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FINAL PROJECT REPORT

LIFE CYCLE ASSESMENT OF TRITIUM IN THE SYSTEM OF THE GRAND CANAL D'ALSACE AND RHINE RIVER

Submitted to fulfill the requirement for the degree

MASTER OF SCIENCE

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Company Profile

The Institut Pluridisciplinaire Hubert Curien (UMR7178, CNRS-IN2P3-INC-INEE, University of Strasbourg) is a research laboratory with multidisplinary appoaches. It has three main departments in different field of studies (eco-physiology, chemistry and subatomic physics). The main objectives of this institute are to develop high-level multidisciplinary programs with the basis of scientific instrumentation. Many researchers from different sciencetific background are involved in IPHC in order to get many perspective to answer scientif problems.

The three main laboratories are divided to three different department: The Department of Ecology, Physiology and Ethology (DEPE), the Department of Subatomic Research (DRS) and the Department of Analytical Sciences (DSA). In 2016, the Department of Radiobiology, Hadron Therapy and Molecular Imaging (DRHIM) was born to make wider researh field.

DRS is one of IPHC departement that has the scientific objectives to do research in nuclear physics and particle physics. Furtheremore, this department has another research interest in radiochemistry, radiation protection and biomedical imaging.

This master subject is part of the multidisciplinary studies that are carried out in the IDeX Consolidation "Juxta Rhenum" of the University of Strasbourg, within the Institut Pludridisciplinaire Hubert Curien. The main objective is to calculate a fate factor of Tritium in order to model transfer mechanisms between water and sediments.

Introduction

Life Cycle Assessment (LCA) is a standardized tool for assessing the environmental impacts of a system from materials extraction to final deposit and treatment of wastes (Grekula, 1999). LCA is a systemic approach to quantify the direct and indirect environmental impacts of chemical compounds entering and leaving the anthropogenic activity studied. Current LCA methods can assess impacts and damage to final targets with a high degree of relevance and advanced sophistication of evaluation models. These mathematical methods for evaluating life cycle impacts focus on pollutant transfers and impact categories such as global warming, terrestrial/aquatic ecotoxicity, or human health. They mainly apply at a global scale referring to global data databases but increasingly concern site-specific scale with local databases. These databases make it possible to characterize the pollutants, including micro and nanoparticles, by a characterization factor.

Simple or complex mathematical models elaborate on the characterization factor. It is the product of two factors; the first factor is the Fate Factor (FF), which represents the transferred fraction of the substance from the source to the environment system and its residence time; and the second factor is the Effect Factor (EF), an expression of the effect of the substance on organisms. Many kinds of literature have been done to get an understanding of fate factors of organic compounds and trace metal elements. In recent years, several studies focused on the behavior of tritium in the environment (CNSC, 2009). However, there are no studies related to the fate factor of tritium in the aquatic system

Tritium is one of the hydrogen isotopes and can be produced either by a cosmic ray or human activities. When neutron from cosmic radiation interacts with nitrogen, nitrogen-15, which is radioactive, is produced and disintegrates into carbon and tritium. This tritium will reside in the atmosphere in a gaseous form (HT) and as water vapor (HTO). Tritium also can be produced from nuclear facilities such as nuclear power plant (NPP) and nuclear reprocessing facility (Kim et al., 2013; Mazor, 2003). Some chemical industry also can release a little amount of tritium in the environment. This tritium is called "technogenic" tritium because it is mainly released by pharmaceutical industries, in luminous paint residues by the watch industry, or with residues by factories manufacturing luminous safety lighting (Eyrolle et al., 2018a).

The nuclear power plant is the main producing of tritium. International Atomic Energy Agency (IAEA) reports showing that one nuclear power plant facility can release 11

to 27 TBq/year tritium in liquid form and 0,2 to 0,8 TBq/year tritium in gaseous form depends on types of the reactors (IAEA, 2007). In the environment, it can exist as tritiated water (HTO) and organically bound tritium (OBT). Growing amounts of studies on the environmental behavior of tritium indicate different behaviors dependent on chemical speciation (OBT, NE(non-exchangeable)-OBT, HTO) as shown in the study of Rhone river, France. Latest research has shown that tritium in OBT form can be trapped in the sediment and reside in water (Ducros et al., 2018; Eyrolle et al., 2018a, 2018b; Kim et al., 2013; Péron et al., 2016). The tritium trapped in sediment has long period biological time, which can lead to an aquatic ecotoxicity potential.

