

Baha'i Institute for Higher Education (BIHE)

Department of chemical engineering

Literature Review on Heavy Metal Pollution in Southern Caspian Sea Basin and Phytoremediation as Treatment Method

Final Project as the Requirement for Bachelor
of Science Degree in Chemical Engineering

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Abstract:

This review mainly focused on heavy metal related pollution of the Caspian Sea in the southern drainage basin which is located in Iran, and proposing a remediation method which is suitable for the situation. Total of 150 papers were reviewed for this matter. Seven of the main rivers of the basin were selected and related field studies were reviewed for heavy metals concentration and hazardous risk. Most high-risk metal was reported to be nickel and lead. For the next objective, phytoremediation was chosen to study. Although there was not a common agreement on the type of the plant for this method, but overallly phytoremediation was reported to be an effective method for removal of contamination. Beside lack of real situation experiments, there was also lack of attention to the separation timing of plants after remediation. Alongside these two matter, removal technique for the contaminated plants from the site are also a matter for future research.

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1. Introduction:

1.1. Project Selectin, Definition and Scope:

Environmental issues are one of the most widespread and universal challenges which is influential on everything that takes benefit of it. In another word, most of the raw material for processes that human's life is depended on, is based on environment, raw material for edible ingredient, clothing, farming and agriculture industry and many man-made industry. Throughout recent years industry progress and urbanizing has led to polluting and misuse of environment more than ever.

Water crisis is one of the most considerable issues all around the world which is not only about the minimum amount of freshwater available, as world water vision reports "There is a water crisis today. But the crisis is not about having too little water to satisfy our needs. It is a crisis of managing water so badly that billions of people - and the environment - suffer badly". The poor management skills and strategies in all the field of water use (domestic, agricultural and industrial) has resulted in lack of clean water and polluting the significant water bodies. As the population and industries growth, the equivalence between water demand and water supplies grow farther and the crisis become more and more intense.

This project was chosen, regarding the world wide crisis of clean water. As for the Caspian Sea, the biggest landlocked basin (lake) in the whole wide world which is beneficial for five coborder countries surrounding it (Iran, Russia, Turkmenistan, Azerbaijan and Kazakhstan) the crisis is tangible for us as one of the coastal resident in the southern Caspian Sea region. The main focus of the project is on the heavy metal sources of pollution inside the drainage basins of the southern Caspian Sea.



Figure 1. Geographical position of the Caspian Sea basin

1.2. Environment:

Environment in its public literal definition means everything in the surroundings, and in more academic and scientific definition, environment represent every element and objects which have consistent influence on any living organism and effect their life and development. Thus the importance of environment role on preserving and conserving the life and growth rate of all kinds of living organism; humans, animals and plants is evident. Basically it would be accurate to say environment –rather natural or man-made- provides natural habitat and basic requirement of living for all of us.

Environment in its natural categories which also may be referred to as the term ecosystem, includes, the air (atmosphere), water, climate and the landing beneath us. All type of environment is essential to maintain their organic and natural sustainability in order to preserve healthy life of living organism and biodiversity.

Amongst different forms of environment, water bodies and their preservation has a crucial role. Water is the habitat of thousands and millions of plant and animal species. Almost 70 percent of the earth is covered by water in any form of ocean, wetlands and rivers. For instance rivers water and their natural movement are the native habitats for different fish species to grow and breed, these fishes also feed from sediments of wetlands and rivers. Other animals such as frogs, turtles and water bugs also use wetlands as their natural habitat, also migration and breeding of water birds and woodland birds are Dependent to wetlands quality and plants life surrounding them. And more importantly, due to water influence on different type of living organism, water plays a critical role in preserving these species along the food chain from contamination and extinction risk. (Heritage 2016)

Through the recent ages, industry and urban progress has had tremendous influence on any form of environment. Population growth has led to increasing in needs and supply and demands, which make humans the biggest consumers on earth. They use plants as their raw material for keeping the industries going which in recent years has led to deforestation. According to UN report on deforestation, the net amount of forest in global rate in 1995 was 4128 million hectares which this amount has dropped to 3999 million hectares within the year 2015. (TehranTimes 2018), these industries also use water from different sources (ocean, river, pond, etc.) and bare lands in order to advance the production, and in return the pollution and wastes -whether solid or water- come back to the environment and pollute the surrounding without any further plan to retreat and retrieve the natural sources.

1.3. Pollution:

Pollutions are defined as any material and substances that enters undesirably into the environment and causes harmful effects on nature and living organism. These contaminants unbalance the natural growth and quality of environment whether they enter from an outside and anthropogenic source such as factories and urban sites or from inside the nature such as soil washing and rock weathering. Regardless of the main sources of contaminants, they may have short term (or easily identifiable) or long term effect on different aspects of environment depending on the type of contaminants and

other factors such as contaminants half-life and bioavailability¹ of them inside the soil or water. (COKER n.d.) (Menon n.d.) (IIT 2009)

Pollution types can be categorized by different perspective, but mainly there are five category of pollutions which can harm the environment:

- 1- Water pollution
- 2- Land pollution
- 3- Air pollution
- 4- Noise pollution
- 5- Radioactive pollution

1.3.1. Water Pollution:

Any undesirable substances and contaminants that enters a body water like ocean, river, lake or sea can cause water pollution. These contaminants can exist in any kind of physical (plastic bottles, paper and napkins), chemical (organic: pesticides like DDT and inorganic: heavy metals like lead and mercury) or biological (microbial like E-coli and coliform) which brings danger and threat to aquatic life by poisoning the food chain and also harms the human's life in long term as the highest step in food cycle. (Menon n.d.)

As it was mentioned before, these contaminates can appear rather by naturally occurrence such as soil and rock weathering and acid mine drainage, or more likely, they can be anthropogenic such as industries and factories waste pollution, urban and municipal wastes and sewage, agricultural (pesticides and fertilizers) or oil leakage as offshore or onshore source inside the water. Generally, sources of water pollution can be narrowed to two main category; point and nonpoint pollutions. (COKER n.d.) (Menon n.d.). There would be a brief explanation on water pollution and its related danger on the next pages.

¹ This term is define in page 10

Point Source:

Point pollutions are identifiable and determinable and are from a known and direct source, thus they can be reduced and treat more easily. (Menon n.d.)

The most common sources of point pollutions are:

Factories and industrial wastes: discharge of solid or water waste of industrial processes inside the water which carries high concentration of heavy metals (cadmium, arsenic, mercury, chromium, lead, iron, and manganese), suspended solids and oils.

Municipal waste: such as urban sewage and discharge which is disposed into body water like rivers located near the disposal bank.

Oil: leakage of oil wells into the ocean and sea water.

Thermal: usage of water stream as coolant for industries and power plants.

Diffuse Source:

Another source for water pollutions are those type of contaminants which are not associated with a direct or determinable source or a specific location.

The most common sources of diffuse pollutions are:

Runoff from agricultural lands: runoff of fertilizer and pesticides from farms and crop lands.

Movement of pollution: relocation of pollution alongside the river by the means of rain and snow movement through the lands. (Menon n.d.) (COKER n.d.)

Table 1. Summary of type of point and diffuse pollution and their origin

Source of pollution	Nature of contamination
Point source	Industrial - Inorganic pollutant(Heavy metals), suspended solid
	Municipal - Microbial, suspended solid, COD
	Petrochemical industry - COD, organic pollutant (aromatic compound, naphtha)
Diffuse Source	Urban runoff - Heavy metals, COD, suspended solids
	Agriculture runoff - Phosphate, nitrate, COD,

These contaminants inside the water body can cause several diseases and thread to aquatic life when is available inside the water as suspended solid, and enters the tissues of aquatic creatures rather by food chain or skin contacts. Heavy metals which exist in the water will end up in human's body through the food chain and will cause health problems such as cancer, kidney problems, skin problems and many others. Harms which are done to the marine animals and also amount of chemical absorption and effect on organism is closely related to the term bioaccumulation, biomagnifictaion and bioavailability of contaminants inside the water.

*Bioavailability and Mobility of Heavy Metals:

Bioavailability is a common term in pharmacology and environmental scientist specially toxicology. The term refer to fraction or amount of bioavailable chemical compound (in this case contaminants fraction) which can be absorbed by an organism system and consequently cause toxicity (Kirk T. Semple 2004). Metals get fractionate within the food chain. It will transfer through the sediments – since the most bioavailability occur in sediments- of sea water to the fish and aquatic organism, then to the human body. (Naji 2015). Since this concept is closely related to solubility of metals, there are also different chemical reaction and agents that can cause immobility and reduce the bioavailability of heavy metals including precipitation, ion exchange, reduction, and oxidation. (Cynthia R. Evanko 1997) Depending on chemical properties of the available compound and contaminant each reaction rather mobilize or immobilize the metals. (A. Violante1 2006)

*Bioaccumulation and Biomagnification:

Transferring heavy metals from one specie to another through the food chain will cause them to be accumulated. Accumulation of metals occur when rate of absorbing elements by a living organism is more than the rate associated with excreting or burning of the metals by natural metabolism. (Sandner, Fatkin and Lacy 2007) Thus bioaccumulation is a result of high concentration of heavy metals in water body and sediments which is taken up regularly by living creatures for a long period of time.

It became biomagnified by increasing in trophic level and by higher concentration, toxicity of each elements become more and more significant. Humans' body as the top level of trophic level is

sensitive to even low concentration of heavy metals such as mercury, lead and cadmium which have the most toxicity among the heavy metals. (Sandner, Fatkin and Lacy 2007)

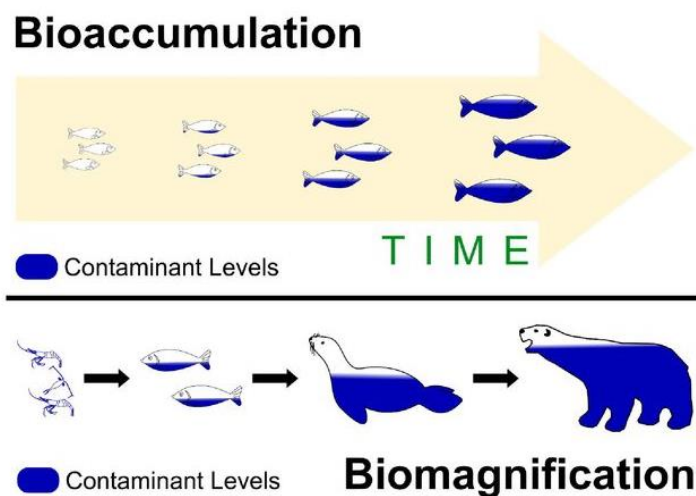


Figure 2. figurative diagram of bioaccumulation and biomagnification of contaminants inside the body of living organism

1.3.2. Land Pollution:

Addition of any substances that causes contamination and degradation of soil, thus causes fertility reduction of it and brings danger to microorganism, and other living creature who their life is dependent on that contaminated soil is called land pollution. The most crucial problem associated with land pollution is soil erosion, which is a result of rather misuse of the land –which is an anthropogenic reason- or erosion which is caused by wind or water which is naturally occurring; and in result soils productivity reduces by removal of essential nutrient and mineral inside the soil. (Menon n.d.) (IIT 2009) (COKER n.d.)

There are three main sources of land pollution:

Industrial: industrial wastes, rather solid or water, which excreted into land. Wastes such as paper, dyes, textile, pulp, cement and metallic contaminants which mostly contains chemicals such as Fe, Pb, Cu, Zn, Hg, Cd, CN.

Agricultural: any contamination of soil which is done due to agricultural activity. Addition of fertilizers and pesticides and insecticides, which also are a source of heavy metals like Pb, As, Cd, Hg, Co.

Domestic and urban: domestic wastes is a result of population growth and urbanization through the years, disposal of kitchen wastes, plastic bags and bottles, paper and glass are the day-to-day types of domestic wastes.

1.3.3. Air Pollution:

Any gaseous and suspended particles which enters the air and accumulate on atmosphere, which high concentration of them can bring danger to living organism and even death to human, animals and plants which consume the air to live, is called air pollution. Major air pollutants are carbon dioxide, sulfur dioxide, hydrocarbons, carbon monoxide, nitrogen oxide and CFCs (Chlorofluorocarbons).

Like other type of pollution, air pollution can also be categorized into two sources:

Natural sources: ashes and flames from volcanoes, natural occurring wild fire in, for instance local and global forests, pollen diffusion of flowers.

Anthropogenic: industrial processes, burning fuel like coal (it can be originated from several sources like burning fuel for generating heat in households, using for engines and power stations, for running the furnaces), transportation and exhaust gas and gas coming from burning solid wastes. (IIT 2009)

Table 2. Overall description of type of air pollutant, their sources and effects on Ecosystem and biota

Pollutant	Sources	Damage to Ecosystem and Biota

Carbon dioxide	Combustion of fuel (industries, households and automobile)	Global warming and thermal greenhouse effect
Carbon monoxide	Incomplete combustion of fuel (coal petroleum and wood)	Respiratory diseases, headache, heart failure in long term
Sulphur dioxide	Combustion of fuel (automobile and industries)	Respiratory diseases like asthma, eye irritation, acid rain, chlorosis and necrosis of plants
Nitrogen oxide	Heat generation of factories, fuel combustion (automobile and aircraft)	Skin cancer, eye irritation, reduction of demanded oxygen by blood
CFCs	Burning of plastics, spray can, leaking refrigerator equipment	Depletion of the ozone Layer.
Hydrocarbons	Automobile and petrol engine	Eyes and lung irritation, possibility of cancer

1.3.4. Noise Pollution:

Any type of excessive sound which is made by human activity and cause inconvenience is called noise pollution. It is ranged between loud urban speaker and stereo system to the aircraft noises. Intensity and radius of sound is measured by the standard unit of decibel (dB). Minimum amount of intensity a person can hear is 20 dB while by increasing the intensity, the amount of time a person can handle the noise decrease.

