obtained with a quench QIP of 396. Thus a quench QIP of 114 or below would result in essentially very close background counts (efficiency < 10%).

The reliability efficiency and methodology verification was accomplished by participation in the Brazilian Intercomparison Analytical Results Run, called Programa Nacional de Intercomparação (PNI), following the same procedure. For

the runs participation, the obtained results for Tritium quantification presented an excellent agreement with the real value.

No environmental or financial costs were added by this operational and *in loco* radiotracer assay. The concentration of ^3H was analyzed by LSC, three spectra evaluated and calculated the concentration average and their respective standard deviations. The found value for Tritium concentration was $56881 \pm 3255 \text{ Bq L}^{-1}$ before planned effluent discharge. The flow rate effluent discharge retention tank was estimated by measuring the inside tank liquid high. The estimated value of $10.9 \pm 0.9 \text{ m}^3 \cdot \text{h}^{-1}$, for liquid controlled dispenser was determined.

After the initial sampling effluent tank, continuous samplings were carried out in the discharge point, simultaneously to the effluent tank controlled release. The ^3H concentration was obtained by LSC, for each discharge point effluent sample and spectra evaluated for calculation of the ^3H concentration average and their respective standard deviations.

The ^3H concentrations obtained, for effluent tank and for the effluent discharge point, were compared and the pertinent dilution factor was estimated by equation 3. The Table 2 presents the results of the ^3H radiotracer concentration and uncertainties (Bq L^{-1}), for each sewerage point collected effluents samples, during the retention tank controlled effluent discharge, for two consecutives study days period. The Table 2 shows also the estimative and average effluent dilution factor, for sewerage effluent point.

Table 2: Concentrations and uncertainties of the ^3H radiotracer in sewerage point effluents samples and estimated dilution factor.

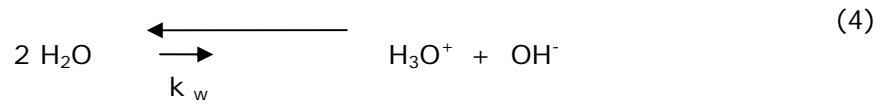
Day	Time	^3H (Bq L^{-1})	Dilution Factor
1	9h37	10361 ± 518	5.5
1	10h35	14881 ± 748	3.8
1	11h31	21963 ± 1098	2.6
1	12h37	14629 ± 732	3.9
1	13h33	11247 ± 563	5.1
1	14h30	11913 ± 596	4.8
	average		4.3
2	9h35	9727 ± 486	5.8
2	10h30	9849 ± 493	5.8
2	11h20	5367 ± 269	10.6
	average		7.4

As shown in the Table 2, the estimated dilution factor for the aqueous effluent, in the discharge sewerage point was of 4.3 and 7.4 respectively to day 1 and 2, consecutive for planned release and diluted effluents sampling.

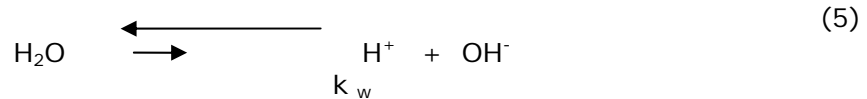
Tritium is a hydrogen atom that has two neutrons in the nucleus, in addition to its single proton, giving it an atomic weight near three. Although tritium can be a gas, its most common form is in water, because, like non-radioactive hydrogen, radioactive tritium reacts with oxygen to form water. Tritium replaces one of the stable hydrogens in the water molecule, forming tritiated water.

Tritium readily forms water when exposed to oxygen. Like H_2O , tritiated water is colorless and odorless. Tritium has a half-life of 12.3 years and emits a very weak beta particle and transforms to stable, nonradioactive helium.

Tritium atoms can exchange with any hydrogen atoms. If the hydrogen atom is part of an organic molecule, the tritium becomes organically bound and is transported with the molecule rather than moving freely like water. Thus, the equation 4 and 5 present the mechanisms for Tritium dispersion and dilution in aqueous medium.



In a simplified way it can be written as the equation 5



Where:

k_w : self-ionization water equilibrium constant

The ion H^+ present could be formed starting from the atoms of the Hydrogen (^1H) or Tritium (^3H), which possess same properties and behavior physical, chemical and energy, besides all the characteristics of the element Hydrogen ($Z=1$). The dilution factor estimated for Tritium radioisotope corresponds to the water dilution factor. Emphasizing that water is the solvent or macro constituent of the effluents release at storage tank.