It has thus been found that the influence of a nuclear facility on tritium levels is expressed at a local scale and is visible in the aquatic environment. However, to our knowledge, no study has attempted to quantify the fate of tritium from discharges (leaving a nuclear power plant) to the "natural" aquatic environment. The present work is included in a research project aiming at understanding the transfer of tritium from Fessenheim nuclear power plant to Grand canal d'Alsace and the Rhine River. The specific objectives of this research project are to acquire first data to determine the fate factor of tritium in the Grand Canal and Rhine River system for future modeling of the impact of the tritium life cycle.

This study is devoted to exploring the dynamic / transfers of Tritium along the Rhine River (with the distance ±40 km from Fessenheim NPP) and the Grand Canal, and to gaining first data into physico-chemical parameters that are expected to affect the transfers in these aquatic systems, i.e., pH, nanoparticles and organic matter. This report will be divided into three main sections as follows:

- Analysis of waters in the Rhine and Grand Canal Alsace systems : water chemistry and tritium concentrations;
- Analysis of nanoparticles : occurrence, zeta potential, nature, and influence on tritium in the systems;
- Experiments on sediment collected in the Rhine river to get a first understanding of sediment adsorption capacity towards tritium in the presence and absence of organic matter.

I. General Framework of the study

I.1. Study Area

Fessenheim nuclear power plant is a nuclear facility located in Fessenheim, Haut-Rhin department in the Grand Est region, France –See Fig. 1 and Fig. 2. This facility is using the Grand Canal d'Alsace as cooling water for the reactors. It has two reactors and each reactor produces 900 Mwe. This facility releases 0,71 GBq/year tritium in gaseous form and 11,6 GBq/year tritium in liquid form (EDF, 2017; IAEA, 2007). Although the concentration is below the regulatory limits, the release is expected to induce a local increase of tritium concentration. The tritium can be bound with organic matter and may potentially accumulate or trap in the sediments.



Figure 1. The study area in the Haut-Rhin department in Grand Est, north-eastern France



Figure 2. Photo of Fessenheim Power Plant from Grand Canal Alsace

I.2 Background Of The Study: Current Understanding Of Tritium Forms In The Environment

In the environment, because tritium is an isotope of hydrogen, tritium is present in all part of the geosphere, including the atmosphere, hydrosphere and lithosphere, the biosphere and the anthroposphere. It is present in many physical and chemical forms.

I.2.1. Tritiated Water (HTO)

Tritiated water (HTO) is the most common form of tritium in the geochemical systems and in living organisms. This form can be found throughout the whole hydrosphere cycle in the environment. It is very mobile since it has similarity with normal water. HTO concentration in hydrosphere depends on many factors such as latitude, season, the age of the water mass, hydrology, drainage basin size, precipitation rate of minerals, and altitude. (Eyrolle et al., 2018a).

The mean concentration of HTO in French river water (1,4 Bq/L) is less than HTO concentration in rainwater (1,6 Bq/L) due to radioactive decay during the mass transfer from atmosphere to hydrosphere (Ducros et al., 2018). The concentration of HTO is varying because of a rapid transfer of hydrogen and water molecules with different components in the environment. HTO can also be found in the atmosphere in the form of water vapor.

I.2.2. Organic Bound Tritium (OBT)

Inorganically bound tritium can be linked either by covalent bound or weak hydrogen bond. Organically Bound Tritium (OBT) initially integrates organic matter cycle mainly during the photosynthesis process. Thus it will move to the biosphere through the food chain. Many research has been done to investigate OBT in the environment. Because tritium is part of the organic matter cycle, OBT is accumulated in organic matter storage media, especially in the sediments of streams and rivers. (Eyrolle et al., 2018b). Tritium can persist in both terrestrial and aquatic environments according to the recycling rates of organic matter. A study showed that the mean Organically Bound Tritium (OBT) concentration in the sediments of Rhone river in France, is not significantly different from the mean HTO concentration recorded for rainwater (2.4 ± 0.6 Bq/L and 1.6 ± 0.4 Bq/L, respectively) (Eyrolle-Boyer et al., 2015). The authors have the hypothesis that regional differences are expected depending on the biomass inventories affected by the global fallout and the recycling rates of the organic matter in the various affected watersheds. Hence, there are possibilities that seasonal factors also affect the OBT concentration. Several studies have been done on the behavior of tritium in the aquatic systems. Tritium behavior in aquatic systems is influenced by its various forms and biogeochemical exchanges among aquatic components, as can be shown in Figure 2. Tritium is bound to dissolved, colloidal or particulate organic compounds either through exchange reactions or enzymatically catalyzed reactions. In exchange reactions, tritium is bound to oxygen, sulfur, phosphorus or nitrogen atoms through weak hydrogen bonds, resulting in forms that are more or less exchangeable with ambient oxide hydrides known as Exchangeable Organically Bound Tritium (E-OBT). In the case of enzymatically catalyzed reactions, tritium is bound to carbon atoms and is permanently fixed to the resulting molecules until they are metabolized. Such forms are referred to as Non-Exchangeable Organically Bound Tritium (NE-OBT). (Cossonnet, 2014)



