PRESENCE AND IDENTIFICATION SCREENING OF PRIORITY/PRIORITY DANGEROUS SUBSTANCES IN MUNICIPAL SEWER DISCHARGES OF ROMANIAN ECONOMIC AGENTS – PROGRAM'S ACTIONS IMPLEMENTATION INSTRUMENT FOR MEETING ENVIRONMENTAL QUALITY STANDARDS BY 2027

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Abstract

Aspects of environmental actions taken by economic agents are presented in order to comply with Water Directive regulatory bases and the Romanian corresponding laws for meeting the 2015' and 2027' targets of preserving the good and very good water quality for the majority of water bodies in Europe. In this respect a program for progressive reduction and elimination of priority/priority dangerous substances in municipal sewage system should be implemented. Pollution pressures put by hazardous substances should be analyzed. The analysis is required by Governmental Order 31/2006 and Governmental Decisions 351/2005 updated with 1038/2010 and is view as a technical document that identifies and evaluates the potential hazards for sewage system and water bodies receiving the wastewaters from sewage system. The presence of pollutants is analytically determined at the final point of discharge before the sewage system and it is assessed in relation to the site activities/products and services to assist the appropriate environmental actions to be taken. It is a link between site investigation activities and response actions carried out to address hazards posed by the presence of dangerous substances/priority dangerous substances to the sewage system. During over forty performed screenings in different Bucharest sewage system areas, where

economical agents discharge their urban waste waters, we founded interesting practical aspects for regulatory authorities, for industry and for the organization that has in administration the Bucharest sewage system. Those aspects have been recorded, analyzed and their results are discussed considering the risk for human consumption as final target to be assessed. Conclusions are finally presented in relation with the general consensus that should be reached in order to fulfill the sustainable development principles and to meet the set targets.

Keywords: screening, priority/priority dangerous substances

1. Introduction

The Water Directives 60/2000 and 90/2009 [1] implemented through a set of Romanian laws such are: Governmental Decision 458/2002 [2], Governmental Decision 352/2005 [3], Governmental Decision HG 351/2005 [4], Governmental Order 31/2006 [5] and Governmental Decision HG 1038/2010 [6] along with their connective environmental legislation, represent the legal frame for the fulfillment of the program of measures for progressive reduction and elimination of priority/priority dangerous substances from water bodies. They are in the attention of regulatory water bodies for posing risk for water ecosystems, human general consumption and ultimately for the human health. They are toxic by their intrinsic nature; they are persistent having a very long half life time in the water ecosystems and they are bio-cumulative because the ecosystems of usual water bodies are not able to transform them in less dangerous substances. Classified into three general categories as volatiles, semi volatiles and heavy metals they have been listed according with their corresponding CAS Number (Chemical Abstract Service Number) for the correct identification. In practice the real challenge that arises is due to the fact that rather rare than often waste water discharges contain pure substances. Instead mixtures of any physical state like suspensions, emulsions, solutions from waste water discharges should be assessed for their toxic, persistent and bio-cumulative characteristics based on available data for pure components of the same or similar mixtures. Unfortunately, is generally recognized by environmental regulatory bodies that is impossible for world wide chemical producers' community to offer environmental and toxicological data for each type of mixture. In this situation the Audit Analysis, Screening is an endeavor that should help through a well documented basis to assess the hazards put by those discharges when they consistently and constantly exceed the required environmental standard limits. The paper will focus on biological effects some of those substances might have when exceeding certain limits and the way they are regulated in past and present legislation. The present technical possibilities of decontamination that can be used by economic agents in order to preserve the sewage system are also discussed emphasizing the costs efficiency.

2. Experimentals

We designed a methodology to be used in hazards pre-assessment/assessment starting from the practical need of helping industrial economical agents to correctly assess sewage water pollution related to their

activities/products/services in order to benefit from an appropriately set permit discharge limits according to the legal regulatory system current in place in Romania and in Europe following the next flow of information.