Below is a graph associated with capability of human ear to be exposed by noises higher than 80 dB:

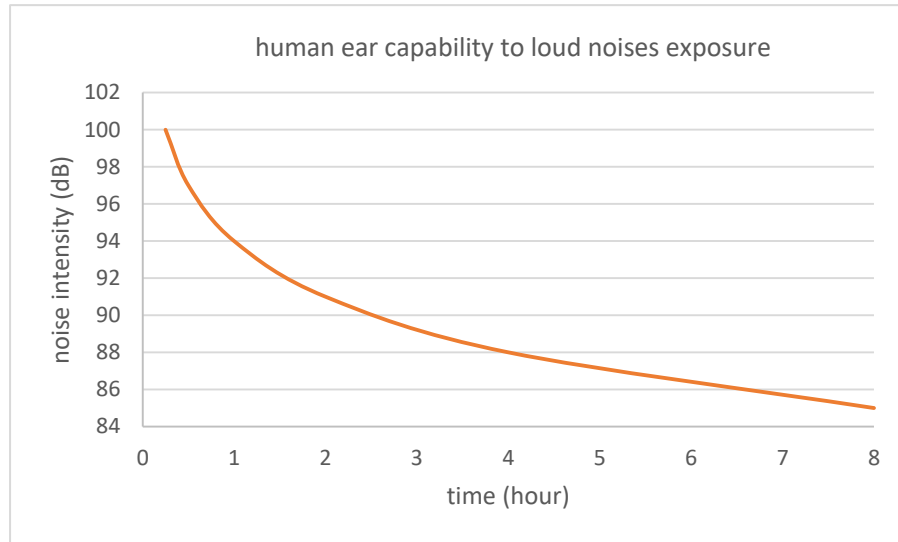


Figure 3. Sensibility of human ear to the loud noises regarding the time being exposed

The major sources of noise pollutions are: Industrial machinery, transportation and road, load speakers in public places and automobiles. (ERIKSEN 2017)

1.3.5. Radioactive Pollution:

Any release and emission of ionizing and nonionizing radioactive substances mostly alpha beta and gamma ray of nuclear elements is called radioactive pollution. These type of pollution are hazardous to living creatures due to their ability of bioaccumulation in bones. These effect vary from radioactive isotope types, but they are very likely to destroy human cells, cause cancer and bring genetic threat to next generations. (COKER n.d.) (M.M. Ghangrekar n.d.)

Major sources of radioactive pollution are: nuclear explosion, mining of ores and radioactive substances such as radium, uranium and plutonium, test and explosion of nuclear weapon and being exposed to medical X-rays.

1.4. Pollution in the Southern Basin of the Caspian Sea

1.4.1. Geography:

The Caspian Sea is one of the most well-known and largest lake around the world. It is a landlocked basin without outflow which is located between Asia and Europe. The Caspian Sea is bordered with Russia (at north and east), Iran (at south), Azerbaijan (at west), Turkmenistan (at southeast) and Kazakhstan (at northeast). It is most famous for its various fishes, caviar and oil production and also provide habitat for so many people in its coastal cities. (غیپشای 1382)

Southern region of the Caspian Sea ends with three Northern Province of Iran, Golestan, Mazandaran and Gilan. Because of the geographical conditions and climate situation of the area population density is rather high and respectively various industries and industry parks are located surrounding the sea border line. These industries use and produce chemical materials in different forms and eventually considerable fraction of these chemicals enter the sea water through the untreated waste water and effluents of industries and also municipal and urban sources, and unfortunately the treatment and filtration services and plans are as a low consideration for the industries and disposal system within the area.

1.4.2. Pollution Sources:

Caspian Sea has been affected by various source of pollution during years and since it is a closed basin and has no external duct to the other seas or oceans its ability to absorb, annihilate and dilute the pollution is less than an open water source, and pollutions mostly become stabilized and localized and become a significant threat to aquatic life. One of the major considerable threat for the sea is pollutions associated with oil extraction processes (Jafari 2010) But since coastal area of Caspian Sea is residential, people is also threatened by industrial and municipal wastes which is thrown into the sea rather directly or through river flows along their way to flowing into the sea. According to scientific estimation about 60,000 metric tons of petroleum byproducts, 24,000 tons of sulfites and 400,000 tons of chlorine are discharged into the Caspian Sea. (Aghai 2003) (Nadim, Bagtzoglou and Iranmahboob 2006). These pollutant have endangered living organism and marine species. There has been lots of plans, Implementation projects and protocols in order to reduce and control pollutions in Caspian Sea over the years, but over the past 10 years, aquatic and marine

species life's has been under the risk of extinction and reduction, and residents of Caspian coastal cities has been faced environmental issues more than ever.

Also another problem related to geographical condition and climate situation is high amount of tourists and traveler which usually reside near sea area or surroundings of the river thus, consequently another significant pollution source of the Caspian Sea is pollutions related to municipal and urban wastes. (Nouri, Karbassi and Mirkia 2007)

According to my study in this field, main threat and danger of industrial wastes (and partly municipal wastes) to the water bodies around them, is entering the heavy metals inside the water.

There was reports of waste minimization programs and strategies that has been done on number of industries in order to minimize the effects but the results as the reports indicates, were only focused on reducing the amount of COD by reducing the use of chemicals that have toxic effect on the surrounding by disposing the wastes related to them. The chemical which were excreted by the means of wastewater was accumulated on the surface water and reduced amount of required oxygen and reflected on the odor ascending the water body. Another plan was focused on collecting the black liquor which were a result of filtrate tank leakage into the wastewater from wood and fiber industry of CHUKA in Gilan which were high in COD amount. Another significant plan that was mentioned, was focusing on reusing the wastewater for another processes. Wastewater of industries were reported to be high COD container even if the chemical treatment were applied to them, thus, they were not a good option for using as basic water but reusing in processes was an efficient method. all the plans and reports above was focused on reducing the amount of COD, color and odor of wastewaters but yet, there is no significant practical program for reducing the amount of heavy metals inside the wastewater that Exit the factory and enter the environment. (Jafari 2010)

1.4.3. Description of Contaminants (Heavy metal):

The greatest danger disposal of wastes causes to sea water and consequently aquatic life and respectively food chain, is entering significant amount of heavy metal compounds in different

chemical types regularly. These heavy metals such as Pb, Cd, Cu, Cr, Mn, Zn, Ni and Fe has high density and higher atomic number than 20. These chemicals can be toxic and cause health problem and is a worldwide issue since they are available in many sources such as industrial wastes, municipal wastewater, landfill leaches and electronic disposals. (Jafari 2010)

Since one of the main sources of nonpoint source pollution of sea water is rivers flow first main focus of this project was studying main rivers water flows, whether they are located in the proximity of any industries and indicating which kind of contaminant is threatening these rivers –water and sediments- the most.

1.5. Treatment Methods Considered - Proposed and Practiced in the Literatures

Coastal area of the Caspian Sea receives significant amount of municipal or industrial wastes through the river flows and directly as it was mentioned above. Since the process of waste disposal is threatening the marine life and the hydrological condition of the rivers and wetland associated with the Caspian Sea, close attention and systematic treatment plans are needed to being applied.

There are different category of treatment and remediation plans which each one is suitable for different site with different characteristics. As for the first step, type, level, amount and form of the contaminants should be determined. One of the best method in characterizing the metals inside the contaminated site that is widely in use recently is called sequential chemical extraction.

This method (SCE) is a selective process of removing the metals (usually from the sludge) using different reagent in order to determine the mobility and distribution of heavy metals in order to determine the most efficient remediation method. This technique includes five step which during each one different form of chemical extractant is used by sequence of reagent, and each step removes heavy metal in a specific form. These steps are briefly known as: exchangeable phase, carbonate phase, reducible phase, oxidizable phase and residual phase. (Ukiwe and Nwoko 2010)

Most of the remediation technique are available in two category called in situ and ex situ. In situ is referred to method which is applied inside the contaminated soil or water while ex situ method is applied after excavation of contaminated site by pumping them out.

Remediation techniques can be categorized as three major method: physical, chemical and biological.

1.5.1. Physical Method of Remediation:

Isolation:

Isolation technique uses capping or different type of barriers in order to prevent the surface water, groundwater or soil to face further contamination. Contaminants get restricted into a contaminated site and not flow into the clean water or soil. This technique can also be used as a temporary restriction while other remediation technique is being applied to the contaminants.

Capping system use different material to restrict contaminated soil and prevent surface or groundwater contamination. It also can be used in order to control the gas and odor which is exhaust from the contaminated site.

Barriers also is a method of capping which is to be applied and reduce the movement of the contamination by using vertical or horizontal barrier which also can be combined by capping. Barriers are not to be applied for deep sites usually more than 30 ft. which is off limit for this technique. In order to achieve best result using this technique, barriers should be extent to low-permeability layer, such as clay or competent bedrock.

Generally physical method is being applied by combining them with chemical methods.

Immobilization:

Another physical technique for remediation of contaminants is called **virtification** this method is associated with reducing the mobility and bio accessibility of contaminants. This method use high temperature in order to destroy, immobilize and even volatilized metals and contamination which should be collected for disposal afterward. Although this method is applicable for soil, but it has

been pretty effective method for removing heavy metals. This process briefly use electrodes which is put inside the soil to produce thermal energy and by carrying the current and then solidify. This process is applicable for soil with only specific amount of water.

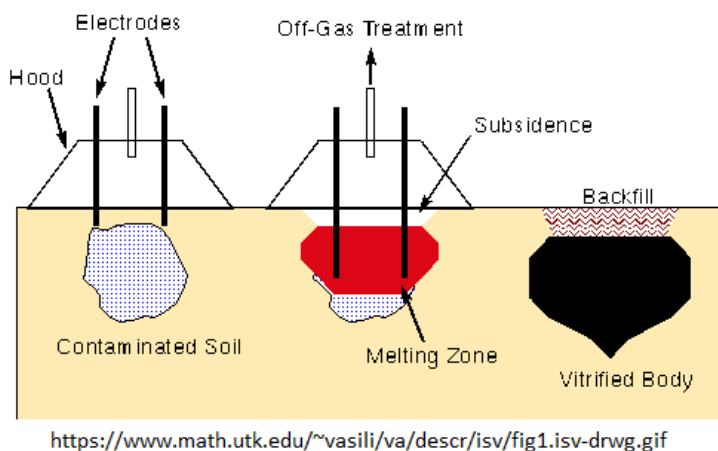


Figure 4. An example of in situ vitrification of contaminated soil using electrodes

One of the other same like process in physicochemical phase for especially water and wastewater contamination remediation is **electrocoagulation**. This process uses anodes and cathodes where three main reactions of reduction, oxidation and neutralization take place. It is also categorized as a method of toxicity reduction.

1.5.2. Chemical Method of Remediation:

Immobilization:

Solidification/stabilization technique is another method which is based on immobilizing the contaminants in contaminated site. Solidification is formation of solidified matrix physically and stabilization is addition of chemical reagent and performing reactions which reducing the mobility of the metals. S/S is achieved by mixing the contaminated material with appropriate amounts of binder/stabilizer and water. Also this method is not applicable for all kinds of metals and contamination. For instance only metal with certain amount of solubility and non-organic contaminants are suitable of this technology. This technology is also applicable for soil. The

dominant mechanism by which metals are immobilized is by precipitation of hydroxides within the solid matrix. (Bishop, Gress and Olafsson 1982) (Shively, et al. 1986)

Toxicity and mobility reduction:

Addition of chemical reagent and chemical reaction to decrease metals mobility and toxicity. There are three major type of chemical reactions which can be used in order to reduce the toxicity inside the wastewater: reduction, oxidization and neutralization reaction. During oxidization reactions which is basically loss of electrons inside the atoms, detoxification of wastewater and precipitation of metals take places by using reagents like potassium permanganate, hydrogen peroxide, hypochlorite and chlorine gas. Reduction reactions which is chemically define as atoms, gaining electrons, use alkali metals (such as Na and K), sulfur dioxide, sulfite salts, and ferrous sulfate as reagents. This process also is able to detoxify, precipitate, or solubilize the metals. Neutralization reaction is applied to adjust the pH inside the wastewater. This type of reaction can be used as a pretreatment method for reduction and oxidization reactions or also for another technologies such as S/S. all three type of chemical reaction techniques can be applied to soil or water as a combination or pretreatment for other techniques. Most important caution in using this method is prevention of adding further contamination into the contaminated site especially when the method is applying in situ by injecting the reagent inside the wastewater or groundwater. Another problem associated with this technique is that addition of chemical reagents is not selectively appropriate. Reagents can effect on other metals and increase the toxicity and mobility of treatment site (NRC 1994). One of the most common reduction reaction is Reduction of Cr(VI) to Cr(III) which is necessary for remediation of wastes containing Cr(VI) by precipitation or S/S. also the stability of reaction in long-term treatment plan is one of the main concern, regarding using this technology.

Permeable treatment walls or permeable reactive barriers (PRB) is an in situ technique for removing, precipitating, adsorbing and reducing the mobility of contaminants inside a contaminated water body. Barriers contain reactive materials which can trap the contaminants while the water flows through the wall. Reactive area is processed rather physically, chemically or biologically; or a combination of these. Most known material investigated as effective reactive is zeolite, hydroxyapatite, elemental iron, and limestone. Primary investigation has shown that element iron can be used for chromium reduction and limestone for lead precipitation. Also as it was mention above, one of the recognizable advantages of application of this technique is that it is an in situ technique, and also applicable for wide range of metals.

