Buletinul Ştiinţific al Universităţii "Politehnica" din Timişoara

Seria HIDROTEHNICA
TRANSACTIONS on HIDROTECHNICS

Tom 55 (69), Fascicola 2, 2010

NATURAL ATTENUATION – A METHOD FOR AQUIFERS REHABILITATION

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Abstract – Contamination of soil and water by various forms of pollutants is a fact in this industrialized age. Pollutants threaten the health of biotic and environmental receptors so their effect should be minimized or even removed if possible.

So far in Romania no one did detailed studies on natural attenuation. Therefore in this paper, we propose to present the phenomena occurring in this process. The natural attenuation process is very complex and includes transport processes of pollutants, degradation processes and reduction of contaminants in soil and aquifers.

This paper aims at presenting natural attenuation phenomena and to highlighting the need for monitoring these processes.

Keywords: natural attenuation, monitored natural attenuation (MNA), enhanced natural attenuation (ENA).

1. INTRODUCTION

In the U.S., already in the 90s, natural attenuation was seen as a process of rehabilitation, in Europe it was ignored. Europeans regarded the natural attenuation as a remediation process left to nature. This concept is not wrong but is far from complete - Natural attenuation is only a first step in the overall objective of reducing pollution and bringing up to the level allowed by EU rules limits. After much controversy natural attenuation has found followers in Western Europe.

The exact definition of this process is given by the U.S. EPA (Environmental Protection Agency) (1997) which states that: "The natural attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants."

Process known as natural attenuation (NA) can be differentiated into two specific areas namely: Monitored Natural Attenuation (MNA) and Enhanced Natural Attenuation (ENA).

Monitored Natural Attenuation (MNA) consist in observing restraint and chemical degradation processes, physical and biological as well. One condition, for this method is to exclude jeopardizing the environment (Müller 2005).

Enhances Natural Attenuation (ENA) – represents stimulation of natural self-cleaning processes. Transition from this method to rehabilitation in situ is fluent, because in both cases we introduce nutrients or oxygen to support degradation process (Steiner 2005).

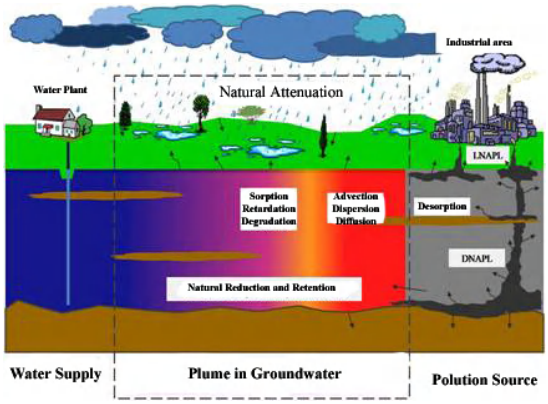

Fig. 1 – Schematic presentation of natural attenuation

2. PROCESSES WITHIN NATURAL ATTENUATION

Processes that occur within natural attenuation can be classified in two categories:

1. Processes that do not diminish pollutant mass but have an effect just on pollutant transport, Advection, Diffusion, Dispersion and Adsorption. Figure 2 represents the evolution of a pollutant plume in different situations.

2. Degradation processes which have the effect of reducing the amount of pollutant. These processes are usually chemical or biochemical reactions which amend stock pollutant, but it will not have an effect of reducing toxicity because through biodegradation we can obtain compounds that are more toxic than the initial pollutant..

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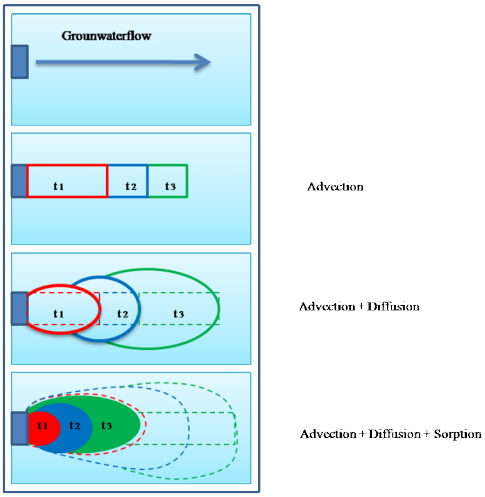


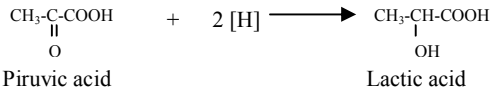
Fig. 2 – Pollutant transport effect.

Base biological reactions can be classified in two categories: processes that use organic material as primary substrate and Co-metabolism.

Processes that utilize organic material as primary substrate are:

- *Fermentation* – is a process by which hydrogen is released from its compounds and energy is produced. First phase of fermentation is anaerobic; here aromatic hydrocarbons are reduced to organic acid. Primary microorganisms decompose organic acid producing hydrogen and secondary substrate (ethanol, lactic acid, etc). Secondary substrate is degraded still till obtaining hydrogen. These processes occur in soil and aquifer where we can find fermentation microorganisms and methanogene bacteria.

