

Wetlands in the Petroleum Industry

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ABSTRACT

Wetlands have been studied for many years and their effectiveness as well as economical nature is great for wastewater treatment. They have specifically been shown to be very good at treating wastewater with petroleum, typically higher in hydrocarbons and other compounds. However it has been shown time and again wetlands are great for this compound, if not the best. The following will describe the design considerations, how to set up the bed, and the processes that are at work in your wetland. It is also imperative to keep in mind that wetlands are not only those made by man, but also the natural ones created by nature with equal if not better treatment. Wetlands are a great if for nothing else than you can enjoy your treatment plant in operation.

KEYWORDS

Wetlands, Petroleum, Microbiology, Wetland Plants, Natural Wetlands, Biodegradation, Bioremediation

INTRODUCTION

Marsh, swamp, biological filter, bog, and mosquito haven are all terms used to describe a wetland. Wetlands are basically a very moist, soggy environment with an entire ecosystem enclosed in sometimes a small area. In nature they tend to act as a border between dryer land and free flowing water, such as a stream river, or lake. Humans have also learned to recreate these systems for use in treating wastewater. Recently, industrial uses including the petroleum industry have taken a look at using wetlands for primary and/or secondary treatment. Wetland research began back in the 1950's in Germany, moved to the US in the 1960's, and took a huge spike in interest during the 1970's (DeBusk, 1999). These biological land-intensive systems provide quite predictable effluents (Knight et al., 1999), considering all the interactions going on. Biological treatment and removal of pollutants is quoted as being the most important mode (DeBusk, 1999), however physical and chemical are also at work constantly. Plants provide the primary, and most popular, method of biological treatment; however microorganisms also provide uptake and synthesis of pollutants (DeBusk, 1999). The role of

microorganisms play is primarily metabolism, conversion of carbon sources into carbon dioxide and methane (DeBusk, 1999). It was stated by Moore (1999), that because of the enhanced microbial potential in wetlands that biodegradation of organics is great. However some may also play a part of the nitrification and denitrification process, such as those discussed in elementary microbiology. The chemical process is mainly the sorption of ions to the soil particles (DeBusk, 1999). This can provide a long-term or

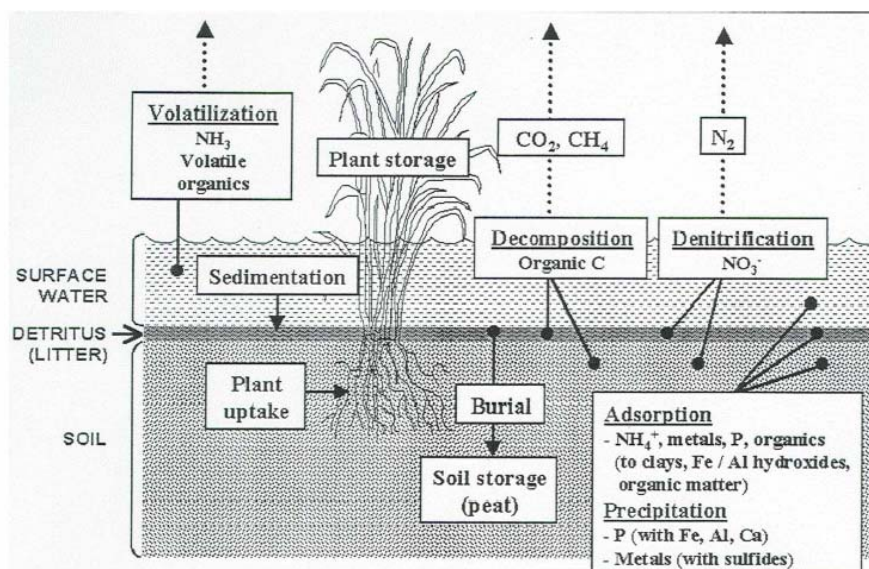


Figure 1. Summary of the major physical, chemical and biological processes controlling contaminant removal in wetlands.

short-term storage of pollutants. Physical processes are mainly settling of flocs. These flocs can then be trapped in the soil or other media and either stored or broken down by other processes. Figure 1 above, adapted from the University of Florida, shows all the processes of a wetland working together (DeBusk, 1999). Because of all the processes going on including death of plants and microbes metabolism, it is rare that contaminants reach zero concentration (Knight et al. 1999). This shows both free-surface and subsurface reactions. Free Surface, or surface flow, wetlands water flows about the media, soil or gravel typically, from inlet to outlet (Knight et al., 1999). These systems are typically designed with high surface areas with alternating zones of deep and shallow water depths (Keefe et al., 2004). Subsurface, or submerged, wetland forces the water to flow through the media and typically has many plants throughout the bed (Knight et al., 1999).