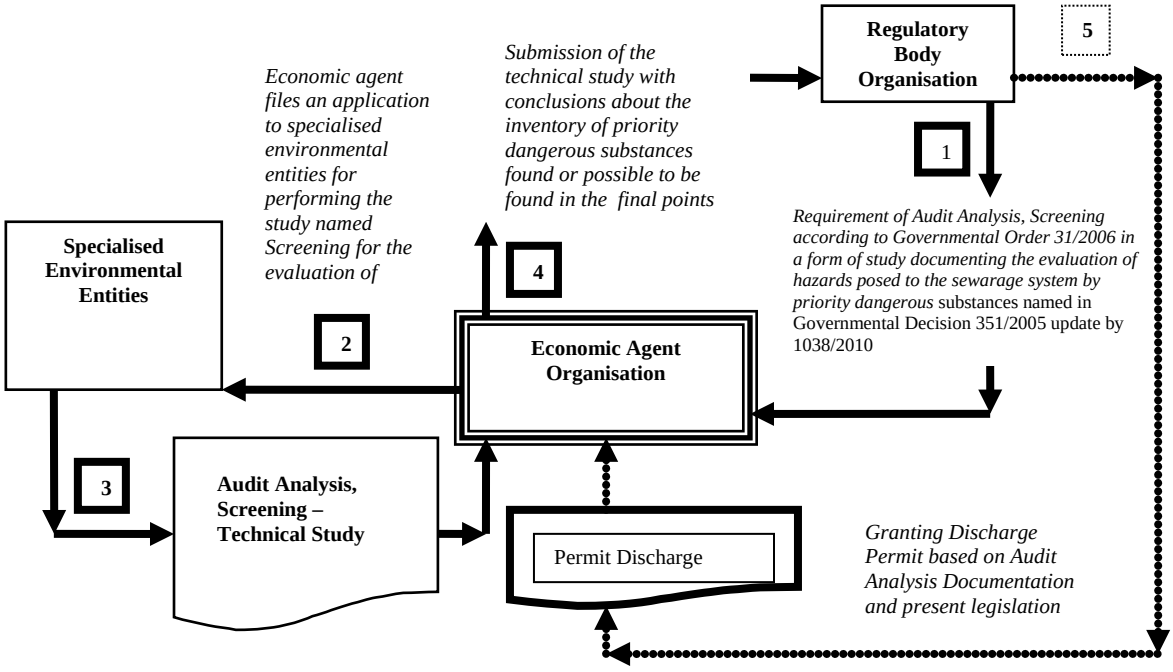

Fig. 1 – Methodological flow of information in screenings

European laws - Water Directives 60/2000 and 90/2009 - encourage each country to apply "polluter pays principle" "precautionary principle" and "inter-generational equity" in establishing the environmental standard limits in a specific way for each country situation taking into account the type of pollution, the hydrological specific regime, the hydrographic potential and last but not the least the possibilities for the actual local de-pollution, BAT type techniques that by definition should be economical feasible for implementation in order to reach the required limits. Those limits should be measured with the appropriately analytical techniques able to reach those limits giving results of known and defensible quality. In the audit analysis approach that we proposed, the used methodology has two basic steps: one step in which the presence of substances from updated HG 351/2005 with HG 1038/2010 is identified at the final point of discharge before municipal sewage system trough specific laboratory analytical tests procedures and the second step in which those substances are identified among the used substances during current activities trough a theoretical site documentation realized as an audit type procedure. First step is carried out through two analytical methods ICP-OES – (English

Acronym for Inductively Coupled Plasma – Optical Emission Spectrometry) for the metals and GC-MS (English Acronym for Gas Chromatography and Mass Spectrometry) for volatile and semi volatile compounds. After test results are ready, one goes for the second step which is a site audit where the documents about raw, auxiliary, intermediate and waste substances are examined in relation to the existing activities/services and products. The possibilities of those substances to make contact with water and reach the sewage system are also considered. The way the Audit Analysis is conceived might be an ante-factum practical assessment (before a remediation – e.g. any program measures to progressively eliminate substances from Governmental Decision 351/2005 and Governmental Decision 1038/2010 in order to fulfill Water Directive objectives) or, might be a post-factum (after a remediation was performed). Our methodological approach offers in either case a course of action to serve the assessment purpose in order to be able to offer an inventory of relevant substances that put environmental pressures on the sewage system and further on Dambovita river. The audit analysis is based on specific criteria such are: 1) the potential of target exposure - in this case Dambovita river - to the direct or indirect pollution considering the current accepted qualitative standards of the water resources according to HG 352/2005 and HG 1038/2010 and 2) the possibility of downstream pollution extension - i.e. the migration and amplification of pollution beyond the existing assessed municipal sewage area - due to discharges made by many similar polluters justifying stricter monitoring and control measures than those normally applicable for the type of water use - sewage system. It should be mentioned that the law limits that should be detected by those high-performance methods should reflect both the environmental awareness /concern posed by discharges of those substances but also technological possibilities for reaching the imposed limits. Strengthening the law limits does not ensure by itself the practical implementation of those standards by each presumptive polluter because they should be able to reach them by using the actual general international recognized depollution techniques. By using usual waste waters depolution techniques involving physic-chemical mechanisms such are: precipitation and co-precipitation followed by coagulation, flocculation, sedimentation, flotation, filtration, oxidation, ion exchange and seldom biological processes, some of those limits that are in the range of the almost mountain waters natural background, cannot be reached without extra costs. It should be noticed that in the new regulation law HG 1038/2010 the limits (see Table 1 column 5) are even stricter than actual limits for potable water (see Table 1 column 3) that are currently stated both in Romanian legislation and in other countries and hardly can be reached trough normal methods most probably requiring the use of more sophisticated techniques. It is also obvious that using the state of the art techniques should not be cost prohibitive for each economic agents in the context of applying "polluter pays principle" as Water Directive recommends in order to recover sewage and water decontamination costs. The law limits required by the latest law regulation HG 1038/2010 (see Table 1 column 5) are commented in the next section having as debating material the recorded conclusions from over 40 audit analyses performed at different economic agents discharging in Bucharest municipal sewerage system.