The **Fig.4** shows a procedure protocol for use of the practical dilution factor generated applying the tritium radiotracer for operational estimative dilution factor of liquid effluents.

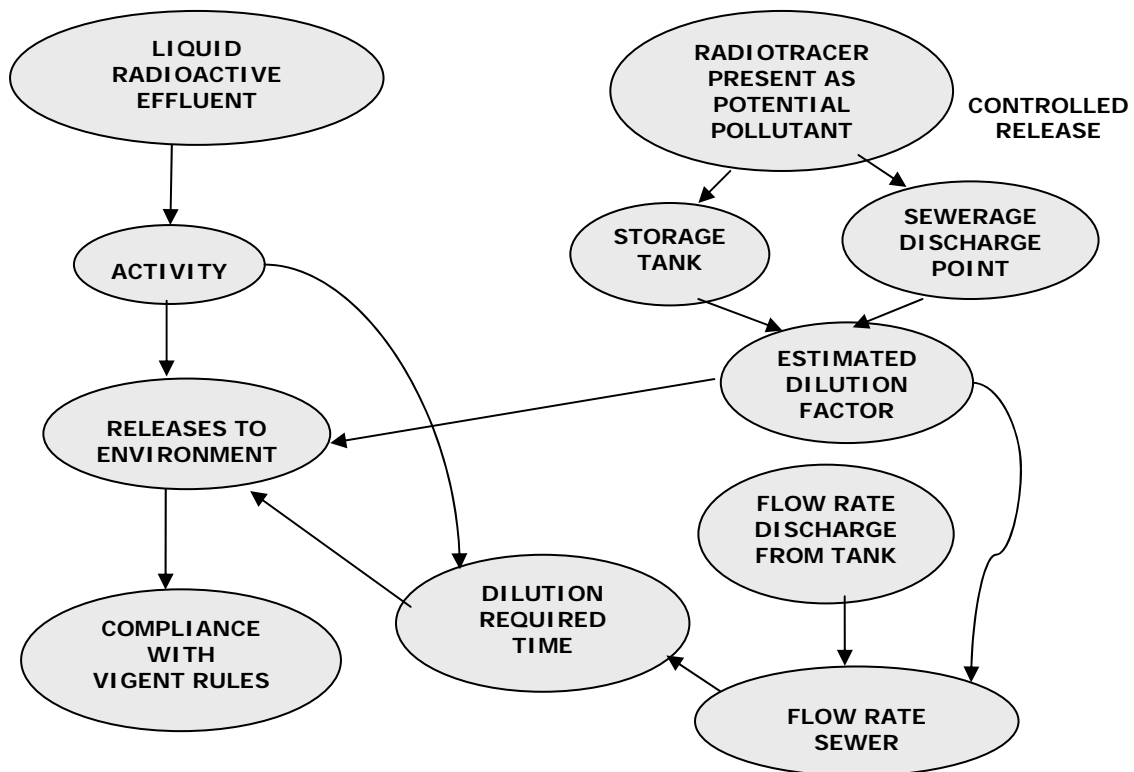


Fig.4. Possible environmental management procedure for liquid effluents, after potential pollutant Tritium use as a tool for dilution factor determination.

3 Conclusions

This paper shows that the cleaner production is the continuous application of an integrated preventive environmental strategy to management services that need procedures to increase eco-efficiency and to reduce risks to humans and environment. Its require attitudes changing, ensuring responsible environmental management, creative conductive companies policies and evaluation technology options.

The Tritium, generated as operational unfavorable specie was used as a able radiotracer. No environmental or financial costs were added by this operational and *in loco* radiotracer assay. The procedure for dilution factor estimative was cleaner, without radioisotope increment concentrations into sewage and environment. Carried out without additional environmental or monetary costs, accomplished the cleaner production practices and procedures propose.

In this case was used a radioisotope Tritium for operational estimative dilution factor of liquid effluents. The use of a potential pollutant to estimate the dilution factor of the aqueous effluents is able to conventional industry, radioactive or nuclear plants. Could be carried out for all chemical species, generated in process and sent for storage effluent tank or treatment station. Able for human production field, such as mining, milling, engineer, agricultural, public urban area policy, transportation and tourism actions. In addition, a table of expected dilution volumes may be prepared by continuous monitoring, case to case.

The dilution factor estimative came possible a procedure protocol for use of the practical dilution factor generated in optimization discharge of liquid effluents in production.

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