For this area of emphasis within wetland treatment is best to start with an idea of what is in petroleum, for the basis of this report. There are typically four compound divisions for petroleum (Harayama et al., 2004). The first is saturated hydrocarbons, this is the primary component and these contain no double bonds. Aromatic hydrocarbons are the second constituent; these have at least one aromatic ring within the molecule. The last two are not hydrocarbons, they are resins and asphaltenes. Both are mostly unknown, however they are quite large molecules and tend to possess small amounts of nitrogen, sulfur and/or oxygen (Harayama et al., 2004). Many times sulfides, phenolics, and other trace metals are also found in petroleum (Knight et al., 1999). Nutrients can also persist in the petroleum substance (Campagna et al., 2001) so as to provide some benefit to nature. As evident the substance we call petroleum is quite complex and can persist for quite awhile in the environment. Lucky for us though it is a compound derived from the earth. As time passes the petroleum does weather (Harayama et al., 2004) and utilizes the different processes to change into other, more beneficial, compounds. In the following pages we will examine the processes used in natural and constructed wetlands. There are many present day examples of wetlands in use and wetland recoveries studied, which will be reviewed.

NATURAL WETLANDS

As stated previously, natural wetlands seem to act as borders, or transition zones, between dryer soil lands and flowing waterways. They can be located in low areas along rivers (Mills et al., 2003), with peat bogs (Moore et al., 1999), or along island shores (Chaillan et al., 2004). Natural wetlands rarely experience petroleum products, unless exposed to by artificial means. However along the Gulf Coast there are many seams and weathering of indigenous material (Mills et al., 2003). Typically wetlands experience petroleum compounds when a spill occurs; some of the more famous include the Exxon Valdez spill in Alaska. Contact can also occur from improper disposal of wastes from refineries or leaks in petroleum waste treatment units. Runoff on a petroleum site or hydrostatic test water (Wallace, 2001) can also be dangerous if not properly treated. Therefore we must not only understand the wetlands designed by humans but we must also have knowledge of natural wetlands in order to protect the environment when our projects break and potentially harm mother nature.

Failures will always be noticed and those with drastic impacts to the environment will be newsworthy. Take for instance the current situation in China, an explosion at a plant led to the leak of chemicals into a waterway. Turns out this waterway is the drinking water source for many towns downstream. These areas are now left without potable water until the plume continues downstream to the next village. Lucky for man, nature is much more smarter and has created ways to take care of itself. Nature utilizes all the processes discussed above in different capacities to achieve an efficient clean-up.

Biodegradation is the primary means by which nature is able to remove hydrocarbons (Chaillan et al., 2004), which are the primary constituents of petroleum. The biodegradation is accomplished through all sorts of creatures; bacteria, fungi, and yeasts (Chaillan et al., 2004). In an analysis by Chaillan (2004) of a previously contaminated site in Indonesia a total of twelve bacteria, four yeasts, and twenty-one fungi were isolated and characterized as hydrocarbon degraders. An additional nineteen bacteria were found to initially reduce the levels of hydrocarbons, however upon further examination they were not found to provide substantial degradation. These bacteria typically belonged to the *Bacillus* family. The same result was reported by Chaillan (2004) in a study by J. Oudot. Of the bacteria characterized as hydrocarbon degraders, only four were already identified. The identification process used by Chaillan (2004), was a GenBank search using the software BLAST. Five of the unknown species were *Dietzia*, which also turned out to be the most common bacteria found in the samples. Two new species, one