3. Results and discussions

In the Table 1, we listed the metals that have been found with higher prevalence in sewerage discharges from economic agents involved in a variety of industrial activities and services such as: metals' processing, plastics, building and construction materials, food, textile, production of paintings, coatings, chemical products, cosmetics, pharmaceuticals and also services in food, printing, and auto industries etc. Column 2 presents usual concentration ranges found in those audit analyses and column 5 presents standards/limits from HG 1038/2010 Romanian law considering also the recommendations of European Directive 105/2008. The law is stipulating that for the substances of interest included in its Annex 2 -Table 1 according to art. I point 5 "the program of measures against pollution with chemical substances for specific pollutants" should be applied in order to comply with yearly average stated limits. The law doesn't mention any specific dead line except for the Annex 2 -Table 3 were the dead-line is 2027 but this law is made considering the fact that Directive 60/2000 has as target the year 2015 for reaching the potential good and very good for water quality for 80% of the water bodies in each country member. In the Table 1 of this paper we present a relevant comparison between the values ranges found in the performed test analyses pre-assessments (see Table 1 column 2) and the law requirements at level of May 2011 for different water resources uses (potable waters - HG 458/2002 - Table 1 column 3 , sewerage waters-HG351/2005 Table 1 column 4). When examine the limits stated in HG 1038/2010 column 5 of the presented Table 1 we observed that most of them are in the order of ppb (< 8 μg/L) ranging generaly speaking from 0.7μg/L –for cobalt to maximum 100 μg/L – for Zn. Those limits are very low ones to reach with normal techniques in the field of waste water treatment technology. The reason for such strict limits might be justified by the biological importance of those metals at similar order of concentration in our body. To be able to comment the results from different audit analyses with the above-mentioned law references for the listed heavy metals we should mention that metals are required in trace amounts as micro-functional elements being involved in many different physiological functions with reference to the human body being classified in biological useful and biological detrimental. But even those included in the biological useful category such are: Fe, Cu, Zn can be dangerous when homeopathic doses are not met. This means that deficit or excess of them comparing with normal metabolic equilibrium concentrations can produce different type of acute or long term damages for the organism. Other metals that are not part of the biological useful category such as Cd, Hg, Pb, As, have not known benefits and their accumulation over time depending on metabolic specificities can cause acute, chronic illness and premature death. Information from technical reports of international organizations such is World Health Organization that include the best known general recognized

Table 1

Substances/ Metals/Compounds) - CAS Nr. (Chemical Abstract Service Nr)	Ranges of Substances/Metals/ Compounds found in performed screenings in μg/L	Limits stated in HG 458/2002 - Table 2 - Potable Water System <in μg/L>	Limits stated in HG 352/2005 - Table 1 - Sewer System of Localities <in μg/L>	New Limits according to HG 1038/2010 <in μg/L.> Table 2	Previous Limits according to HG 351/2005 - Table 2 - <in μg/L.>
1	2	3	4	5	6
Cu - 7440-50-8	1-100	100 (2000 when elements of system are made of Cu)	200	1.3	1300
Zn - 7440-66-6	1- 400	5000 (Table 3)	1000	100	-
Ni - 7440-02-0	1- 100	20 (Table3)	1000	20	2100
Mo - 7439-98-7	1- 50	-	-	3.6	3600
Co -7440-48-4	1- 100	-	-	0.7	700
Cr - 7440-47-3	1- 100	50	1500	2.5	2500
Cd - 7440-43-9	1- 100	5	200	200	1000 (Table1)
As - 7440-39-3	-	10	-	7.2	7200
Hg -7439-92-1	-	1	-	8.05	1000 (Table 1)
Pb - 7439-92-1	1 - 10	10	500	7.2	1700 T2