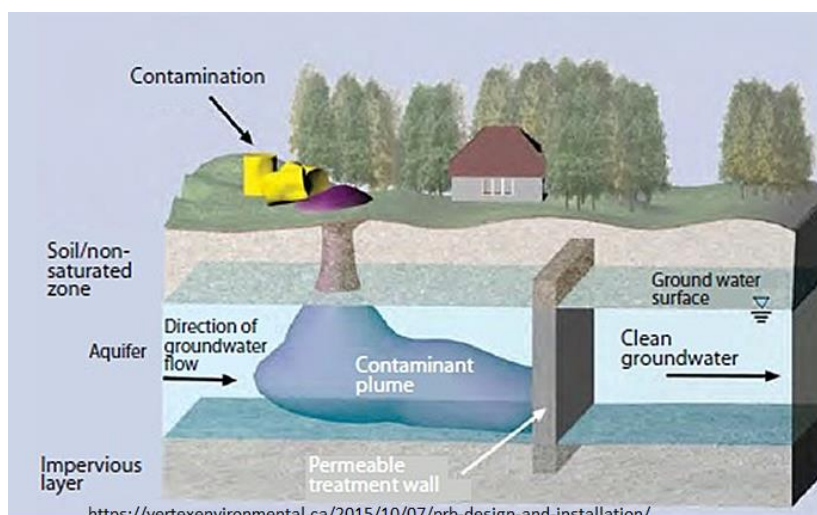
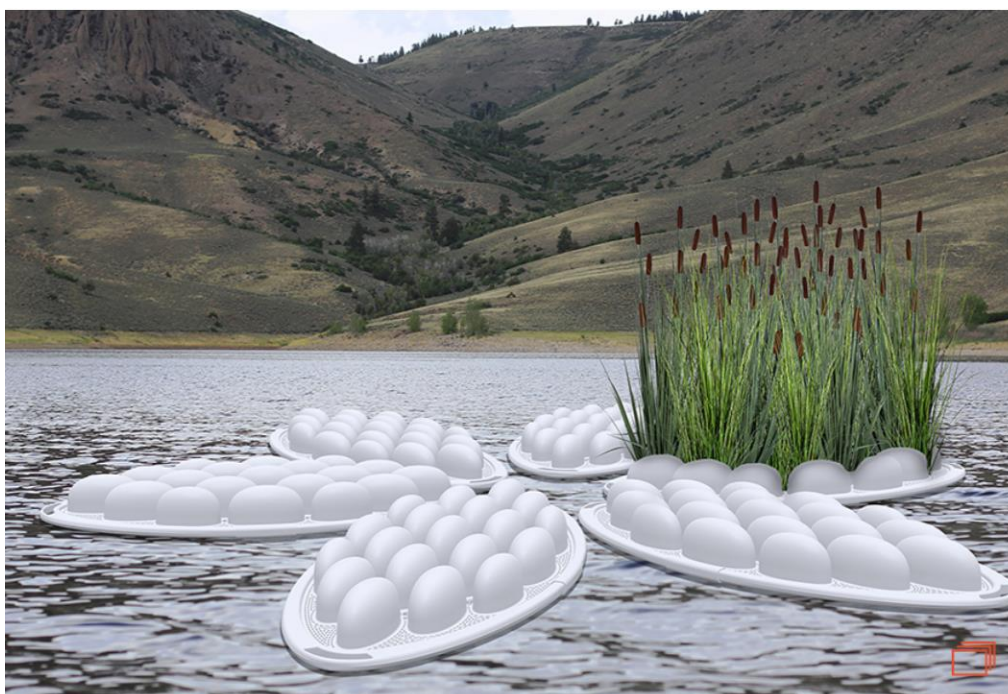


Figure 5. Visual diagram of a horizontal PRB

1.5.3. Biological Method of Remediation:

One of the most considered method of contamination remediation, especially for cases which are contaminated by heavy metals, is using plants as treatment means which is called **phytoremediation**. Plants in this technique uses their natural ability to uptake and accumulate metals in their tissues and roots by absorption. The ability of up taking and immobilizing the metal inside the soil or water body in this technique is selective and specific type of plants are proportional for specific type of metal and ion to remove.



<https://www.globalgradshow.com/projects/rafts-for-phytoremediation-of-surface-water/>

Figure 6. Sample of a raft which is designed for phytoremediation purposes. According to designer's explanation, plants will be located inside the rafts which is float in water surface. This particular design is suitable for phytoremediation of water pollution.

Table 3. Summary of accessible treatment method regarding their type and main technique

Treatment method	General focus	Type of treatment
------------------	---------------	-------------------

Capping and Barriers	Isolation	Physical
Vitrification	Immobilization	Physical
Electrocoagulation	Detoxification and Immobilization	Physiochemical
Solidification/Stabilization	Immobilization	Chemical
Reduction, Oxidization and Neutralization Reaction	Detoxification and Immobilization	Chemical
Permeable Reactive Barriers (PRB)	Immobilization	Chemical
Phytoremediation	Immobilization and Stabilization	Biological

1.6. Pollution by Heavy Metals

1.6.1. Why Heavy Metals?

Environment, especially water bodies due to their currency, are exposed to all kinds of pollution and contaminants whether physical, chemical or biological. Controlling and treating these contamination is definitely time consuming since mostly, finding the exact source of the contamination is a real challenge itself. Among all the contamination types, this project is focused on heavy metals as one of the most threatening contamination source for the Caspian Sea water.

Heavy metals or metalloids, as a major contaminant inside the industrial and municipal wastes are known to have high atomic weight and density (5 times higher than water) thus high toxicity level. Even a small amount of these metals are able to accumulate and bring danger to living organism. These contamination won't be degraded but rather would be accumulate and biomagnified through the food chain and trophic level and bring harm to aquatic life within the first steps and human within next level and in longer amount of time. For instance some type of heavy metals such as zinc

(Zn), iron (Fe) and mercury (Hg) are necessary in a controlled amount for human bodies and aquatic metabolism but other types like lead and cadmium are mostly harmful for human and also fish's liver and muscle tissues even in smallest dosage. (Hoseini, Tahami and Askari Hesni 2015) (Tchounwou, et al. 2014)

As for the Caspian Sea region in Iran which is a coastal area and is residential for about ten million people surrounding the water, it can be recognized as one of the main food product supplier for these people and even local Sea birds. According to Food and Agriculture Organization (FAO), fish consumption in Iran is about 6400g per capita (FAO 2012). This amount can be considered as 17.5g of fish products per person which is consumed daily.

One of the other significant danger of heavy metal is that these contaminants usually precipitate on the water sediments thus most of the fishes which feed from benthos consume large amount of the metals. According to an experiment done by Mirzajani in 2015 with the objective of Metal bioaccumulation in representative organisms from different trophic, five fish species were studied on, and three of the species called Sander lucioperca, Liza aurata and Cerastoderma glaucum were detected to be in the risk of high concentration of Respectively, Cd, Cr, Co and Ni for L. aurata and C. glaucum and Cu ($9.3 \frac{\mu g}{g_{water}}$) in S. lucioperca. It was utterly mentioned that the most probable reason and justification for the increased amount of metal concentration inside the fish tissues compared with previous studies, since these fishes are benthivorous, is increment in the concentration of metal in sediments of the Caspian Sea. (Mirzajani A.R 2016)

Another reason for choosing the heavy metal as the main study and analysis objective for this project is that the half-life of the heavy metals such as lead, cadmium and mercury is very high inside the human and aquatic animals tissues and body organs and it would be rather accurate to say, once they enters the body -with high bioavailability-, they will be absorbed by body tissue and they will not be degraded or Excreted.

Baku bay and Kazakhstan is an example of the environmental threat to fishes and aquatic life. Due to the proximity to all kinds of pollution especially industrial discharges which has been estimated to be more than 40 factories, there is no trace of aquatic life in the coastal area. Considering about

350 large and small river flow around the coast line in the Caspian Sea area in northern part of the Iran, the Caspian Sea is facing contamination regularly.

1.6.2. Chemical Properties of Heavy Metals:

1.6.2.1. *Lead:*

Lead or Pb is one of the most toxic heavy metals which is produced by industries, agricultures specially pesticides and urban wastes. Industrial sources of lead includes metal smelting and processing, secondary metals production, lead battery manufacturing, glass, piping, Intesticides, pigment and chemical manufacturing, and lead-contaminated wastes. It was also being used as the main elements in paint and as an anti-knock ingredient in the gasoline but since the high level of toxicity of lead for environment has been recognized industries tried to minimize their use of lead but still high amount of lead elements are contributed through the electronic wastes into the groundwater, surface water and soil. It is estimated that about 40 percent of lead attribution in environment is from electronic wastes.

Lead is usually found in forms of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes. Most common and reactive form of Pb is oxidation state of +2 or Pb(II) and lead-hydroxy (Smith, et al. 1995). although most amount of the lead injecting into environment is staying in the soil but the rest which enters the surface and ground water is highly toxic and usually is present as precipitation and sediment in forms of (PbCO_3 , Pb_2O , $\text{Pb}(\text{OH})_2$, PbSO_4),. It has an accepted toxic level of 0.0012 ppm, although it is not considered safe at any level. By the report of Environmental Protection Agency, maximum allowed and safe concentration of lead is $0.1 \text{ mg} \cdot \text{L}^{-1}$.

Lead toxicity is very high damaging for living organism. It can enter the body through food chain, inhaling and through human skin. It can cause various type of harm to human body. Nervous system damage, kidney and reproductive system failure, damage of hemoglobin synthesis, sterility in men, low fertility rates in women, impaired mental development and as the matter of food chain contamination, lead which exist inside the soil can poison the fruit and water by deposition and bioaccumulation. Same harms as above is done on birds and sea lives.

1.6.2.2. Cadmium:

Cadmium is the most toxic element among all the other heavy metals. Since cadmium is not necessary and essential for human body function, even low concentration level of it, is toxic and harmful for any living organism amongst the trophic level. Cadmium is being used in manufacturing of nickel–cadmium batteries, plastics and pigments. It also is available in by-product from the mining of sulfide ores of lead, zinc and copper. Another rich sources of cadmium is Phosphate fertilizers and wastes. Through all the processes and manufactures above, cadmium enters the environment where it get absorbed by soil and water. Maximum safe concentration reported By the Environmental Protection Agency for cadmium is 0.005 mg L^{-1} (Gautam, et al. 2014)

Alongside the anthropological sources of cadmium which are mentioned above, natural causes such as rock weathering, volcanoes, and forest fires are also rich in cadmium. Within these natural sources cadmium enters the environment commonly in the form of CdS or CdCO_3 . Otherwise it mostly is available in the form of Cd^{2+} , cadmium-cyanide complexes, or $\text{Cd}(\text{OH})_2$ solid sludge. In higher pH the majority form of cadmium is Hydroxide ($\text{Cd}(\text{OH})_2$) and carbonate (CdCO_3) solids and lower pH sources is rich in Cd^{2+} and aqueous sulfate species. In the presence of phosphate, arsenate, chromate and other anions, cadmium precipitation occur. One of the reason why cadmium is extremely harmful and dangerous is that this element is mobile in surface water and groundwater. (Callahan, Slimak and Gabel 1979)

Naturally, cadmium can be removed from the water by sorption and precipitation. sorption of cadmium occur by cation exchange capacity of clay carbonate minerals, and organic matter present in soils and sediments while precipitation of cadmium occur under reducing condition and be precipitated as CdS which is effective on controlling its mobility. (Cynthia R. Evanko 1997)

Cadmium present in soil can be absorbed by plants through their roots and be biomagnified while it is consumed by other animals feeding from them. Cadmium presents in water can also harm aquatic life by reducing the reproduction and growth rate and since even a low concentration level of it is toxic it cause higher death rate among fishes. Cadmium has been recognized as the cause of itai-itai disease in Japan. Most common and wide spread sources of cadmium amongst human is smoking tobacco and cigarettes which can cause lung cancer and by accumulation in the lung tissues and

cause cancer. Another sources for cadmium is through food chain and is highly available in mushrooms, shellfish, fish and seaweed. It can also causes renal dysfunction, osteomalacia, infertility and damage to the central nervous system, immune system, and DNA while it transfer from digestive system to liver and kidney where it remains and accumulate inside them by half-life of at least 30 years. (Gautam, et al. 2014)

1.6.2.3. *Mercury:*

Mercury is one of the other most toxic heavy metal. Natural sources of mercury are mostly volcanoes eruption, degassing, geothermal springs, and rock weathering. It was estimated to be up to 6000 tons of mercury release from natural sources but urbanization and industry progress has led to mercury exposure through sources like the burning of fossil fuels, waste incineration, mining (which mercury is available as byproduct of ore processing and also in sulfide ore cinnabar), industrial uses such as the manufacture of batteries and Releases from manometers at pressure measuring stations along gas/oil pipelines. Among all the natural and anthropological causes of mercury exposure, coal and fossil fuel burning is the most accountable causes which provide about 40 percent of mercury contamination. (Cynthia R. Evanko 1997)

Mercury is mostly exist in forms of exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (Hg_0), or alkylated form (methyl/ethyl mercury) in the environment. Under oxidizing condition, mercurous and mercuric is most stable form while under reduction, mercury compounds and other forms will reduced to mercury elements. Basically $\text{Hg}(\text{II})$ is strongly compliable with both inorganic and organic and is very soluble in oxidized aquatic system (Bodek et al., 1988). Under anaerobic condition, mercury element will be formed by demethylation of methyl mercury, or by reduction of $\text{Hg}(\text{II})$. Also under such circumstances both organic and inorganic forms of mercury may be converted to alkylated forms by microbial activity, such as by sulfur-reducing bacteria. Most toxicity of mercury occur in its alkylated forms due to its high solubility potential inside the water and volatility in air. (Cynthia R. Evanko 1997)

Once mercury disposed into the soil, same like other heavy metal it will be digested and magnified through food chain. As it was mention above under anaerobic condition, bacteria inside the soil is able to transform mercury compounds into methyl mercury which is highly toxic and has a high

bioaccumulation potential. Once it enters the body and get digested through food, enter the blood and then it can be accumulated inside the brain, kidney, heart, lung and vertebrates. Mercury accumulates in brain more than other organs where it can cause physiological stress, mental retardation and defecting nerve cells. Other effects of mercury on human system is abortion and tremors, blindness and kidney damage. Mercury was also diagnosed as the major cause of Minamata disease in Japan. (Gautam, et al. 2014)

1.6.2.4. *Chromium:*

Chromium is another heavy metal which unlike other metals, mostly doesn't appear in its element form and usually form compounds. Primary ore products of mine is rich in chromium in the form of FeCr_2O_4 . Other sources of chromium includes disposal wastes from industries with chromium as their main substances like leather, pulp and paper, tanning and rubber manufacturing industries. Also releases from electroplating processes is also great cause of chromium contamination.