Figure 3. Tritium behavior in aquatic system. (1) NE-OBT will become E-OBT through biodegradation of organic matter after a long time of retention. (Cossonnet, 2014)

E-OBT is tritium bound with sulfur, oxygen, or nitrogen atoms and can be removed by washing with Tissue Free Water Tritium (TFWT). E-OBT equilibrates very quickly with TFWT, which is itself at equilibrium with the water molecules in the surrounding environment (Eyrolle et al., 2018a; Kim et al., 2013). Also, E-OBT is in equilibrium with HTO in the plant or animal and behaves the same as HTO. This fraction of OBT depends strongly on the HTO concentration present at the time of sampling and can exchange with water vapor during analysis. (Kim et al., 2013). NE-OBT is tritium covalently bound with carbon atoms, and it makes stronger bound than tritium bound in E-OBT. Unlike E-OBT, tritium in this form has a biological period that depends on the molecules on which it is bound. If the tritium is bound with fast metabolism species of organic matter such as carbohydrates, it can stay in this form from few weeks and few months until it degrades. On the other hand, tritium can be bound with slow metabolism species of organic matter, and in this form, tritium can be bound for several years or decades. (Eyrolle et al., 2018b, 2018a).

Recent studies have shown that NE-OBT causes tritium to persist in organic matter and that the fate of NE-OBT depends on the reaction kinetics, particularly the decomposition and recycling dynamics of the organic compounds. Higher OBT concentrations than the HTO concentrations of the surrounding environment have been widely observed in terrestrial plants and river sediments collected away from the influence of releases from nuclear facilities. For example, OBT concentration observed in the Loire river ranges from 10 to 23 Bq/L, and the HTO concentration ranges from 6,9 to 21 Bq/L (Péron et al., 2016). This shows the persistence of tritium initially integrated into the organic matter within these matrices. (Ducros et al., 2018; Eyrolle et al., 2018a, 2018b; Kim et al., 2013). Another study in Qinshan Nuclear Power Plant, China, showed that for soils collected at ± 2 km from the nuclear power plant, there is a correlation between NE-OBT and HTO ratio in soil samples. They concluded that this could happen because of living organism converting HTO into OBT. (Zhang et al., 2018). This indicates that NE-OBT exists in an environment not only because of organic matter but also because of living organism.



Figure 4 Tritium form in the environment (Eyrolle et al., 2018a)

As noted before, tritium in NE-OBT can cause resistance during several years. It o can be bound with many types of organic carbon, and there is a possibility that tritium can be bound in close association with organic molecules sorbed at surfaces of nanoparticles. Also, research showed that around 70% of the tritium bound to the organic matter is in a non-exchangeable form, and the other 30% is tritium is bound with organic matter as E-OBT (Eyrolle et al., 2018a).

Past research implied that HTO is the most common of tritium form in environment and OBT can reside on the soil and water in a long period depending on the kinetics associated with the cycle of the organic compounds into which the tritium is incorporated. Although tritium resistance in water and soil is well known, there is no clear explanation on OBT resistance mechanisms in the environment. Also, tritium behavior toward organic matter and possibly nanoparticles is still not well known. Until now, there is no research about HTO and OBT measurement in the environment around the Fessenheim NPP.

This research will measure tritium concentration (HTO and OBT) along the Rhine River and Grand Canal d'Alsace with distances \pm 30 km from Fessenheim NPP to gain first data on the tritium behavior in this specific system.