within the *Brevibacterium* and one within the *Mycobacterium* families were also found. *Mycobacterium* has been identified before as hydrocarbon degrading organisms. On an interesting note, it is suggested by Chaillan (2004) that a new taxon similar to *Actinomyces* and *Thermoleophilum* was found. Sequence was not close enough to place into either of the taxons. Of the yeasts tested one in particular was newly identified as a degrader of hydrocarbons, *Candida viswanathii*. It had previously not been known to degrade hydrocarbons. The unique fungal species found was only one from a mat growing in the contaminated area. All other fungi species were native to and found in the soil. This unique species was *Fusarium oxysporum*. A few other organisms were first found to be in the highly hydrocarbon environment and thought to be degraders, but upon further testing were found to be not. Possibly the organism just being opportunistic in an environment with low pests was the solution proposed by Chaillan (2004). In a study by Cohen (Harayama et al., 2004) it was reported that the *Cynobacteria* are also well known oil degraders, especially in the seawater areas. However Harayama (2004), believed these to be mat growers and opportunistic organisms staying away from possible predators. As you can tell the organisms listed above are from varying families and include many species. It was originally hoped by Chaillan (2004) to determine a nomenclature based on hydrocarbon degrading, however it was later conceded that hydrocarbon degradation potential may be something adopted by organisms. Although not particular to a species the interesting thing to note was that the organisms appeared to have followed the same pattern when degrading the hydrocarbons (Chaillan, 2004). This once again shows us that nature is very much connected between not only species but across species and families. The multiple of organisms as well as the variety show that many organisms can be used to treat for and clean up a majority of petroleum.

Due to the apparent prevalence of organisms that can degrade petroleum, or at least part of it, we now have a method for the natural clean-up of petroleum products. And yet, although we have a pathway a time line has not been placed on it. We all know that plastics and just about everything can degrade, but as with plastic time can be a very precious thing to its degrading process. It was found that recovery occurred within a month for the aquatic biological activity, primarily benthic invertebrates, and within three months vegetation with direct contact to vapor and gas. The soils were also studied extensively by Wemple (2000). Impacts seemed to be only to the upper four feet of soil, however it spread horizontally at least ten feet in channel regions and upwards of thirty feet in more marshy soils.

Although it appears that the nature degradation process occurs quickly, this is not always evident. Sugai (1997), studied the effect of the Exxon Valdez oil spill in Alaska and came to the conclusion that hydrocarbon degradation is much less dependent on the actual reactions taking place than it is on the process occurring in the surrounding ecosystem. It was proposed that in order to properly evaluate such degradation an ecosystem level study and model must be created. And although biotic reactions are much quicker and influential, abiotic must also be accounted. In order to possibly control and influence these ecosystem wide processes, addition of fertilizer has been advocated by many. A few studies reported in Miles (2003) seemed to provide a variety of points regarding the addition of fertilizer to increase biodegradation rates. A study by Venosa (Miles et al., 2003) proposed that the adequate amount of nitrogen in the pore space of sand allowed for the major removal mechanism of hydrocarbons. One could make a case that this would imply that if the environment was not in supply of the proper amount of nitrogen some amount would need to be added. However a study by Lee (Miles et al., 2003) of the St Lawrence River controlled spill showed no difference in nutrient enhanced versus controlled treatment. And in fact Lee Miles et al., 2003) reported that an increase in toxicity occurred with the nutrient added areas. This brings to the point even more what Sugai (1997) was mentioning about knowing the ecosystem in order to best promote natural degradation, and to assure the environment is not harmed by our actions to help it along. A study in the United Kingdom by Swannell (Miles et al., 2003) demonstrated that enhancements did encourage biodegradation and in fact no toxicity was reported. This data is very encouraging but one wonders to what other items were in play in the surrounding ecosystem. In relation to specific nutrients nitrogen and phosphorous are said to speed up biodegradation as reported by almost fact by Harayama (2004). There are some very encouraging data, as well as much room to speculate as to whether or not an addition of nutrients are needed. It seems that a lot of data is needed with regard to what is going on in a specific ecosystem for a good estimate of whether an addition, and how much, should be used.

The ways in which pollutants are removed are very numerous and yet can be, for the most part, separated into aerobic and anaerobic processes. Both processes types can derive the same molecules, however the nutrients and organisms needed may be very different, as well as the time needed to