Chromium like other metals are available in different form and depending on its oxidation state, its toxicity level varies. Most common form of chromium is Cr(VI) which is mostly available in shallow aquifers where aerobic condition. Cr(VI) is very mobile and highly toxifying. The toxicity of it effects all living organism; plants, animals and humans with significant matter. Thus, reduction of chromium into Cr(III) is very important. Major form of Cr(VI) are include chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) these two species have ability to precipitate in presence of metal cation. Reduction of Cr(VI) to Cr(III) is under control of organic materials such as sulfide and ferrous species while the most stable form of it can appear by soil organic matters. While chromium is transferred into surface water by surface runoff it become soluble and will appear as precipitation. (Cynthia R. Evanko 1997)

Major harms and damages of chromium specially Cr(VI) inside human body is studied. High level of chromium can cause nasal septa defect, liver and kidney damage, skin ulceration and it can also cause central nervous system damage. Also for plants it can effect on their photosynthesis process and reduce its rate. Also as for aquatic life, it has toxic effect on hematological problems and immune response in freshwater fish. (Tabari, et al. 2010) (Fendorf 1995)

1.6.2.5. Zinc:

Zinc is one the less toxic heavy metals which in contrary to cadmium, chromium and lead is essential for organism of body in a controlled amount. Zinc does not naturally appear in its element form while it rather extracted from mineral ore in the form of ZnO. Zinc is also main substance in brass and bronze alloys, copy paper, pharmaceuticals, batteries, galvanized products, cosmetics, rubber, tires, metal coating as corrosion resistant for iron and steel (it can be considered as the primary use of zinc in industries) and paints. Thus, disposal of any wastes, effluent and leachate from these type of products can cause zinc to enter the environment. Also coal and waste burning and natural ore wastes is rich in zinc. (Cynthia R. Evanko 1997)

Zinc is mostly appear in its oxidation state of +2 and is able to react with anions, organic acids and amino acids. Most available form of zinc inside wastes are zinc chloride, zinc oxide, zinc sulfate and zinc sulfide. Zinc as its precipitated form can appear as $\text{Zn(OH)}_2(\text{s})$, $\text{ZnCO}_3(\text{s})$, $\text{ZnS}(\text{s})$, or $\text{Zn(CN)}_2(\text{s})$. Although zinc is not as toxic and harmful as cadmium, lead and chromium but it is hazardous due to its high mobility inside the surface eater and groundwater which is because of its solubility in natural and acidic water body. (Cynthia R. Evanko 1997)

Zinc unlike cadmium has low bioaccumulation capacity and is less likely to accumulate and settle in the muscles and tissues, but as it was mentioned earlier, since it is highly mobile and soluble, it has high tendency to enter the food chain through suspended materials and is more bioavailable. Large amount of zinc inside the body can cause nausea and vomiting in minors. In adults it may cause anemia and cholesterol problems. (Gautam, et al. 2014)

1.6.2.6. Copper:

Copper is one of the other essential elements which participate in activation of enzymes during photosynthesis mostly found naturally in lands which is appeared through mining basically, and in a form of copper sulfide and oxide ores. Copper also is mainly available inside sandstone and minerals like malachite and chalcopyrite. Copper usually transfer to the groundwater and surface water by the lands run off. Other anthropological sources of copper includes fertilizers, building materials,

rayon manufacture, pesticide sprays, municipal and industrial wastes, algacides, chromated copper arsenate (CCA) pressure treated lumber, and copper pipes. (Gautam, et al. 2014)

Copper is basically binding with organic matters like clays and minerals. Due to its sorption to mineral surfaces and binding with organics, copper mobility decreases. Most potential forms of copper for the sorption is cupric, Cu^{2+} . Dominant forms of copper in aerobic condition is CuCO_3 while dominant forms for anaerobic condition is CuS . Most toxicity of copper have be demonstrated for Cu^{2+} , CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$. (Cynthia R. Evanko 1997)

Like other biologically essential trace metals, in spite of the fact that copper is essential for specific number of biological organism to operate, high concentration of this metal is toxic and harmful for human body. Copper damages on human body includes, nose, eyes and mouth irritation, nausea and diarrhea, long term exposure may cause kidney damage. As it was mentioned it is not necessarily essential for all the living organism, in fact copper can be highly toxifying for aquatic organism. (Gautam, et al. 2014)

1.6.2.7. Nickel:

Nickel is listed beside cadmium and lead as one of the other most toxic and poisonous heavy metal. Nickel is categorized as metals with high accumulation capacity on human muscles and tissue and some plants but not specifically in animals. Nickel is present in soil naturally and appear by volcano eruption. Anthropological sources for nickel includes: wastes from silver refineries, electroplating, zinc base casting and use as alloy combined with other metals, color ceramics, storage battery industries and fuel combustion. Nickel is also available in food uptakes by human (in low bioavailability, lower than it may be present in drinking water): canned vegetables, sugars and preserves, and bread and cereals food groups. (Paremr and Lokendra 2013)

Nickel appears in different forms but one of the most common and toxic one is Ni(II) which is associated with industries and effluent mentioned above. Also Complex nickel oxides, nickel sulfate, and metallic nickel are present in environment by combustion and smelting processes.

It has been demonstrated that nickel is included as essential elements for animal's body although the function is not precisely determined. Regardless of its essentiality, like other heavy metals nickel

with high concentration is harmful and toxic to living organism such as human. Nickel enters the body by food chain and inhalation and it accumulate on heart and liver and bring them damages. It can also cause headache, nausea, chest pain, dry cough and exposure in long term of time causes abnormal cellular morphology and cell reduction, respiratory problems, Decreases in growth and hemoglobin concentration, nervous system damages and cancer. ((ATSDR) 2005)

Table 4. Basic properties and important characteristics of most important and common heavy metals.

Metals	Damages	Sources	Limited Concentration (Based on Environment Protection Agency)	Half-life
Lead	- Nervous system damage - Kidney failure - of hemoglobin synthesis damage - Sterility and low fertility - Brain damage	- Smelting - lead batteries - Glass - Piping - Paint - Chemical manufactures - Insecticide - Electronics - Waste disposal - Fertilizer	0.1 mg*L ⁻¹	20-30 years (body) (WHO 1995)
Cadmium	- Reducing the reproduction rate of aquatic life - Renal dysfunction - Osteomalacia - Infertility	- Nickel–cadmium batteries - Plastics and pigments - Mining of sulfide ores of lead, zinc and copper - Phosphate fertilizers - Waste disposal	0.005 mg*L ⁻¹	17-30 year (body) (Järup, et al. 1983)

	• Central nervous system and immune system damage • Lung cancer	• Steel plating • Volcanoes eruption • Forest fires		
Chromium	• Nasal septa defect • Liver and kidney damage • Skin ulceration • Central nervous system damage • Reduction of photosynthesis in plants • Hematological and immune response damages in aquatic life	• Primary ore in mining • Leather • Pulp and paper tanning • Wood industry • Rubber manufacturing • electroplating processes	0.1 mg*L ⁻¹	35-40 hours (IPCS 2006)
Zinc	• Nausea and vomiting in minors • Anemia • Cholesterol • Abdominal pain	• Brass and bronze alloys • Paper • Pharmaceuticals • Batteries • Galvanized products • Cosmetics • Rubber • Tires • Metal coating as corrosion resistant for iron and steel • Paints	5 mg*L ⁻¹	16-43 days (body) (Tekada, Sawashita and Okada 1995)
Mercury	• Accumulation inside the brain, kidney, heart, lung and vertebrates. • Physiological stress	• Combustion of fossil fuels • Waste incineration • Mining • Batteries	0.002 mg L ⁻¹	70 days (blood) (US Center for Disease

	• Mental retardation • Defecting nerve cells • Abortion and tremors • Blindness • Kidney damage	• Manometers at pressure measuring stations along gas/oil pipelines. • Volcanoes eruptions		Control and Prevention 2005)
copper	• Nose, eyes and mouth irritation • Nausea and diarrhea • Kidney damage • Cause damage to aquatic life	• Mining (copper sulfide and oxide ores) • Fertilizers • Building materials • Rayon manufacture • Pesticide sprays • Municipal and industrial wastes • Algaecides • Chromated copper arsenate (CCA) • Pressure treated lumber • Copper pipes.	0.1 mg*L ⁻¹	

Nickel	• Headache • Nausea • Chest pain • Dry cough • Abnormal cellular morphology and cell reduction • Respiratory problems • Decreases in growth and hemoglobin concentration, • Nervous system damages • Lung cancer	• Volcano eruption • Wastes from silver refineries • electroplating, • Zinc base casting • Use as alloy combined with other metals • Color ceramics • Storage battery industries • Fuel combustion • Canned vegetables • Sugars • Preserves • Bread • Cereals food groups.	0.1 mg*L ⁻¹	20 to 34 hour (Friberg, et al. 1986)
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2. Review of Published Literature:

2.1. Specific heavy metal pollution in the rivers that leads to the Caspian Sea:

Amongst different type of water basins and water bodies, rivers plays and important role in preserving the ecosystem which is going to be explained below. Providing natural habitat is one of the rivers main role, flowing water of rivers provides habitat for different animal and aquatic plant species. River waters are being used as drinking water for many local people and also for animals which usually passing along or reside beside the river path. Rivers water and food sources – local fishes- can be their main source for water and food. Farmers use water from nearby rivers to irrigate their cropland and farmlands regularly. Many industries and factories are placed near rivers thus, the water flowing by rivers is being used for industry matters, such as using as coolant water and disposal of their wastes. One of the other natural benefits of rivers is that, they provide a potential source for tourism and recreational purposes. (Srinivas 2019)

Beside all of these importance and natural and social benefits of rivers, most important role of the flowing water of rivers from the viewpoint of this research, is transferring water to the larger basins, mostly to the seas -rather landlocked or open water- and oceans. Most important characteristics of rivers regarding their transferring role is their flow rate which means average amount of water which they transfer into the final destination (sea) by cubic meter.

As it was mentioned before rivers are being used for different application along their way and through each of these state, they are continuously exposed to multiple pollution and contamination risks. Disposal of agricultural such as fertilizers, wastes from urban and surrounded city sludge, and as this paper is focused on, disposal of waste water and solids from industries into the nearby seas without filtration and pretreatment. Thus it will endanger any living organism which their life is dependent on rivers water and lotic ecosystem, and it will ultimately endanger sea water by contamination from any forms which was explained in introduction section. As it was explained at

the beginning of introduction section, pollutions associated with heavy metals are the main focus on this paper.

2.2. Rivers:

For this research, specific number of rivers were selected to be studied which all of them were part of drainage basin and watershed of the south region of the Caspian Sea which is boarded with Iran's three northern province; Golestan, Mazandaran and Gilan. About 100 small and large flow rivers are included in the Caspian Sea drainage which some of them are particularly stems from mountains in Iran and some of them are common between Iran and Common border countries such as Turkmenistan and Azerbaijan. Main River basins located from northeast of Caspian Sea watershed to Northwest includes: Atrek, Gorganrud, Haraz, Sefidrud, Tajan, Aras and Chaloos.

Importance of these main rivers were signified by determination of their irrigation potential, fish farming, length and flow rate into the Caspian sea. Also there are others characteristics for rivers which make them ecologically important and exposed to pollution. For instance their proximity to mining processes. For this research all the above rivers were studied regarding their heavy metal pollution, its sources and danger rates, and also overall experiments on the Caspian Sea situation on three province were gathered and reviewed for the sake of this project which is not included in the report but the related articles and reports will be present on bibliography section.

The Caspian Sea includes six main basins surrounded it which is accounted for its total flow rate. Volga basins in north Russia with 273 km³/year (80%) of average flow rate which is majority of the inflow, Terek basin in west Russia by 7.4 km³/year (2.5 %) average flow, Ural basin in Kazakhstan with 8.1 km³/year (3%), Kura Aras basin in Azerbaijan with 17 km³/year (6.3%), and Turkmenistan and Iran basins which all together is accounted for the other 8% of the annual flow rate. Average flow rates of Iran basins were reported to be 5.3 km³/year from 1980 to 2015 (Ataei, et al. 2018)

2.2.1. Haraz River:

Haraz River is one of the most strategically and geographically important river in the Caspian Sea watershed located in Iran. Based on Caspian Sea National Research Center report, the annual flow rate of Haraz River into the Caspian Sea in 2015 were 0.72 km³, and its length is estimated to be 185

km which is originated from Alborz Mountain and outflow in the Caspian Sea in Sorkhrud city. During recent decades Haraz has been exposed to contamination since it's mostly surrounded by cities and significant disposal amount of municipal, industrial and agricultural wastewater is threatening the water quality.