II. Methods and Materials

II.1. Sampling Area

The water samples are collected along the Rhine River, Old Rhine and Grand Canal d'Alsace with distances \pm 30 km from Fessenheim Power Plant. There are three sampling points in Rhine River (2 points before the Rhine split into Od Rhine River and Grand Canal Alsace, 1 point after the confluence), six sampling points in Old Rhine, and six sampling points in Grand Canal. The samples were taken during different seasons, the first campaign was in March, and the second campaign was in May. On-site measurements were done to acquire data on pH, temperature, dissolved oxygen, and conductivity. For each sampling point, 1 L of water is collected to make water chemistry measurements in the lab, and 40 mL filtered water with 0,45 µm filter is stored in dark vial glass to remove colloid and prevent tritium from light.



Figure 5 Sampling area of the study

II.2. Samples Processing and Measurement Methods

The 500 mL water samples collected in March were filtered with 0,45 μ m filter then 250 mL filtered samples were ultracentrifuged at 9000 rpm during 2 hours. Both filtered samples and ultracentrifuged samples were concentrated with evaporation methods. The concentrated samples were then used for trace metal analysis with Inductively coupled plasma mass spectrometry (ICP-MS). For the water samples collected in May, 500 mL of water samples were filtrated with three levels of filtration, 2,7 μ m, 0,45 μ m, and 0,2 μ m. The filtrated samples were then measured with ICP-MS, for trace metal analysis, and Inductively coupled plasma atomic emission spectroscopy (ICP-AES), for major elements analysis. Filtrated was done to detect whether there is the presence of nanoparticles on which trace metal elements can bound in the water samples. Each raw sample in both campaigns were analysed for its anion and total organic carbon concentrations.



Figure 6 Scheme of centrifuge threatment (top) and scheme of filtration threatment (bottom)

To determine tritium concentration, 8 mL of water samples were mixed with 15 ml high-efficiency LSC cocktail (Perkin-Elmer 'Ultima Gold LLT') then the samples was measured with Liquid Scintillation Counting (LSC) to count the activities of tritium in water samples. The counting time was 7200 s and three-time measurements were done for each sample. The measurement efficiency ε was determined by inner standard source method. After the measurement, the water samples which have tritium concentrations above the detection limit were distilled to see whether tritium is in the form of HTO or not.

The experiment of tritium adsorption on the sediment was done with extracted organic matter (from the Rhine water) and a pre-treated sediment from the Rhine river system. The sediment collected in the Rhine was washed three-times using water to remove free tritium. After that, organic matter was removed using hydrogen peroxide. Then, the « model » sediment obtained was dried for 6 hours to remove excess water. The sediment was used for two experiments with tritium. The model sediment was used to make two experiments : the first experiment consisted in a 15 mL solution in contact with 20 mg model sediment only, and the second consisted in a 15 mL solution with 20 mg model sediment and 302 μ L extracted organic matter from the Rhine river system (the organic matter reconcetrated at a value 623,3 mgC/L). The solution pH was adjusted around 6,5 to 7,5 as measured in the Rhine river system. In these two solutions, we added 10 μ L tritium standard with a known concentration (74,1 Bq/L) and then (after shaking during 2 hs and sediment-solution separation) the supernatants were measured with LSC. The experiment is aiming to

see the adsorption of tritium from Rhine river sediment sample and to reveal whether organic matter may affect tritium adsorption on the sediment.





III. Results Analysis

III.1. Water Chemistry of Rhine River and Grand Canal Alsace

III.1.1. pH Measurement

From the samples collected in March, the global evolution of pH in the Rhine river from upstream and downstream is slighty decreasing. As shown in Fig. 4 below, samples collected in the GCA show no important variation in pH values. However, the pH slightly decreased after the power plant. Samples collected in the Old Rhine exhibit higher pH values (pH>8) than those collected in the GCA, excepted for sample JR10 collected near the NPP. Unlike for GCA, pH varies amongst samples collected in the Old Rhine river. There was observed a sharp pH decrease of more than 1.5 pH unit (from 8.5 to 7) in the Old Rhine water collected in front of the NPP, followed by a steep and regular pH increase (up to a value of 8.5 in waters collected 20 km downstream). There is thus a possibility that of a connection or exchange between the GCA and Rhine river.