complete each step. In the analysis conducted by Mills (2003), it was determined that aerobic processes are order of magnitude faster than anaerobic processes. This is likely to the fact that oxygen can act as the electron acceptor and it is quite prevalent. The main processes for aerobic are biodegradation and volatilization. It almost goes without saying that volatilization can only occur aerobically with an open surface to the atmosphere. Biodegradation is favored in aerobic environment because of its high potential with oxygen, readily available, and the interaction with the root zone (Mills et al., 2003). The root zone is important because many, many microbes live on the roots of plants, assisting and plant and itself in survival. Once the oxygen transfer ability is lost and amount of oxygen drops the situation becomes anaerobic. In this case anaerobic biodegradation takes over. It as found by Harayama (2004), that in this case a nitrate-iron or sulfate can become the electron acceptor. These would replace that previously taken by oxygen. As evident by availability it becomes clear that anaerobic will take longer to complete the degradation. During anaerobic degradation, methanogenesis also occurs and can work as the electron acceptor within this process (Harayama et al., 2004). However in both cases, aerobic and anaerobic, sorption can take place (Mills et al., 2003). This process is simply bonding of the ions to charged soil particles and in turn does not require the aeration or lack of aeration to be completed. After these have been carried out, it was found by Moore (1999) that only inert matter and inorganic are left. Although maybe still a concern Moore (2003) mentioned that these are quite unlikely to reaction in nature and have less ability to cause a problem. As evident natural wetlands have a lot going on, they are of course their own little ecosystem. Constructed wetlands have just as much going and are in many cases tailored to meet a specific goal. Proceeding is information specific to constructed wetlands, mainly considerations to evaluate when designing such a system.

CONSTRUCTED WETLANDS

As compared to natural wetlands, constructed or man-made wetlands are artificial in creation with specific parameters that lead to specific goals. Constructed wetlands use the same processes as natural wetlands; only the specific process can be selected through the design process. Depending upon the goal that is desired different parameters will be set, others will be calculated, and some may even be ignored. The great majority seem to focus primarily on hydraulic retention time (HRT) as the main parameter, with special care for the influent concentration. Of course the bases for these numbers will always what the outflow will permit. There are many other parameters that will be discussed next however many seem to be derivative or closely related to the HRT and/or influent concentration. In fact in Knight (1999) stated that hydraulic load and influent concentrations were most important to treatment in wetlands.

HRT is a simple equation that can provide a large deal about what is or can go on in a wetland, or any treatment process for that matter. The equation is total volume of water divided by flowrate (Simi and Mitchell, 1999). Flowrate is a very important characteristic that can easily be varied when designing a wetland. The slower the flowrate the more stuff that will precipitate out of the stream, however too many precipitates can be troublesome due to build up (DeBusk, 1999). This seems obvious that it gives the lighter particles more time to settle out. DeBusk (1999) later went on to say that this is of particular concern in wetlands because the flow tend to be laminar and therefore further promote settling of lighter material. Correlated very closely to this is the total suspended solids (TSS) requirement as well as influent concentration. The trouble with wetlands, as stated previous, is that hardly ever are pollutants at zero. This is particularly the case with TSS when there is a deep cell near the end of the wetland, outlet (Knight, 1999). Algal cells are likely the TSS being picked up in the final cell of the constructed wetlands (Knight, 1999).

The second primary parameter is the influent concentration. However removal rates are still very high for varying concentrations (Xia et al., 2003). Although the rates may be high it appeared to Xia (2003) that the efficiencies in the treatment went down. It seems only obvious that a consistent influent concentration will help with kinetic equations in order to properly size the wetland.

Although not a mentioned as a major component, plants were discussed throughout almost every literature piece. Many paper submitted research showing that plants produced better results, however when statistics were related to results and confidences introduced little to no difference was evident. The best results demonstrated by Omari (2003), showed that although the top section of the wetlands had

little difference the lower regions were much further apart. Although all the confidence intervals overlapped, see Figure 2. the numbers represent the removal efficiency (%) of hydrocarbons.

Experimental Bed (<i>Typha</i>)				Control Bed (no <i>Typha</i>)			
	Top	Middle	Bottom		Top	Middle	Bottom
Average Overall	80.1	78.0	71.6	Average Overall	72.3	69.1	63.4
Confidence	+/- 9.8	+/- 9.1	+/- 10.0	Confidence	+/- 11.9	+/- 10.3	+/- 9.4

Figure 2

Adopted from Omari, 2003

Although the acieration is still made by Omari (2003) that the bottom removal efficiencies are greater in discrepancy because of the ability of the *Typha* to transport oxygen to the root hairs and therefore promote degradation. Others, such as Campagna (2001) have concluded that plants are by no means harmed by petrochemicals, to the extent that such a substance is not limiting the plant. And in fact in a study by Wass (Knight, 1999) it was found that oil and grease were only broken down in the presence of plant life. Although not entirely conclusive it seems that these lead to the idea that plants do in fact help out the wetland ecosystem.

Microbial activity is very important to the success of any wetland. As discussed for natural wetlands, the microbes interacting in this environment are quite diverse in processes and location. Wallace (2001) noted that in fact there was great microbial activity in the sub-surface flow wetlands. This could easily be due to the idea that in such a wetland the water is forced through the media and primary treatment must occur on the media or items attached to the media. The diversity of the microbial population in constructed wetlands was proven by Ashok and Saxena as well as Alexander (Omari, 2003).