Figure 7. a) A view of urban pollution located in the mouth of Haraz River. b) Mouth of Haraz River from different viewpoint

There are many factory and industries surrounded Amol which is also on the route of Haraz River, which most important of them are Kaleh diary, Amol machinery and paper manufacture (MBA). Although there is no analytical information and field research on how the disposal of these industries are done but according to researches and experiments on Haraz river water quality regarding metallic pollution, it can be assumed that these industries are influential.

According to field study on Haraz River by Nasrabadi, 20 site near the Haraz was selected and water sample were collected from them and analyzed for the heavy metals. Seven main heavy metal elements which were indicated by their analyzation were: Cu, Zn, As, Cd, Pb, Ni and Mn. According to the results and conclusion from Nasrabadi and his colleagues, the correlation between mean concentrations of metals along the 20 sites indicates that the sites which were located surrounding the Amol city (site number 14 to 20) were in higher pollution risk which is meeting the assumption of this paper that was proposed above regarding industrial and municipal waste disposal as one of the main risk associated with heavy metal pollution. However the paper itself represent that the main reason for the difference between concentration of metals through the lower located sites and upper located ones were considered to be related to mining, agricultural and municipal and industrial waste and was matched with previous study done by the same author which is also in accordance to assumption made by this paper (Nasrabadi 2015)

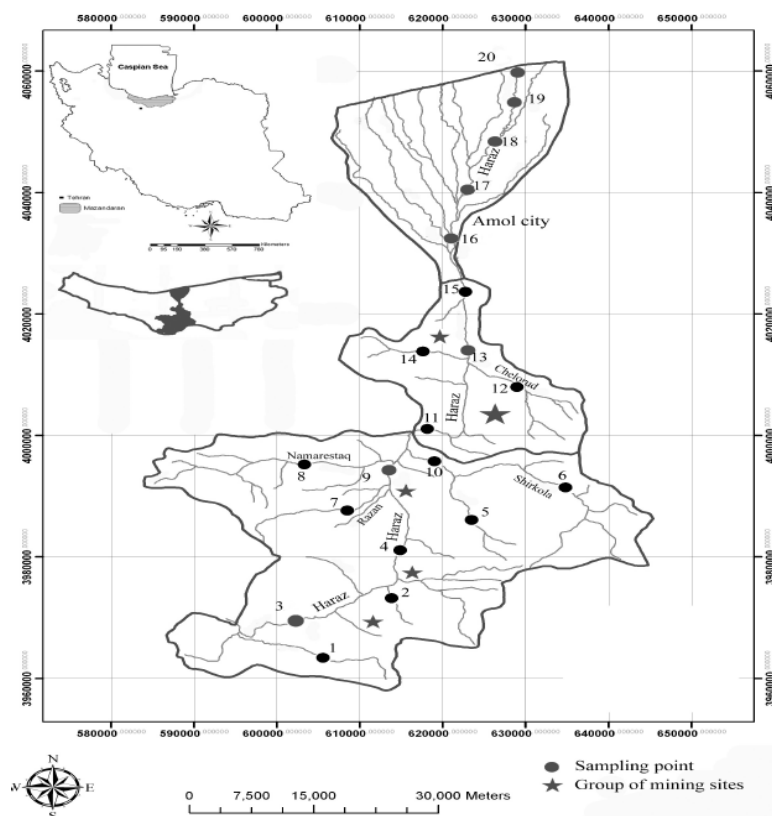


Figure 8. Location of sampling sites of Haraz River as the main study area for Nasrabadi's experiment. (This picture is sited in Nasrabadi's paper)

Mean concentration of metals from highest amount to lowest were reported to be: Mn=116 $\mu\text{g/l}$, As=55.35 $\mu\text{g/l}$, Zn=52.75 $\mu\text{g/l}$, Ni= 22.4 $\mu\text{g/l}$, Cu= 13.25 $\mu\text{g/l}$, Pb=4.4 $\mu\text{g/l}$ and Cd=2.65 $\mu\text{g/l}$. according to the indicated used by paper, which is proportional to the standard permissible value, the amount of Nickel and Arsenic was exceeding the standard value. Also the metals which were indicated, especially Cd, Zn and Pb are associated with same industry sources categorized in section 2.2. Processes such as machinery which includes smelting, alloys related processes, metal coating and steel plating and also paper manufacture is rich sources of zinc, cadmium and lead as it was mentioned. (Nasrabadi 2015)

2.2.2. Tajan River:

Tajan is another ecologically important river in Mazandaran province. Tajan River is approximately 140 km long which is originated from north hillside of the Alborz Mountain locally is called Hezarjarib and after passing Sari city it enters the Caspian Sea alongside the Khazar Abad road which is the location of many villages and urban lives beside the factories and industries.

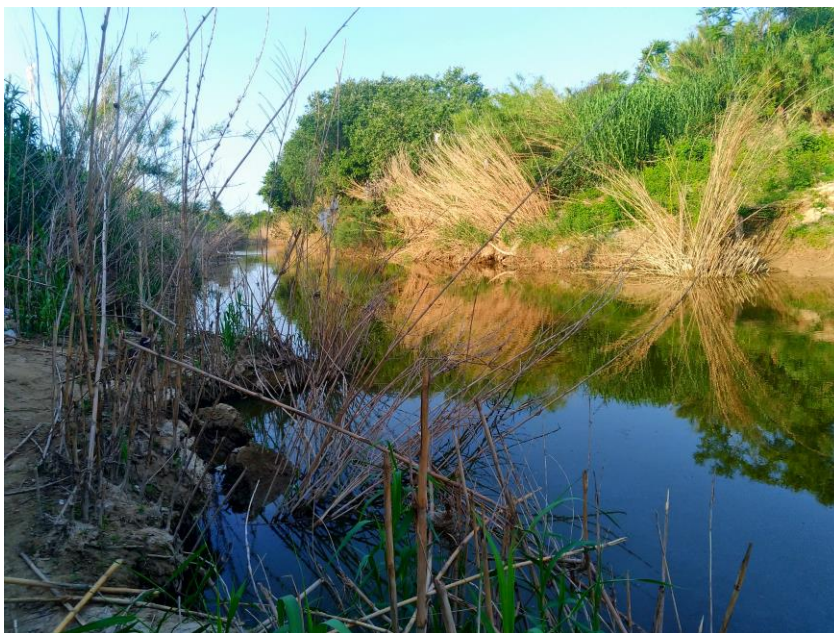


Figure 9. A close view of Tajan River located in sari

Tajan is the natural habitat for the most significant fish species of north Iran *Rutilus frisii kutum* (ماهی سفید) which is economically valued. Another importance of Tajan River, is the irrigation objectives of the water usage in its area. Also its proximity to one of the largest Cellulose industries and MDF products factory in the area called Arian Sina. Throughout the recent years unlimited disposal of urban and industrial wastes and also Non-principled agricultural use of Tajan water due to its proximity to cropland has made it biologically, physically and chemically contaminated and highly turbid, but yet most of the experiments and study were focused on biological contamination of the river and slightly focused on chemicals.

Although there is no precise study on Tajan water flows and sediment, Saeadi from Iran University of science and technology, Narmak branch, analyzed the merging area of Tajan River and the Caspian Sea, showed below from his paper. His study indicates that from the joining area, heavy metals of Mn, Pb, Cd, Zn, Cu, Ni and Co are present in high risk fraction proportions and mostly the sediments were contaminated by Mn, Pb and Cd. reports on mean concentration of metals and the comparison between the reported concentration and "Marine analytical chemistry standard Program of national Research council of Canada" indicates that the heavy metal concentration for the study area is higher than the standard amount. For more accuracy he studied the sequential chemical extraction which was explained before, for reaching a more vivid view of association of contaminations in different bounds and forms. The high risk fraction mentioned in lines above was based on his categorized groups of SCE levels by high risk fraction and low risk fraction. The result indicates that 88% of Mn, 71% of Pb, 51 % Cd, 55% Zn, 53% Cu, 35% Ni and 33% Co was present in high risk fraction group. (Saeedi and Karbassi 2006)

According to Tabel 4 since highest amount of metallic were determined to be related to Mn, Pb and Cd it would be a safe assumption that due to Tajan proximity to farm lands, rice fields and croplands, the high concentration of these metals can be associated with insecticides and fertilizers and also association between copper compounds and fertilizers and wood industry is to be studied.

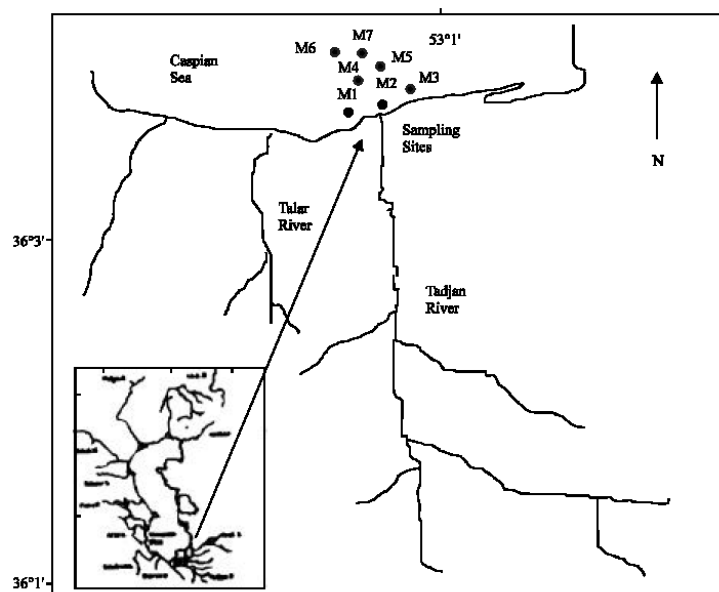


Figure 10. Location of sampling sites of Haraz River as the main study area for Saeedi's experiment. (This picture is sited in Saeedi's paper)

2.2.3. Sefidrud River:

Sefidrud (Sefid (white) River) is the second biggest river located in Iran with the length of approximately 670 kilometer and also one of the highest annual flowrate into the Caspian Sea. Sefidrud is actually the confluence point of two tributary of qezel ozen (originally located in northwestern of iran) and shahrud (originated from southern Alborz mountains). sefidrud is originated from sefidrud dam located in manjil a city in southern part of Gilan province which was built in order to meet with the irrigation and power generation purposes. The river water area behind the dam is 56 km². Sefidrud watershed passes along northwest of Iran; Gilan, Ardebil, eastern Azerbaijan, kurdestan, zanzan, Qazvin and slightly from Tehran and Hamedan. Sefidrud river flows into the Caspian Sea from Kiashahr city with annual flow rate of 1 km³ as Caspian Sea National Research Center announced for 2015. (Ataei, et al. 2018)

Beside geographical importance of sefidrud, it also has a crucial role ecologically and for economics of valleys surrounding it from Rudbar to its discharge point into the Caspian Sea. Upstream lands around the river is implanted by olive plantations of Rudbar while the downstream lands are more and more populated by irrigated rice cultivation. Beside rice and olive which are the main and wide

known products of Gilan province, other agricultural activity and production are also signifying the importance of sefidrud location. There are number of facilities and irrigation channels from sefidrud to irrigate the fertile plain, crops like tea, peanuts, and different kinds of vegetable, cotton, tobacco, and a wide range of fruits and vegetables.

Due to the crucial role of sefidrud on Gilan province and specially the rural life of that area, field study on the contamination rate of the river has been done during the years. One of the last and most updated data on this matter was presented by Vosoogh in 2016 (1394). The study was focused on the heavy metal concentration on sediments of the sefidrud. Sites for sampling process was chosen from the sefidrud dam to the discharge area of the river. The objective of this study was to indicate the concentration and characteristics of heavy metals of Cu, Zn, Cr, Mn, Fe, Pb, Ni and Cd, regarding the particle size of the sediments which the study was conducted on. Thus, four category of particles were studied: $<38\mu$, $38-63\mu$, $63-125\mu$ and $250-500\mu$. Vosoogh mentioned that most of the past studies in the related subject were conducted on particles smaller than 63μ due to higher amount of surface (pore) thus higher amount of metal absorption. But this experiment was focused on studying wider range of particle size (Meers, et al. 2005). According to conclusion and outcome of this study, there were no significant relation between the particle size and metal concentration for all kinds of heavy metal. For this study three indicator was chosen to investigate the contamination rate, ecological risk and toxicity rate of the contaminated area. The results indicates that for particle size of $63-125\mu$ the "intense" contamination rate and "high" ecological risk was approved and by approaching the discharge area to the Caspian sea the contamination gets higher. Also for particle size of $<38\mu$ the highest toxicity rate was shown and the previous result of "smaller the particle size, higher concentration of heavy metal" was replicated. The quality assessment of the indicator of contamination rate was represented by Ibrahim 2005, ecological risk was represented by Hakanson 1980, and toxicity rate by Zanjani and Saeedi 2013 (وئوق, سعیدی و لک 1394).