Unlike the samples collected in March, samples collected in May show pH variation in GCA. The evolution of pH in GCA is a gradual increase along a distance of 15 km after NPP (from 7,4 to 8,2). In Old Rhine, pH in the sample point before NPP shows that pH is increasing sharply from 7,6 to 8,9 then the pH steeply decreases after the NPP. The pH value in Old Rhine is higher than in GCA before NPP and is the same (or slightly lower) as that in Old Rhine after NPP. Although the pH evolutions are not the same between the two campaigns, the data obtained show that both measurements indicate the possibility of water exchange around NPP.



Figure 8 pH evolution along the river and canal

III.1.2. Anions Analysis

The major anions present in the water samples are chlorine and sulfate. Sulfate concentrations are similar in the samples collected in the river and the canal, and they increase from upstream to downstream. The evolution of sulfate concentration along the Rhine and Grand Canal are the same in the second campaign. However, the concentration is higher compared to the first campaign result. The chlorine concentration is generally higher in the Old Rhine than in GCA (except JR15-JR14, and near the NPP). Unlike for the canal, which shows only a small increase in chlorine downstream the NPP, chlorine concentration varies in the Old Rhine regularly from upstream to downstream. In conclusion, for major anions (chlorine and sulfate), the Rhine has higher concentrations than the canal.



Figure 9 Chlorine concentration (top) and sulfate concentration (bottom)

III.1.3. Total Organic Carbon Concentrations

From the data collected during the two campaigns, the concentration of total organic carbon cannot be defined because the measurement provided values below the detection

limit (detection limits is 4 μ g/L). This is certainly because the sample was taken in the winter season (March 12th, 2019), and at the start of the spring season (May 2nd, 2019), when organic carbon concentrations are rather low in rivers.

III.1.4. Total Inorganic Carbon Concentrations (TIC)

From the measurement, TIC in the canal side does not vary between the samples collected in March and May. The data observation shows that the concentration is the same from upstream to downstream. Furthermore, the TIC values during the two campaigns are similar. TIC value in Old Rhine does vary between the samples. When compared with TIC values in the canal, there is observed no significant difference excepted for one point before NPP in Old Rhine.

TIC value is increasing after the power plant. TIC on Old Rhine samples is increasing from upstream to downstream.



Figure 10 Total Inorganic Carbon evolution

The following chemical equilibria relate inorganic element species:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$

The speciation of organic carbon depends on pH: at low pH, the main species is CO_{2} , and at high pH, the main species is $CO_{3}^{2^{-}}$. Also, the inorganic carbon tends to make equilibria with atmospheric CO_{2} . The TIC values from the collected samples during the two campaigns is around the solubility curve of CO_{2} , which explains that the water is equilibrated with CO_{2} in the atmosphere. From Fig. 11 it can be shown that the total abundance of inorganic species depends on the pH of the samples. The pH value of the sample is between 6,9 to 8,9; this means that the major species of inorganic carbon is mainly HCO_{3}^{-} .



Figure 11 CO2 Solubility (left) and carbonate speciation curve (right)

III.1.5. Major Elements Concentrations

The major elements that can be found in the water samples are silica and aluminum. These two major elements have the same evolution both in the Rhine and Grand Canal Alsace system. For the silica, the concentration along the Rhine and the Grand Canal do not varies within a distance of 20 km. The concentration is around 0,4 - 0,7 ppm in Old Rhine, and 1,2 ppm in the canal. Generally, silica concentration is higher than in the canal. Aluminum also shows the same evolution between the two systems, and the concentrations do not differ between Old Rhine and Canal. It can be concluded that the Old Rhine and The Grand Canal Alsace have the same evolution of major elements (silica and aluminum).



Figure 12. Silica concentration and aluminum concentration in the Rhine and Grand Canal Alsace

III.1.6. Trace Metal Concentrations

The trace metal analysis showed that the concentrations of Al, Cu, Co, Pb, and U in river and canal increase after the Fessenheim Nuclear Power Plant. For Pb concentrations, both samples collected in GCA and Old Rhine are similar. However, after NPP, Pb concentration in JR1 is sharply increasing up to 0,07 ppb. Pb concentration in GCA water increases after NPP, too. Analysis of copper concentrations show that the concentration before NPP in Old Rhine is higher than in GCA. After NPP, copper concentration is higher

in the GCA. The copper concentration in GCA also sharply increase to 0,09 ppb after the NPP (JR2). Possibly, increase of aqueous concentrations in these trace metals can partially relate to an increase of pH after NPP.