Although many concerns are raised as to the degree at which organisms can stand the toxicity potential in petroleum effluents, most data seems to suggest these have no impacts. The wetland system at the BP refinery in Mandan, North Dakota has been operation since the 1970's and still no trout have been found to die of toxicity (Litchfield, 1993). Even though there are Chromium, Copper, Nickel, and Lead leaving the refinery. It is estimated that many fall out of suspension during treatment. Additionally a study by Duba (Knight, 1999) at the Chevron Refinery in Richmond, California has shown reduced toxicity to aqua invertebrates and bacteria, however during high concentration effluents some toxicity has been noted in plants. It is proposed by Knight (1999) that toxicity reduction are a secondary benefit in the plethora of reactions taking place in wetlands.

Seasonal changes are expected no matter where the location and it can be easily inferred that changes will occur in the wetland environments. It has been noted in China that seasonal temperature changes and not an annual temperature shift are related to the effluent quality, particular to mineral oil degradation (Ji et al., 2002). This make some sense that organisms can adapt over time to changes but the sudden changes of seasons are not as easily adapted. As well organisms likely align their life cycles with the seasons, assuming they are indigenous to the area. In a study up in Canada in was found the greatest hydrocarbon degradation to be in the summer and winter, via aeration, and drop significantly in the spring and fall (ERAC, 2001). This once again could be due to the sudden changes in temperature and other meteorological effects. However once everything stabilizes in the organisms are able to get back to degradation, effectively and efficiently.

Through the research many papers would publish effluent data from their respective wetlands. Although each report tended to have a different focus or reason for research many still collected like data. Below in Figure 3 is the collection of such data. Each reported gave many data sets and the below are the means of all data sets reported.

	BOD ₅ (mg/L)	COD (mg/L)	Mineral Oil/ Grease (mg/L)	pH	Ammonia Nitrogen (mg/L)	Total Phosphorous (mg/L)
Knight, R.L., et al., 1999	11.65	96.125	3.105		1.98	4.75
Ji, G., et al., 2002	4.95	104	4.15	7.53		0.095
Xia, H., et al., 2003	3.89	43.54		7.962	0.907	
Figure 3						

As you can tell the data is rather spread out and yet some values are very similar. The two bottom sets of data are from eastern Asia and the top set is from a collection of wetlands throughout the world. These of course do not report the influent concentrations, which as noted prior can have a rather large impact on the wetland effluent. It is also worth noting that petroleum is widely varied depending on which region of the globe the product is mined from, and even varied within a region or drill site. The most interesting trend is that although two seem to match well, they do not always. Overall though I think this further demonstrates the point first brought by Knight (1999), that wetlands do provide for a quite predictable effluent. This is especially true if you were to consider the processes and cycles always going on in a wetland.

EXAMPLES

There are many good examples of current wetland being studied and developed around the world. Below is a synapses of the sites that seemed unique and at least interesting.

In Texas, near the coast by Houston on the San Jacinto River a flooded broke four petroleum pipes and released large amounts of petroleum into the river. A study was conducted by Texas A&M University and part of the research is reported by Mills (2003). The objective of the data reported in this paper was to view and account for the natural attenuation of the wetland for the petroleum. Within one year the site was remediated and in fact about 95% was removed in 150 days. The idea was proposed that fertilizing the area could have sped this process up even more. The author cautioned the reader that enough may not be known what the effects will be and in this case an estuarine environment is particularly sensitive. The crash of the Exxon Valdez in Alaska was a tragic thing and some effects are still felt today by the people and animals of the Prince William Sound. Three researchers from University Alaska-Fairbanks studied (Sugai et al., 1997) many of the things done to remediate the spill as well as areas that we less impacted by man-made remediation efforts. Based on this data it was determined that in order for remediation efforts to effective an entire ecosystem model should be created. This would help to determine all the reactions and interactions taking place. Lots of studies were presented earlier in this report about how fertilizers in wetlands worked in some place and not in other, in fact even harmed a few wetlands. This seems sketchy, until you consider the idea proposed by Sugai (1997) and others. A researcher in Canada (Moore et al., 1999) studied four different peat bog wetlands that had been influenced by petroleum, with intentionally or not. Measurements and other information was taken and sythesised regarding influents and effluents, existing conditions, vegetation, and much more. A summary of each site was given, specifically looking at how the site reacted and treated the hydrocarbons. Basic processes in wetland were determined as well as a guide to what parameter are important for proper treatment of hydrocarbons. It was ascertained that a lower flowrate created the opportunity for more natural attenuation. Peat can absorb up to eight times its weight in oil, as compared to activated carbon only 30-50% of that. Volatility requires lots of air and therefore lots of pore space in subsurface flow wetlands. Biodegradation requires lots of microbes in many populations. On the surface aerobic degradation and volatility can occur, deeper anaerobic degradation occur, and sorption can occur anywhere.