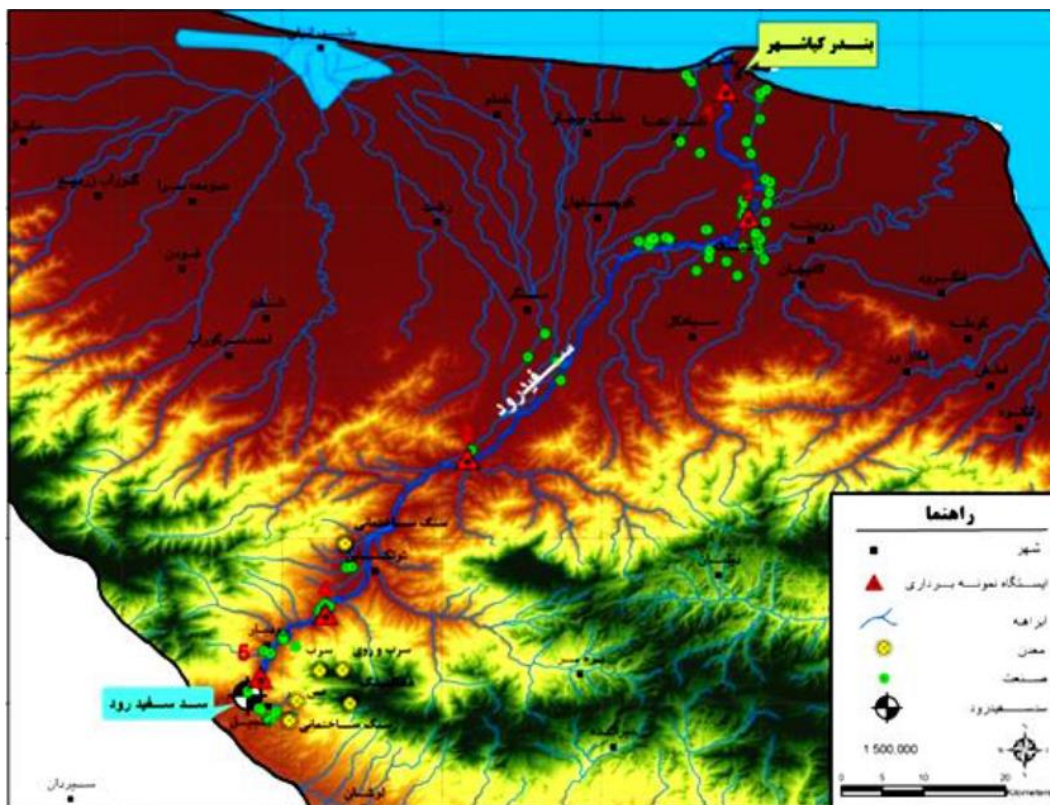


Figure 11. Location of sampling sites of Haraz River as the main study area for Vosoogh's experiment. (This picture is sited in Vosoogh's paper)

2.2.4. Aras River:

Aras River is one of the most geographically and strategically important river located in Iran. Aras River is originated from Binagulaq Mountains based in turkey, then it flows through Turkey-Armenia boundary and from there, it locates as the share border between Iran and the both country of Azerbaijan and Armenia. The total length of the river from its origin to its discharge point into the Kura River in Azerbaijan, is estimated to be 1072 km and the common boundary shared with Iran is 470 km. amongst the four country that shares Aras, Iran's share is more than the others and is estimated to be 40% of the whole river. The total annual flow rate of Aras basin located in Iran is 2.057 km³. (UNECE 2011)

Aras basin is the supplier of water for many cities along its path thus it is under the threat of municipal and urban wastes rapidly. Agriculture is one of the main activity around the river basin in Turkey, Armenia and Iran. The return flow of agricultural run off to the river is pressurizing the basin

by agrochemical waste, pesticides, nutrients and salts. Irrigation system and techniques are also utilized from the basin. Alongside the municipal and agricultural pollution sources, one of the most threatening contamination source for Aras basin is the industrial activities and wastewater. Although it has been a known fact that turkey share of the river's land and surrounding is not highly filled with industrial purposes and factories, the Iranian share of the river is threatened by industrial wastes widely. A great share of the river is located near Ardabil province, where agricultural and irrigation system is very dense, as much as industrial facilities of Pars Abad Moqan and other factories. Altogether, these includes 60 km of Aras River. Mining is also a factor of concern in both and shared area of Iran and Armenia. Due to all the mentioned pollution factors and sources, the water quality and fishes lives in Aras River is exposed to a great danger.

Within the years, many study were conducted on pollution status of Aras River and it was acknowledge the fact that Aras is widely polluted by heavy metals such as Cu, Mn, Fe and etc. which was associated with mining, lack of wastewater and solid management. (UNECE 2011) There is a recent study (2012) on sediments and fishes tissues of Aras River which was conducted by Nasehi and her colleges from Ardabil Islamic Azad University. Objective of this study was to assess and analyze the heavy metal concentration within the Ardabil province. Therefor, 5 site from Aras boundary were selected in order of, entrance to the Ardabil province, after darrehud-Aras junction, after Gurrichai-Aras junction, downstream of pars abad moqan industrial complex and Iran Armenia mutual boundary. Heavy metal analysis shown the high concentration of Cu, Pb, Fe, Ni, Cd and Zn on sediments sample from Aras River. According to their assessment and comparison with the earth crust, sediment and igneous rocks, the amount of cadmium inside the samples were indicates the great risk. The high amount of Fe in all stations were justified to be in related with Fe availability in earth crust and rocks which can be dissolved into the water and also in associated with human activities such as waste disposal and mining activities of songun and Armenia copper mines. Copper, zinc, cadmium and lead has the highest concentration in station 5 while Nickel and iron has the highest concentration in station 4. Station 4 is the in proximity to 15 active industrial units' wastewater including Moghan's Agro-industrial and livestock Company (near Oltan and Tazekand Ghadim) and Pars- Abad's sugar refinery, dairy farm, and cattle feed center which are among the most important and biggest industrial units in the region. (Nasehi, et al. 2012)

The results states than the mean concentration of metals were descending in order of $Fe > Cu > Ni > Zn > Pb > Cd$. Since the station 4 was in proximity to high number of industry and factories, the threat exposure was remarkable in this area and high concentration of nickel (2.72 mg/l) was claimed to be associated with juice, dairy products, edible oil and sugar cane factories as well as soybean croplands, which are located within the Sub-basin of Aras River in the study area. According to categorizing the sources of nickel in table 4 it is compatible with the current study. Justification on iron high availability was explained above. (Nasehi, et al. 2012)

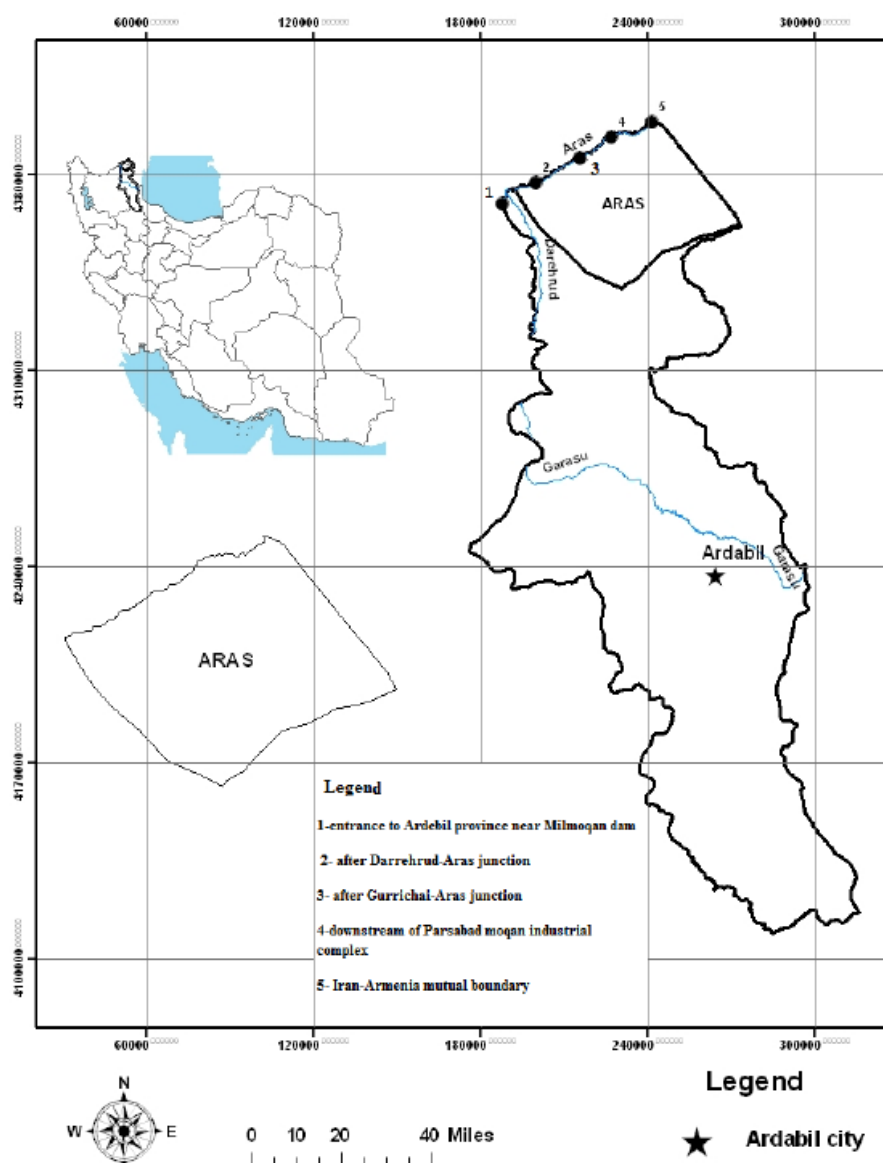


Figure 12. . Location of sampling sites of Haraz River as the main study area for Vossoogh's experiment. (This picture is sited in Vossoogh's paper)

2.2.5. Gorganrud River:

Gorganrud (Gorgan River) is one of the main river in Golestan province and east side of the Iran. Gorganrud is originated from Aladaq Mountains based in Bojnourd. After passing through Golestan province, the river is discharged into the Caspian see through Gorgan Bay located near khajeh nafas area by the total length of 200 km. one of the main importance of gorganrud is the irrigation of Gorgan's plain (Dasht-e-Gorgan). There is lots of industry and urbanizing surrounding the Gorganrud which is jeopardizing the water and other member of ecosystem inside the Gorganrud. Near the river's delta, surrounding the Torkaman port and khajeh-Nafas port the density of industries and urbanizing is higher.

There is a study focusing on the heavy metal contamination of Gorgan bay that has been done by Tabari and his colleagues. The study area was categorized as 4 sites, Gomishan wetland, eastern beach (which includes the 2 sampling site from Gorganrud), western beach and Goran coast itself. The analysis was done on fish, water and sediment samples. According to the analysis, from the four heavy metal investigated (Cr, Zn, Cd and Pb) lead has the most, mean concentration amongst the others in water samples. And between the four sites, the eastern site which includes Gorganrud has the highest amount of Pb (164.84 ± 33.05 ppb). Respectively the mean concentration order was shown to be $Pb > Cr > Cd > Zn$. Also for sediment samples the order changed to $Zn > Pb > Cr > Cd$ with highest mean concentration of zinc in four sites. The justification on the metals which were found and the highest concentration of them in sediments were associated with the sedimentation and precipitation tendency of heavy metals which in other papers were also indicated. According to my studies and the shared idea of the Tabari paper, the four heavy metals of Zn, Cr, Cd and Pb are all related to the paper and pulp industries as well as paint and pigments and electroplating, which are related to the industries surrounding the experimental area. Also the runoff of agricultural lands is also a concern of fertilizers entrance into water which also contains lead and cadmium. (Tabari, et al. 2010)



Figure 13. Location of sampling sites of Haraz River as the main study Area for Tabari's experiment. (This picture sited in Tabari's paper)

Although according to the comparison that was made in the paper by the FAO/WHO food standards program it was announced that the Pb, Cd and Zn level is below standards (standard limit for Pb and Zn is about 0.1_0.2 mg/L and for Cd is 0.5 mg/L) while for Cr is 0.5 mg/ml and is higher than the standards limit. It was finally mentioned that however the contamination risk is not currently very high in the area, but since the filtration and wastewater treatment for the industries and runoff from agricultural lands and fertilizers and quality assessment of the output water of each is neglected, the area has risk potential. This study was conducted on 2010. (Tabari, et al. 2010)

There is also another newer study by Bagheri and his colleagues which was mainly focused on gorganrud itself. 10 sites were chosen for sediment sampling process regarding the industrial areas and municipal density. Result of heavy metal analysis indicates that the concentration of heavy metals of (Al, Cr, Ni, Cu, Fe, Co, Mn) was higher near the discharge area of the river into the caspian sea. The Muller indicator was chosen to differentiate between the natural and anthropogenic causes

of contamination. Since most of the heavy metals is already present in the earth crust and could enter the water by runoffs from rainfalls and drainage. According to muller indicator, site number 1 which is the discharge area of the river, is contaminated higher than the other sites ($Al(2.16) > Cr(1.53) > Co(1.17) > Cu(1.17) > Ni(1.01) > Fe(0.79) > Mn(0.56)$) and is respectively threatened by all the metallic which were study in the analysis .The conclusion was at the same position to the Tabari's paper. Generally Gorganrud is not as highly contaminated by heavy metal as other main river of the Caspian Sea. (باقری, و غیره 1390)