Zinc concentration in Old Rhine before NPP is higher than the concentration in GCA and the concentration increases sharply from 10 to 29 ppb after NPP. In contrary, zinc concentration in GCA after NPP is higher than the concentration in Old Rhine. Like in Old Rhine, the concentration also sharply increase (14 to 31 ppb), and both concentration in GCA and Old Rhine after NPP have similar values.

Aluminum measurements showed that aluminum concentration is higher in Old Rhine before the NPP, and the concentration decreases significantly (37 to 2 ppb) in JR5 to JR10. After the NPP, aluminum concentration is lower than the aluminum concentration in GCA. The major species for each trace metals are $Al(OH)_4^-$ for aluminum. Cu(OH)₂ for copper, PbCO₃ for the lead, and Zn²⁺ for zinc. These results were obtained from speciation calculations using PHREEQC with the WATQ4F database.



Figure 9 Trace metal concentration

III.1.7. Tritium Measurement

Tritium analysis was done using Liquid Scintillation Counting (LSC). Water subsamples were taken (8 ml) and mixed with 12 ml of Ultima Gold LSC Cocktail. Then, the samples cocktail was shaken until solution was homogenous. The counting time for the measurement was 7200 for each sample to reach the detection limit of 1 Bq/L. Figure 13 below shows the result of tritium counting from the samples collected in the Rhine River and Grand Canal Alsace.



Figure 13. Tritium counting result from water samples collected

The result from the first campaign data measurement shows that tritium can be found in the Old Rhine River and Grand Canal Alsace. In the Old Rhine, tritium can be found in JR5 and JR9 which are have distance ± 10 km from Fessenheim NPP. However, the tritium cannot be found at the point located between those two points (JR11). This can happen with several possibilities; tritium concentration can be diluted due too the high flow rate of the Canal, or tritium bounded with other elements such as organic matter or trace metal elements are trapped in sediments there. In Grand Canal Alsace, tritium can be found in JR10, which is the sample collected in Fessenheim NPP. This tritium possibly comes from the Fessenheim NPP operation. Another sample point that has tritium is a sample collected in Rhin River (JR20). This sample located 40 km before the Fessenheim NPP has a high concentration of tritium (7,2 Bq/L) compared to other samples. It indicates possible another tritium source than the Fessenheim NPP in the Rhine River system.

The second campaign was done in a smaller area than the first campaign (± 10 km from Fessenheim NPP). The result showed that tritium can be found in Old Rhine 5 km before the Fessenheim NPP. The data result from tritium counting collected in Grand Canal Alsace show that tritium can only be found in JR24 located 5 km before Fessenheim NPP. Besides of that, a sample collected in JR3 River (sample located in the small river beside the Rhine River), showed a tritium concentration of ca. 3 Bq/L although the river has no direct contact with the Rhine . The data from both campaign indicated that tritium could be found

in both Rhine River and Grand Canal Alsace near the Fessenheim NPP. It seems that the tritium transport in both systems is dynamic and possibly there are several sources of tritium because tritium could be found at a relatively high concentration (7 Bq/L) 40 km before the NPP.

III.2. Nanoparticle Analysis on The Water Sample

III.2.1. Zeta Potential

Result of electrophoretic mobility measurements on the water samples suggested the presence of small particles having negative zeta potential values from -8 mv to -14 mv (surface potential) in both systems (Rhine River and Grand Canal Alsace). These values suggest that the particles present in the samples may not be stable, and will tend to combine to form aggregates. It can be concluded, in general, that both systems display similar zeta potential ranges, which suggest the presence of unstable particles.



Figure 14. zeta potential meassurement

III.2.2 Filtration Samples

Sample collected near the Fessenheim power plant with a distance of ± 10 km were filtrated using different size of filters. This was done to know if nanoparticles to which trace metal are bound are present in the sample. Aluminium concentrations in these samples was under the detection limit. Thus, the samples were analysed to determine the concentrations of trace metals like nickel, copper, and zinc. These trace metal elements are possible trace metals that can be beared by nanoparticle beside than aluminum. The size of the filter used was 2,7 µm, 0,45 µm, and 0,2 µm. If the concentration of a trace metal element in the water filtration, it shows that there are no particles bearing the trace metal element in the water sample. In the opposite, if the concentration is changed after the filtration, it can be an indication of presence of particle of small size.