In figure 5 is shown the decomposition of benzene, meta fission path leading to pyruvic acid, from there is decompose again to lactic acid.



Lactic acid is then decomposed to methane (CH_4).Reduction or dechlorination – process is made in two stages:

- Fermentation of organic substances with forming of hydrogen. Produced hydrogen is uses as electron donor and the accepting are chlorinated carbohydrates

- Consumption of hydrogen by microorganisms that performs dechlorination. Dechlorination is in fact the process of replacing a chlorine atom with a hydrogen atom.

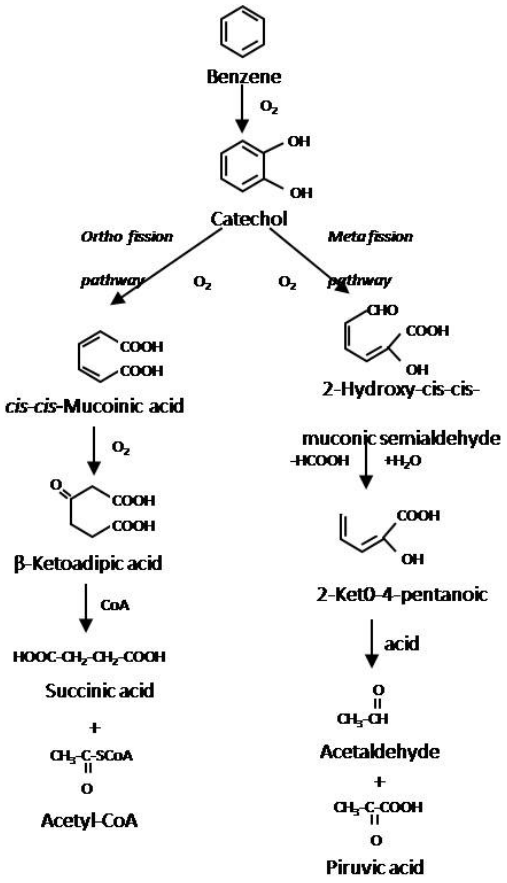
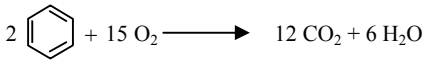


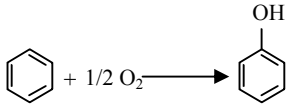
Fig. 3 - Microbial degradation of aromatic components (example of benzene)

Environment most favorable for these reactions is the anaerobic and the one that has a low redox potential. The process is obvious where, in the ground and aquifer can be highlighted a high concentration of chloride and ether

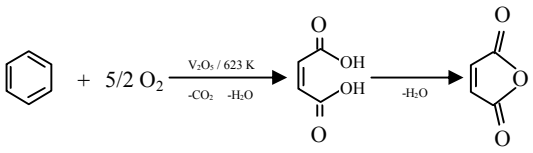
- Oxidation – biologic oxidation can occur in aerobe as well as anaerobe conditions. In aerobe conditions the process is very fast because of oxygen, which is a good electron acceptor. When the process takes place in anaerobe conditions the electron acceptors are nitrite, manganese, iron and sulfur, in this case we are referring to direct anaerobe oxidation. Oxidation of organic substances is highlighted with the help of benzene just like in the case of fermentation. Benzene can be oxidized completely, and then we can obtain carbon dioxide and water or it can be partially oxidized to phenol or maleic anhydride.



-Complete oxidizing with forming of carbon dioxide and water



- partial oxidize with forming of phenol



-oxidation with forming of Maleic anhydride

Co-metabolism – is a process by which pollutants or intermediary products of them are degraded with the help of enzymes developed by organisms for other purposes. This is not an energy production process for the enzyme developing organisms. The primary substrate used is represented by carbohydrates which are used as a source of natural carbon or anthropogenic (Wiedermeier et al. 1999).

3. REDOX POTENTIAL

Bacteria require a substrate to use as a source of nutrients and from which to extract needed energy to achieve biological functions.

The required energy is acquired from redox reactions when an exchange of electrons between donor and acceptor, takes place. The energy obtained is stored in the form of adenosine triphosphate, and used for cell growth and reproduction. Besides energy bacteria needs other nutrients like carbon, and phosphorous in order to function.

Bacteria with a high redox potential are found in near proximity of the pollution source or within the pollutant plume. (EPA, 2000).

In the substrate decomposition `redox reactions from different areas; each area represents a certain redox potential, which shown in figure 4.

4. HIGHLIGHTING NATURAL ATTENUATION

The reduction of contaminants is distinguished with the help of different parameters. The most important parameter is extension and concentration of pollutant, respectively degradation and presence of resulted metabolites. Normally with time, concentration of pollutant decreases and concentration of metabolites increases.