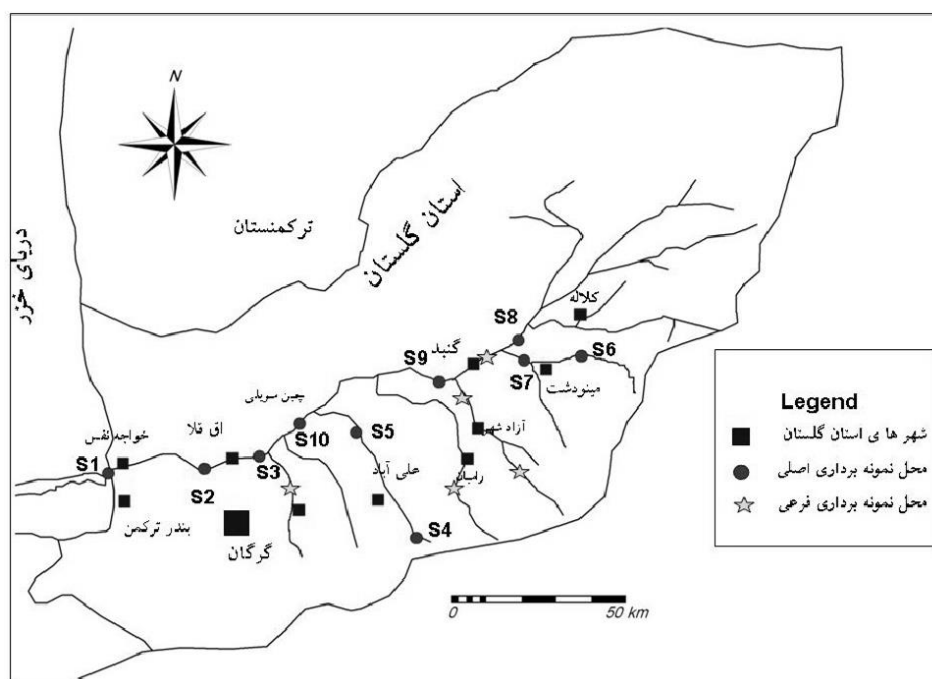


Figure 14. Location of sampling sites of Haraz River as the main study Area for Bagheri's experiment. (This picture is sited in Bagheri's paper)

2.2.6. River Atrak:

Atrak River is another mutual basin based in Iran which is shared by the countries of Iran and Turkmenistan. Atrak/Atrek is originated from north eastern mountain in Iran, after joining to Tersakan tributary in Turkmenistan it flows into the Caspian Sea. Total length of the River is 530 km.

it's estimated that about 79% of Atrak River is based in Iran which contain the basin area of 26500 km². The annual discharge of Atrak River into the Caspian Sea (in Turkmenistan) is 0.1 km³. (UNECE 2011)

The main usage of the Rivers in northern states of Iran is for agricultural purposes and irrigation of the land but the problem is the returned flow and runoffs of the lands into the river without any treatment and further observation. From another point of view, industrial and municipal wastewater are also threatening the River water. According to presses, concerning amount of industrial and municipal wastes are entering the Atrak River regularly which endanger the water quality and causing high level of contamination. According to Tasnim news and Fars news, discharge of waste water and sludge from industrial, municipal and agricultural sources are the main reason of river contamination and also cause water drought at some level (Tasnimnews 1396) (Farsnews 1395). According to these reports and reports from academic study, main threat to the Atrak River is bacterial and biological pollution and most experiments and study also focused on this aspects.

Eastern parts of Iran is one of the main industrial lands in the country and amongst them the wastewater and solid discharging from petrochemical industries in Bojnourd has the main role in polluting the environment surrounding it according to Yazdanmehr. Thus he and his colleague has done a study on the sites surrounding the petro chemistry factory of Bojnourd in order to assess the soil quality of the 16 site for contaminants and trace metals. These sites and the factory are located at the proximity to the Atrak River. The results shown that amount of heavy metals of As, Ni, Zn, Pb and Cu are more than standard amount for earth crust (Pb=91 ppb, As=29 ppb, Zn=344 ppb, Cu=107 ppb, Ni=252 ppb, Cr=163 ppb). According to the analysis done by the study, lead have mainly anthropogenic sources while nickel, arsenic and copper are associated with both anthropogenic and natural sources but generally it would be accurate to presume wastes from different sources of industrial, municipal and agricultural has a crucial role in polluting the surrounding by heavy metals.



Figure 15. Location of sampling sites of Haraz River as the main study Area for Yazdanmehr's experiment. (This picture is sited in Yazdanmehr's paper)

Since I could not find any precisely related article and study associated with Atrak River, I assume the results and conclusion regarding type of heavy metals inside the soils sample around the atrak river (bojnourd) can be accommodated into the Atrak River water since it is located in proximity to the factory mentioned above and the article also mentioned the possibility of the pollution entrance into soil and water. Further studies is suggested be conducted on this area. (یزدان مهر و قربانی 1396)

2.2.7. Chalus River:

Chalus River is another main river in the Caspian Sea watershed from north Iran. Chalus River is originated in mountains of Kandovan and Taleghan and discharged into the Caspian Sea from the Chalus city located in Mazandaran. The length of the river is approximately 72 km and the annual flowrate into the Caspian Sea is estimated to be 0.33 km^3 by the year of 2015. (Ataei, et al. 2018)

Chalus River is threatened by the wastewater from municipal sources the most and is highly turbid, since the margin of the river is one of the main touristic area in the province, but little precaution and treatment plans are being conducted.

According to a study done by Azimi and his colleagues the concentration of lead in three main river of the Caspian Sea (Babolrud, Chalus and Gorganrud) was investigated. Three sample site from upside of the river, middle way and mouth of the river was chosen and the sediments were analyzed for lead (Pb). The results shown that Chalus River has the minimum lead concentration between these three rivers. The concentration for Chaloos, Babolrud and Gorganrud were 13.81, 15.30 and 17.68 $\mu\text{g/g}$ dry weight respectively. (Azimi, Riahi Bakhtiari and Parsayi 1398)

Table 5. summary of concentration and origin of the contamination inside main river's of this study and a reportage of most threathening heavy metal which was reported in each field study

rivers	state	Type of contaminant	source	High risk indicator metals
Haraz	Mazandaran	E-coli, Coliform (biological) color , COD (physical) Ni Pb Cd Cu Zn Mn As	Municipal and industrial waste, tourism industrial (wood and paper and textile iran poplin) mining and quarrying activities, urban and industrial discharges	As, Ni
Aras	gilan	Fe>Cu>Ni>Zn>Pb>Cd Cr Zn, Al Mn	sugar refinery, dairy farm, cattle feed (pars abad moqan), juice, dairy products, edible oil and sugar cane factories	Ni
Gorgan rud	Golestan	Cu, Cr, Cd, Zn Odor and color	Industrial (paper, electroplating,) Brick production and cotton wiping (پنبه پاک کنی)	Cr

		Al, Cr, Ni, Cu, Fe, Co, Mn	industrial park	Cr>Ni>Fe>Al>Mn>Cu
Sefidrud	Gilan	Fe, Mn, Al, Li Zn, Pb, Cu, Cr, Cd	Natural Municipal and industrial	all
Tajan	Mazandaran	Mn>Pb>Cd>Zn>C>Ni>Co	-	Mn, Pb and Cd
Chalus	Mazandaran	Pb	municipal	Pb
Atrak	Golestan	Zn>Ni>Cr>Cu>Pb>As	Petrochemical factory of bojnourd	As, Ni, Zn, Pb and Cu

2.3. Identification of Major Contaminants Reported:

Seven main rivers of the Caspian Sea watershed based in Iran was investigated through the papers and field examination. Different areas were exposed to different metal contamination and different concentration of each. Concluding a uniform result respecting the concentration of metal in all study area is rather hard since each indicator which was used in papers were different, but it would be roughly accurate to state that the **nickel** (Ni) and **lead** (Pb) metallic were mostly present in all the area.

3. Proposed Treatment Methods – Phytoremediation:

Phytoremediation as an alternative plan to retreat the industrial wastewater which are reach in heavy metal are being considered lately since it is a green technology and has lowest cost amongst other treating methods and plans. Another advantage of this method is that phytoremediation is a selective way of removing heavy metals.

Although there is some limits and disadvantage to this technique such as low efficient age of plants, being a time-consuming method, and as it will be explained below low biomass production for some plants, but, since the study area was chosen to be Northern provinces of Iran which is known for its massive and diverse vegetation and fertility, the most efficient and applicable method as proposed remediation technique is decided to be phytoremediation. (Voijant Tangahu, et al. 2011)

This method use plants to absorb, extract and excrete the contaminants from the soil body or water body. This process generates by the use of different organism part of a plant: roots, shoots and leaves. Each part participate in translocating, accumulating and degrading of contaminants. Generally through the process of phytoremediation, contaminants get absorbed by the plant's roots and tissues and the toxicity level of metals gets lower in soil or water. Since heavy metals cannot be degraded, plants can accumulate and immobilize them by up taking them through their roots and tissues. In better chances and best case – for specific type of plants-, plants can even convert and detoxes the contaminants into lower toxicity level. (Carolyn Beans 2017) (Voijant Tangahu, et al. 2011)

Generally, there is two category for plants which are being used for phytoremediation processes. First category are consists of plants such as *Thlaspi* which have a high capacity of metal concentration inside their biomass although the annual biomass provided by these type of plants is not very high. Second category consist of plants such as *Brassica juncea* (Indian mustard) which have a lower potential for metal concentration but higher biomass production so it would be accurate to conclude that actual amount of removed metal is higher. (Robinson, et al. 1998)

Phytoremediation divides into different mechanism regarding type of the contaminants – organic or inorganic. For organics mechanism involves phytostabilization, rhizodegradation, rhizofiltration, phytodegradation, and phytovolatilization. For inorganics, mechanisms which can be involved are phytostabilization, rhizofiltration, phytoaccumulation and phytovolatilization. (Voijant Tangahu, et al. 2011)

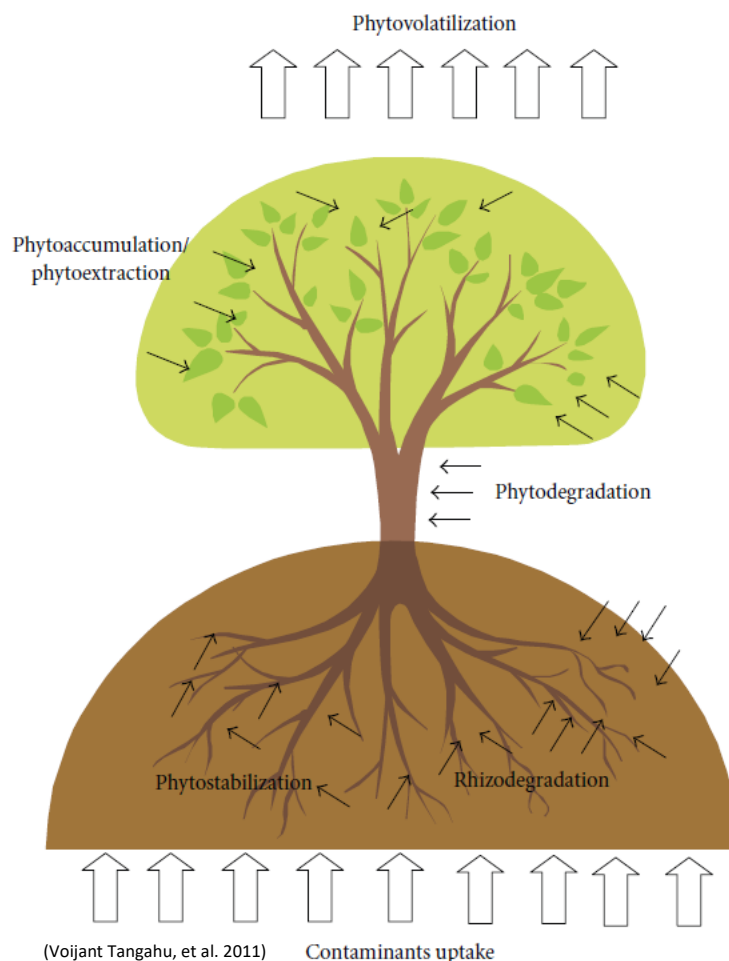


Figure 16. General mechanism which is being used by plants after up taking heavy metals from soil or water in phytoremediation technique

3.1. Phytostabilization:

The first step, phytostabilization, which is common step for organic and inorganic compound is immobilization of contaminants in soil, by means of root plants. Roots of plants accumulate and absorb the contaminants from the soil and also precipitate them, thus reduce their bioavailability.

This mechanism is applicable for soil, sediments and sludge. (Voijant Tangahu, et al. 2011) (Faraji 2014)

3.2. Rhizofiltration and Rhizodegradation:

Through the next level which is Rhizofiltration, the contaminants and pollutants which specifically are metals, excess nutrients, and radionuclide contaminants in groundwater, surface water, and wastewater medium, in this specific process, be absorbed by the plants root from the aqueous solution underneath the soil, thus the contaminant get excreted form the soil or water. There is another excess step between two previous ones for organic compounds and contaminants including organic carbon bind which is called rhizodegradation. Through this step organic substances existing in the soil get cracked and breakdown by the microorganism inside the soil body In order to produce the energy and food for them. The broken down contaminants also get ingested by plant tissue as nutrient which is called **phytodegradation**. These two steps is applicable for soil, sediment, sludge, ground water, surface water and wastewater. (Voijant Tangahu, et al. 2011) (Robinson, et al. 1998) (Faraji 2014) (EPA 1999)

3.3. Phytoextraction and Phytoacumulation:

Contaminants and pollutants which are broken down in the soil, gets up-take by the plants and be accumulated inside their roots and shoots tissues through phytoextraction and phytoacumulation level. Within these levels some special plants with higher absorbing and accumulating capacity, called hyperaccumulator is being used. These kind of plants usually have a shoot to root metal concentration ratio of more than 1 while this ratio for other normal plants is less than 1. This is for metals, metalloids, radionuclides, nonmetals, and organics contaminants in soils, sediments, and sludge medium. (Voijant Tangahu, et al. 2011) (Robinson, et al. 1998) (Salido, et al. 2010)

3.4. Phytovolatilization:

The final step contains ability of plants to volatilize and transfer the contaminants into the atmosphere. This process which is called phytovolatilization is for metal contaminants in groundwater, soils, sediments, and sludge medium. Within this step, contaminants move from shoots to leaves by the water and be volatilized there. (Voijant Tangahu, et al. 2011) (Salido, et al. 2010)