Figure 15 Measurement of trace metal elements with different size of filter in Old Rhine.

Figure 15 above shows the different concentration of nickel in the Old Rhine water samples. The concentration of nickel, copper, and zinc in the Old Rhine sample show the evolution of the trace metal concentration does not change after the filtration. this suggest that there is no presence of nanoparticles higher than 200nm bearing trace metals.



Figure 16. Measurement of nickel with different size of filter in Grand Canal Alsace

The graph in Figure 16 shows the concentration of nickel after filtration in the Grand Canal Alsace. Nickel concentration after the filtration shows that there is a possibility of nanoparticle present in near Fessenheim NPP (JR10 and JR24). The data show that the concentration is changed after the sample was filtrated at 2,7 μ m whereas the concentration does not change after filtration with 0,45 and 0,2 μ m filter size. It means that we have an indication of presence of particles with sizes lower than 2,7 μ m in JR10, and JR24. The same behavior also can be found in data observed from the copper concentration in JR10 and JR24 sample, and data from zinc concentration in JR10 sample. The analysis shows the data collected from sample located near the Fessenheim NPP (JR10 and JR24) have a possibility that nanoparticles are present in waters.

III.2.3. Ultracentrifuged Samples

Samples collected in Rhine and Grand Canal Alsace at distances ± 30 km from Fessenheim NPP were ultracentrifuged. This was detect the present of nanoparticles to which trace metal elements were bound. The estimate trace metal bound with nanoparticles is calculated by subtracting total concentration measured in the filtered sample (with 0,45 µm filter) and in the ultracentrifuged sample (this sample was centrifuged before with 9000 rpm at 2 hours to separate big sized particles and leave the smaller particles in water).

[Estimated bound nanoparticle] = [F sample] – [UC sample](1)

Some calculation gave negative values because concentration after centrifuge was higher than the concentration of the filtrated sample. The negative values were due to the detection limits and the concentration uncertainties associated to the analysis. The estimated aluminum concentration associated to nanoparticles and the total concentration of aluminum show a similar trend (Figs. 17 and 18). This suggests that there are nanoparticles containing low amounts of aluminum in the river and canal. Moreover, aluminum concentration associated to nanoparticles in the canal is increasing after the Fessenheim Power Plant. In contrary, nanoparticle concentration is reducing after power plant in the Old Rhine. From the simulation result using PHREEQC, it is shown that aluminum precipitate in a water sample as Boehmite (AlO₂H), Gibbsite (Al(OH)₃) and Diaspore (AlHO₂). From Gibbsite equilibrium curve, shown that samples are near the equilibrium curve. The majority of samples are oversaturated and gibbsite precipitation in water is a possibility.



Figure 17. Estimate nanoparticle concentration (left) and the total concentration of aluminum (right)

When comparing concentrations, it appears that there is a correlation between aluminium associated to nanoparticles and the total concentration of aluminum (Fig 18).



Figure 18 Aluminum concentration comparison

III.2.4. Tritium Distillated Samples

Samples from JR4 and JR23 were distilled to detect whether tritium was in the form of HTO in the samples. If there is a difference in tritium concentration between the raw sample and the distillated sample, it indicates that tritium is not present as free tritium. Table 2 below shows that after filtration tritium in JR23 was below detection limit and the concentration in JR4 was the same as that of the raw sample. It seems that tritium in JR4 is free tritium.

That tritium in JR23 was under detection limit after the distillation indicates that tritium in JR23 is not free tritium, and it might be possibly associated with nanoparticles. It is also an indication that the two systems have different forms of tritium; free tritium in the Grand Canal Alsace and bounded tritium in the Rhine River.

Sample	Sample		ample	Distillate Sample		
Name	Location	Activities	Error (Ba/L)	Activities	Error (Ba/L)	
		(БФ/С)	(bq /L)	(B4/L)	(B4/L)	
JR4	Canal	3,0	1,3	2,2	1,2	
JR23	Old Rhine	2,0	1,3	-	-	