Degradation of pollutants starts with consuming all of the free oxygen and leads to installation of anaerobe conditions. In anaerobe conditions nitrate is reduced through denitrification, then iron oxide and manganese oxide are reduced, and last sulfur is reduced.

Methane genesis (production of methane) runs only after all of the free oxygen as well as the oxygen from the above compounds . Methane is produced through decomposing organic compounds. When the consumption of electron receptors starts, redox potential starts to decrease.

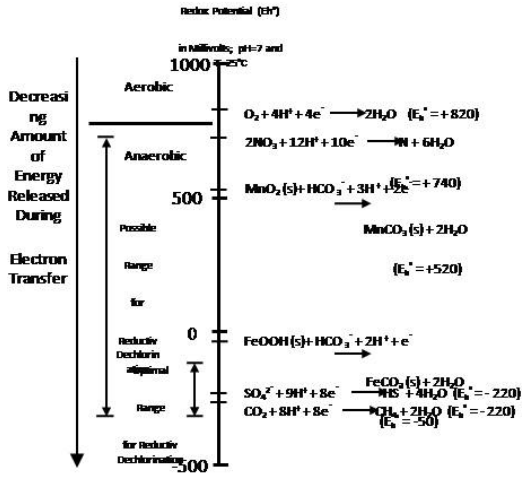


Fig. 4 – Redox-Potential of most important microbiological processes (Wiedermeier et al. 1999)

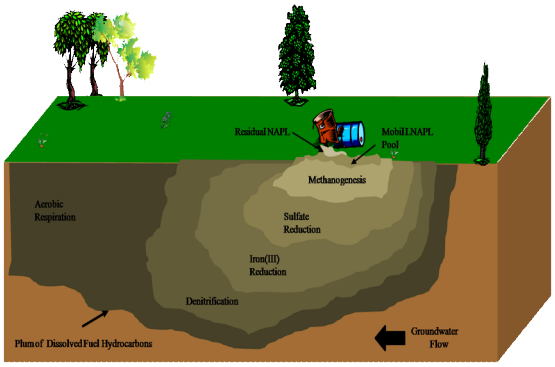


Fig. 5 – Areas of oxidized decomposition (Lovely et al., 1994)

Degradation processes that occur inside the pollutant plume take place on several areas. We can distinguish the following areas starting from the source of the pollution:

- Methanogene area
- Reduction of sulfurous area
- reduction of iron area
- reduction of nitrates area
- Aerobe area.

In the following table we find the quantity of electron acceptors used for carbohydrates degradation (benzene in our case). In the case of oxidize degradation:

Table 1 – Quantity of electron acceptors used in the case of oxidize degradation (Weinberg).

Fundamental Balance (C_6H_6)	
Aerobic Respiration	1 mg/l
Denitrification	1 mg/l
Manganese Reduction	11 mg/l
Iron(III) Reduction	22 mg/l
Sulfate Reduction	1 mg/l
Methanogenesis	0,8 mg/l

5. ADVANTAGES AND DISADVANTAGES OF NATURAL ATENUATION

Advantages

The most important advantage of natural attenuation is the fact that the pollutant is degraded irreversible. This method requires a minor quantity of energy compared to traditional methods of depollution. Given the fact you might say that economy is good argument in favor of natural attenuation usefulness.

Disadvantages

Monitoring and analysis of natural attenuation only postpone costs. Another disadvantage of this method is the complicated prognosis and modeling of the pollutant plume, respectively degradation rate.

The biggest disadvantage of natural attenuation is the possible appearance of toxic metabolite.

Natural attenuation is limited by the factor of time and size of the contaminated area.

6. CONCLUSION

Natural attenuation processes were most studied for: benzene, toluene, etylbenzene, xylenes (petroleum hydrocarbons) and chlorinated solvents. Other substances, as phenols, halo aromatic compounds and pesticides, can also be depredated but we don't have so much information about these processes.

Natural attenuation is considered in USA, to be used as a rehabilitation method were the effects of it leads to permissible concentrations of pollutant to the environment and human life. In Europe is considered to be a natural process that occurs by local conditions. Natural attenuation processes must be studied and monitored because they can help at describing actual situation and choosing the best engineering method for rehabilitation. The processes described above contribute to very active decrease of contaminants.

For an effective monitoring we must determine geological and hydrological conditions from the area we must rehabilitate. Efficiency of natural attenuation processes must be demonstrated with the help of a complete enquiry.

In our country many areas are affected by historical pollution (inadequate waste landfills, industrial areas, craft areas, military sites, mining sites) therefore it shows a necessity to applicated these presented techniques. Monitoring the current situation of the affected land is important because then you can take all appropriate measures to rehabilitate and reintroduce the land in agricultural or other area of use.

7. ACKNOWLEDGMENT

This work was partially supported by the strategic grant POSDRU 6/1.5/S/13, (2008) of the Ministry of Labour, Family and Social Protection, Romania, co-financed by the European Social Fund – Investing in People.

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