works of renowned qualified experts in different fields of interest is used to document the present debate and it is fair enough to say that establishing those type of environmental standards is not a routine work. It involves the use of scientifically works covering many fields of interest whose results proved to be defensible over the time and updated in the light of new progress made in different interest research fields maintainig however a good precautionary approach for what actually should mean the safest recommended daily intake doses. The bioavailability and the toxicity of different metals are judged in the reciprocal interactions. The assessments are based on intensive studies and recommendations of safe intake and are documented in the corresponding volume of WHO Environmental Health Criteria Series. The ranges do not represent individual requirements but are the limits of adequacy and safety of the mean intakes of whole population. Used in conjunction with other criteria, biochemical, environmental and socio-economic, the guidelines offered may not only serve as means of assessing probable trace-elements status but also contribute to the more effective diagnosis and control of such problems". WHO states also the definition of the term "requirements" which is the lowest continuing level of nutrient intake that, at a specific efficiency of utilization, will maintain the defined level of nutrition in the individual. WHO states also "basal requirement". "This refers to the intake needed to prevent pathologically relevant and clinically detectable signs of impaired function attributable to inadequacy of the nutrient… The trace element utilization is inversely related to the status or dose and little inference about normal metabolic dynamic of those metals in organism can be made from this information. However, WHO mentions that it is already evident that, as for iron, the absorption of copper, zinc and possibly of chromium is influenced by pre-existing status". In this respect stating a single level for recommendation intake is for sure not advisable [7]. Heavy metals can be solubilized in industrial discharges at the level that depends on their nature but also on the presence of other ions in the system and they trend to form different products more or less soluble at the usual required sewerage pH of 6.5 - 8.5. Using normal treatment techniques and considering solubility products for the precipitated species (most frequently hydroxides) and computing the concentration at the pH 6,5 -8,5 we can still find metal species in solution. They might be the result of an incomplete precipitation or the result of a complexation reaction with the ligands that exist in the solution. This way they can reach our body through recommended daily drinking water consumption of 1.5 - 2.5 liters where they find a variety of ligands normally existing in the body fluids exerting influence on the bodily metals solubility. The majority of body fluids are slightly alkaline (pH 7,5) except the stomach which has an acidic pH between 2 - 6 and the intestinal tract that has an almost neutral pH. Experimental data on the solubility of metal species in biological fluids are limited. In human body most of the heavy metals are usually part of proteins: storage proteins, transduction proteins, enzymes. In enzymes the metal is a cofactor and through them the metals have a large involvement in the most important physiological functions. The normal metabolic homeopathic concentrations are depending on: age, gender, status of already existing metal in the body. It is depending also on the specific expression of enzymatic system characteristic of each person. That means enzymes are the essential instruments for managing the energetic resources of our bodies. They are

expressed during our life time in a manner that depends on endogenous and exogenous factors. That is precisely why they represent unique instruments for each individual. This way is explained the difference in risk for eliciting illnesses among individuals when exposed to different dietary or non-dietary environmental factors. It is generally recognized that "modulation of detoxification enzymes is one mechanism by which diet may influence the risk of different diseases including the risk of cancer" [8].That is the major obstacle to be overcame when it comes to find one rule to fit all. In this respect, the legal established doses for human consumption use should be harmonized with the mentioned daily recommended safety ranges. They represent actually the limits for daily intake that is supposed to preserve a person with normal metabolism for detrimental effects due to either overdoses or deficit comparing to the normal homeopathic necessities of the body which is named basal requirement [8].

4. Conclusions

Applying to the sewerage system stricter limits than stated for potable water is hard to be explained. Even when considering the local area discharge context the differences are of orders of magnitude. This is the case with copper. For potable water it has a limit of 2000μg/L – when the water distribution system is made of copper - and for waste waters discharged in municipal sewer system It has a limit of 1.3μg/L. From what we found in those audits, we concluded that in a proactive environmental protection attitude, the current laws offer a flexible approach in order to reach European Water Directive objectives by enforcing stricter limits to the sewer system discharges only when the local pollution context requires them.

Bibliography

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