Table 1. Comparison between raw sample and distilled sample

The sample JR23 was then used for examination using Transmission Electron Microscopy (TEM) detect presence of nanoparticles in the sample. The TEM imaging results showed that several types of nanoparticles were present in the sample JR23. The majority of the nanoparticles present are calcite (CaCO₃), and clay nanoparticle possibly as smectites (containing iron). The particle sizes vary from 10 nm up to 1 μ m which indicates there are many groups of calcite and smectite in the sample. Firgure 19 showed that pictures of nanoparticles that can be found on the JR23 sample. The left picture is nanoparticle of clay

nanoparticle present in the sample with the size of $\pm 1 \ \mu\text{m}$. The big particle was identified as a clay material concist of aluminum, silica, and iron. The right side picture shows calcite nanoparticle with the size of $\pm 5 \ \mu\text{m}$ present on the edge of particle with size of 20 nm. The picture also idicated there are many group of nanoparticle with different size. We know that surface of smectite bear hydroxyl groups (OH⁻) so that there may be isotopic exchange between the hydrogen of the surface hydroxyls and tritium. In summary the result from the distillation JR23 sample indicated that tritium in this Rhine sample is not free tritium; and TEM analysis suggested that free tritium can be absorbed by smectite and possibly also by calcite of very small sizes.



Figure 19. Different size of nanoparticle present on the sample; nanoparticle of clay mineral (left) and calcite (rigth)

III.3. Sediment Experiment Result

The experiment used the "model sediment" sample (sediment from which organic matter was removed) from JR23 and organic matter extracted from water of the Rhine River (and reconcentrated at a value of 623,3 mgC/L after extraction). 20 mg of sediment sample was brought in contact with 15 ml solution. One of the solutions was added 302 μ L of extracted organic matter solution. After, by 10 μ L tritium standard with activities 74,1 Bq/L were introduced in the samples. After shaking and separation, the supernatant solution was measured by LSC to see is there any difference in tritium concentration. The result of the experiment can be shown in Table 2.

Solution	mass of T added (g)	NOM added (µL)	mass of sediment	T Meassured (Bq/L)	T Activities (Bq)	Adsorption (%)	рН
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			added (mg)				
Sediment	0,0196	-	21	15,7	0,235	80	6,7
Sediment +NOM	0,021	302	20	11,3	0,169	86	7,2

The results indicated that the tritium was absorbed by « model sediment » as much 80 %. When the natural organic matter was present in the sample, the adsorption increased to 86 %. From TEM analysis, it is known that in the sample we have presence of smectite. The adsorption of tritium in the sediment might be because of smectite present in the sediment as a nanoparticle or bigger minnneral. The smectite can absorb the tritium because of the hydroxyl group in the surface of smectite. The result also indicates the organic matter helps to increase sediment tritium adsorption. The organic matter can help the adsorption of tritium possibly because organic matter is adsorbed on the surface of the sediment and organic matter adsorb tritium directly. This result suggest that, beside its association with suspended nanoparticles, tritium is expected to be bound to sediment -and organic sorbed to the sediment- in the JR23 sample, ie, in the Rhine River (unlike for Grand Canal).

IV. Conclusion and Recommendation

The analysis of water chemistry result shown that the pH along Rhine and Grand Canal Alsace vary (7 - 8,9) and there is an indication that the Rhine and Grand Canal communicate near the Fessenheim NPP. Furthermore, both systems have same characteristic of anions and its evolution along the Rhine and Grand Canal. The analysis also shown both sytems are highly carbonated water. In the point of view tritium concentration, the tritium concentration are "dynamic" (it varies along Rhine River and Grand Canal). Moreover, the result showed an indication of another source of tritium than Fessenheim NPP, possibly come from chemichal industry and hospital medical waste. the characteristic of tritium is different in both system; tritium found in Grand Canal Alsace is free tritium, and tritium found in the Rhine is bounded tritium.

The sample collected from Rhine River system showed that there are present of calcite and smectite nanoparticle. Bounded tritium in the Rhine system might be absorbed with smectite nanoparticles and possibly with calcite. The experiment results showed that tritium is also possibly absorbed in sediments of Rhine River, and organic matter extracted from the Rhine water can increase the adsorption of tritium in the sediment.

Future research can be done to see the effect of different pH to adsorption of tritium in sediment and organic matter. The experiment can be done with the same procedure in this report but the pH of the solution is varied so that it can be seen whether pH can affect the tritium adsorption. Another experiment can be done is to make variation of ratio between sediment and organic matter in the solution to see the ratio can help the adsorption of the tritium or not.

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ANNEX 1. Anions measurement results

ANNEX 2. Conductivity and Dissolve Oxygen Result