3.5. Laboratory Experiments Pilot Scale Field Trials and Results:

According to experiments increasing of lead concentration in soil will lead to increasing in plant uptake of the metal in the tissue. Lead inside the soil is naturally immobile and rather not bioavailable. Pb is mostly insoluble in soil, consequently, aqueous solutions containing chelating agents such as ethylene diamine tetra-acetate (EDTA) anion are commonly applied to soil in order to mobilize Pb and facilitate extraction. Thus the experiment was conducted in order to discover whether adding a chelator as a chemical enhancement will increase the Indian mustard capacity of up taking the Pb or not. "The application of EDTA, DTPA, CDTA, EGTA, and citric acid to the soil solubilized Pb in the soil and also increased Pb uptake and translocation to the shoots" so the experiment shows that adding a chelator to the soil will increase lead solubility thus leads to increment in Pb concentration in plant shoot. Also this process was effective for Cd, Cu, Zn and Ni compounds too but the most efficiency was for Cu, Pb and Zn (Blaylock, et al. 1997) Pb uptake in roots increase by increasing the pH but Pb in shoots increase by decreasing the pH. In the previous experiment on the same sequence, it was proven that the pH efficiency on As and Pb removal from the soil by phytoextraction is under compromise. Although the relation between pH level and plants ability to transfer and extract the Arsenic and lead was not the same (as it was mentioned above lowering the pH increase the Pb removal and it is the opposite way for arsenic) the mean effective amount of pH level for efficient removal of both As and Pb is 5. The experiment also proved that addition of a chelator is necessary since without enhancement the root concentration of Pb will be much higher than shoots. Within all the chelator the most effective one found out to be EDTA. (Salido, et al. 2010)

As the above experiments and results were related to soils polluted with heavy metals, there is an experiments that indicate same result is feasible for wastewater metal polluted. according to a study by Sampanpanish by the objective of investigating the effect of EDTA in removing the Pb from wastewater by the plant of Elephant Ear' aka *C. esculenta*, it was stablish that the more amount of time and concentration of EDTA being applied to wastewater, will consequently lead to more amount of Pb uptake. It was also suggest that other plants with high potential of Pb uptake such as *Jatropha curcas*, *Meliosmapinnata*, *Leucaenaleucocephala* and *Eucalyptus camaldulensis*, Especially *Pennisetumpurpureum* Schum cv, can be effective. (Sampanpanish and Hongpiriyakul n.d.)

Also another field study was conducted to investigate the effectiveness of using a soil-applied chelator in up-taking the heavy metal for phytoremediation treatment. Addition of EDTA to soils in the field lysimeter studies confirmed the increment of heavy metal uptake. (Blaylock, et al. 1997)

Another experiments by Benin, Benin City, Nigeria, Showed that water hyacinth (*E. crassipes*) act as an hyperaccumulator for metals such as Zn, Pb and Cd, and as the previous experiment for Indian mustard approved, by increasing the pH level, the roots ability to uptake the metal increases too but unlike the Indian mustard the leaves Pb concentration will increases too. (AISIEEN, FALEYE and AISIEEN 2010)

According to assessment of *Typha domingensis* ability of up taking heavy metal and its potential application for phytoremediation which were done by Hegazy and his colleges, the plants and industrial wastewater sample from the waste water pond of industrial zone of El-Sadat city in Menoufia governorate, was collected and further analyze were done for the concentration of heavy metal which indicates high amount for Fe, Zn, Pb and Al. Then, the assessment of plants potential to uptake the metal in its different tissues part were study regarding different season and it was shown that the uptake ability is more in roots than shoots and is decreasing for metals in following order $Pb^{2+} > Fe^{3+} > Al^{3+} > Zn^{2+}$. Also the actual amount of uptake which occur in the industrial pond was higher than the amount in controlled site (laboratory). (Hegazy, Abdel-Ghani and El-Chaghaby 2011)

There is another experiments which state that generating a genetic developed plant based on an existing one can prove the ability and capacity of contaminants up take by plants. For example the

lab experiment following field study on experimental paddy field of Gyeongsang National University, Gyongnam, Korea showed that generated rice of OsNRAMP5 RNAi can act twice as accumulator (specially for Cd) as the wild type existing plant. Although this experiments was also conducting on soil field (Paddy field), but the conclusion is accommodating to any field contaminated by heavy metal. (Takahashi, et al. 2014)

Amongst the articles and experiments which I've studied in this field, one of the most interesting one was the study that has been done by Ziarati and her colleagues on the Anzali lagoon situated on the southwest shore of the Caspian Sea to investigate the potential of the Nymphaeaceae (we known as niloofar-e-abi) high-biomass plants to uptake the Ni and Cr inside the water body. According to studies the industries which threatening the Anzali lagoon water are: Wood and Paper Company in Talesh, Wood Fiber Company in Hassan Rood, Iran Poplin textile, Gilan Carpet, Pars Khazar house ware, Zam-Zam soft drink, and several food industries in Rasht are important to mention. The results shown that Cr and Ni uptake ratio increase by increment in amount of metal concentration. But it was precisely mentioned that "concentrations remained high in roots compared to shoots in Cr (III) and Cr (VI), treated groups, while metal content was higher in shoots than roots in Ni -treated groups." (Ziarati, Asgarpanah and MirMohammad Makki 2015)

One of the other experiments was focused on *Typha domingensis* as phytoremediation plant for up taking Fe, Mn, Zn, Ni and Cd. Municipal wastewater containing mentioned heavy metals was collected and *Typha domingensis* plants were be put on pots containing 7 liter of wastewater for 2 days. Amount of heavy metals inside the water was observed before and after the treatment and was compared for 24 h and 48 h after the treatment process. The order of concentration of heavy metals inside the plant was suggested to be Fe>Mn>Zn>Ni>Cd after 2 days. Amount of heavy metal in wastewater after treatment, for Fe to 50 % of primary concentration, for Cd to 46% Ni decreased to approximately 43% and for Zn and Mn to 25%. Thus the order of effectivity of plants potential to remove the heavy metals from wastewater is Mn,Zn>Ni>Cd>Fe. (Mojiri 2012)

A field experiments done by Sakakibara and his colleagues in a river located in southwest japan which flows from mine tailings area of an abandoned mine has shown the effect of an aquatic plants called

Eleocharis acicularis, in up-take potential for heavy metals. This plant act as hyperaccumulator for Cu and Pb. So as a proper candidate *E.acicularis* was chosen to remediate the rivers water by putting them inside a pond which was made by a dam and end up with flowing into the river. The results was analysed by the indicator of BCF_w which is represented by concentration of and elements in shoots per concentration of an element inside the water (C_{shoots}/C_{water}). It was explained that for values higher than 100 for metal accumulator, it indicates that the plant has positive potential for heavy metal up taking. Results has shown the values of Mn (26,000), Cu (86,800), Zn (4820), As (4370), Cd (8420), and Pb (1,490,000). The ultimate result shown that the concentration of Cu at the end of the experiments fall to half the concentration of it at the first place inside pond and for As it falls down to 0.25. The result was also approximately the same for the river water of downstream (of the pond). (Sakakibara, et al. 2013)

Plant	Area	Metals	Result	Uptake Amount	Image of The Plant
Five aquatic plant species, <i>Lepironia articulata</i> , <i>Pandanus helicopus</i> , <i>Scirpus grossus</i> , <i>Cabomba furcata</i> , and <i>Nelumbo nucifera</i> —aquatic	Water of Tasik Chini	Cd, Cu, Pb	The highest concentration was found in roots of <i>S. grossus</i> . The concentrations of Cd in the leaves and stems of <i>C. furcata</i> , concentration of Cu in the stem of <i>C. furcata</i> was greater than that in the leaf, while the concentration of Cd was more in the leaf than that in the stem. $Pb > Cu > Cd$. The highest internal translocation was found in <i>P. helicopus</i> , while the lowest internal translocation was found in <i>S. grossus</i> .	-	 

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Nymphaeaceae	Anzali lagoon	Cr, Ni	remained high in roots compared to shoots in Cr (III) and Cr (VI), treated groups, while metal content was higher in shoots than roots in Ni -treated groups. *After only 10 days of growth.	300 ppm crIII = 90 mg/kg DW 300 ppm ni = 100 mg/kg DW	
Brassica junkie16 Indian Mustars (phutoextraction) + corn	Lab → field lysimetric the field (at Barber Orchard) and in the WCU greenhouse	Pb>Cu>Zn>Cd>Ni As and Pb	(by adding EDTA as chelate, the pb uptake by shoots will increase significantly by lowering the pH) increasing pH improve As removal but lowering the pH is increasing Pb removal	pH (field)= 8.3 Shoot +EDTA = 785 Root+EDTA=152 pH= 7.8 shoot + EDTA + acetic acid= 1471 root+ EDTA + acetic acid= 466 pH 6.11 As extracted (27.4 mg/fern) pH= 5 Pb shoot concentration (9000 mg Pb/kg shoot) EDTA concentration (10 mmol/kg soil).	
water hyacinth plant (E. crassipes)	Lab	Zn>Pb> Cd	By increasing the pH level (8.5) the amount of metal uptake by root increased	Roots: Pb= 4150mg/kg, Zn= 4870mg/kg Cd= 710mg/kg leaves: Pb=1400mg/kg, Zn=2800mg/kg, Cd=180mg/kg	

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Oryza sativa OsNRAMP5 as Fe, Cd and Mn transporter Generated plants	Lab and paddy field	Cd Fe Mn Zn Cu	ASi plants accumulated twice as much Cd in their shoots as WT plants.	Cd= 60 ng/g Mn=1000 $\mu\text{g/g}$ Fe= 300 $\mu\text{g/g}$ Zn= 16 $\mu\text{g/g}$ Cu= 1.2 $\mu\text{g/g}$	
Thlaspi caerulescens	St Laurent le Minier, Southern France one of the largest metal mine	Pb, Zn, Cd	a biomass production of 5.2 t/ha would yield 60 kg/ha of Zn and 8.4 kg/ha of Cd.	pH=7.3 Zn = 11,627 $\mu\text{g/g}$ Cd = 1618 $\mu\text{g/g}$ Pb =844 $\mu\text{g/g}$ Mn= 61 $\mu\text{g/g}$	
'Elephant Ear' (Colocasiaesculen ta (L.) Schott)	Kanchanaburi Province (laboratory experiment)	Pb	More days lead to more Pb uptake and also addition of EDTA leads to more uptake. The most effective amount is 0.02 mM for EDTA. Also hyperaccumulator will increase the uptake results.	pH=7.1-8.1 pb concentration in roots after 90 days = 502.84 mg/kg	
Typha domingensis	industrial zone of El-Sadat city in Menoufia governorate	Pb2+ > Fe3+ > Al3+ > Zn2+	Higher accumulation in roots and yellow parts of the plants for in field experiment.	For roots Winter: Al= 303.91 mg/kg Fe= 423.20 mg/kg Zn= 117.64 mg/kg Pb= 14.87 mg/kg Summer Al= 350.55 mg/kg Fe= 582.44 mg/kg Zn= 149.60 mg/kg Pb= 20.46 mg/kg	

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Typha domingensis	Greenhouse plants/ laboratory analysis	Mn,Zn>Ni> Cd>Fe.	Decreasing of metal increased after 48 h and accumulation was more than 24 h.	Mn and Zn= 25% primary concentration Ni=43 % PC Cd=46% PC Fe= 50% PC	
E. acicularis	Manmade pond inside a river flowing from a mine in southwest japan	Mn, Cu, Zn, As, Cd, and Pb	Significant decrease in concentration of Cu and As in the river bed and pond water.	BCF _w : Mn=26000 Cu=86,800 Zn=4820 As=4370, Cd=8420 Pb=1,490,000 Concentration of river water at the end As= 50% Cu=0.25%	

4. Conclusion and Recommendation :

Amongst the articles that was chosen for this review, phytoremediation was generally reported to be an effective method for removal of heavy metals. Although there were not any conclusion on a significant type of plant as the best option, but the results of each experiments has shown that each type of plant were suitable for specific metal regarding the situation and condition of the contaminated site, which makes phytoremediation an economic and effective technique in total.

Since the most hazardous contaminant for the southern Caspian Sea was reported to be Ni and Pb, the articles were also reviewed for suitable plant reported for this sake. As for the determination of the best plant for phytoremediation process, regarding the different scale units, mg/kg water was the most proper and precise unit to discuss the most effective plant for up taking metals. Amongst 10 plants and experiments that was studied for this part of the project, water hyacinth plant (*E. crassipes*)-which is a hyperaccumulator- and 'Elephant Ear' (*Colocasia esculenta* (L.) Schott) had been reported to have the most up take amount of Pb. Since the experiments of second plant, elephant ear was a field study rather laboratory, it might be a better proposition for contaminated sites of the Caspian Sea. According to the field experiments of Japan's river using *E. acicularis* as hyperaccumulator for Pb, considering the very high number of BCF calculated for this element, it also reported to be a good option but since at the end of the experiment the concentration of Pb stayed as same as the beginning amount it has shown that this plant is not a potentially effective plant for Pb up-take. Also according to the articles it would be effective to add EDTA as chelator in order to increase the Pb uptake but, it is not a main focus of this paper. And for Ni, *Typha domingensis* was proposed by the author since the amount of nickel up take by this plant is high.

There would still be number of matter to take care of. Most important of all is the fact that most of the experiment which were study for this review were merely a laboratory study, thus same experiments for real situation and fields are suggested to be considered. In such situations it should be taken into account that significant amount of contaminants are feasible to be adsorbed by surrounding and en route media of water flow for water contaminated sites. Another matter is the removal and harvesting the contaminated plants after treatment regarding the effective amount of time which each type of plant can participate in removal process. Although most of the articles which I have studied did not mentioned any further consideration for timing and removal, it has a crucial

role in remediation of wastewater because if plants won't be harvested within the proper period of time, all the heavy metals inside their tissues will eventually goes back to water as it was at the first place.

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