Constructed wetlands on the other hand are designed with specific objectives in mind. They can be judged quite easily on a pass/fail basis. Although most of the interactions and actions of a wetland are

unknown and too cumbersome to account for in a design equation, we assume many things and base out designs on past examples. Below are a few real work examples of wetlands in practice, with real pass/no-pass options.

In order to begin to judge the vegetative capacity as well as other design parameters, two studies in China looked at hydraulic loading (Ji et al., 2002) and a second study comparing four plant varieties and a non-planted bed (Xia et al., 2003). The first study by Ji (2002) compared two reed beds with differing hydraulic loading and a controlled bed. The results, as reported by the author, now allow China to use wetlands as an effective treatment option for "heavy oil-produced water." The test was ran in the Liaohe Oilfields in China. The bed were 15mx60m made of sandy loam soils and then clay as a cap. Tests were ran for three separate seven month periods. The results of the testing provided enough information to create a design guide for others to use when designing for petroleum water treatment. The second study in China was a comparison of four different plant types to determine which may or may not work for petroleum treatment. Overall it was found they all did a good job of removal high strength petroleum waste. Their results may also be a little skewed because one plant was in situ to some petroleum. It took some time for plants to get adjusted, but once done all the rate were approximately the same.

Forced to clean up its act by repeated permit violations a BP refinery in Mandan, North Dakota decided to dedicate part of its property for a wetland treatment/wildlife preserve. The process and recent results were reported by Litchfield (1993). Action was needed when the separator and lagoon were not treating to the quality established by the companies National Pollution Discharge Elimination System (NPDES) permit. Therefore an action was needed. Basically the refinery could install a couple million dollar mechanical unit or try a slightly new wetland technology. Although the wetland is fairly cheap, \$500,000, a lot of land would be needed. Luckily BP had an extra 640 acres adjacent to the refinery. Eleven ponds were created to flow wastewater from the lagoon to the Missouri River, five ponds were used on for overflow and habitat. Litchfield stated that most of the time no flow reaches the river and in fact many other refineries are transporting waste to Mandan. There are numerous wildlife that frequent the area, ranging from the smallest microbe to deer and geese. Testing has been rigorous and so far it was been found that toxicity has not killed any of the fish. As of the published date of the report the NPDEDS permit was not exceeded, and any other deviations prior were due to heavy rain events. Numerous awards from governments, associations, and others have been bestowed upon the project. It is truly a success story of providing a low cost option that works for the client, customers, and the environment.

CONCLUSION

It has now become clear that wetlands are more than capable of handling the treatment of petroleum wastes. Some may ever argue that wetlands are the best; easy to use, cleans up nice, looks pretty. Wetlands either already created by nature or those by man can produce the same results given the same conditions. There are many processes that are always going on in a wetland; degradation, settling, volatilization, sorption, and photo-oxidation. The organisms used in these reactions are very numerous and almost impossible to make it its own taxona (Harayama, 2004). It seems clear that organisms must live in such an environment to gain the ability to degrade hydrocarbons. The concept to study the entire ecosystem and not just chemical reactions (Sugai, 1997) is amazing. The idea sounds so simple and yet probably was glanced over by hundreds before. It make very logical sense that all reactions taking place must be accounted for, this seems to account for why so many people have different results for the use of fertilizer to speed up the degradation process. The use of hydraulic load and influent concentrations (Knight, 1999) as the basis for wetland design makes good sense and workable numbers can be developed based on these assumptions. As evident by all the successful wetlands treating petroleum waters now, it only seems natural that wetlands will continue to be used for years to come. Imagine owning a large industrial part only to find out that there are hydrocarbons everywhere. The two options are expensive treatment or another method. The ability to turn an industrial site into grassland and wetlands was just what Chevron did on the outskirts of Cincinnati. Now the area is teeming with broods, ducklings, red tailed hawk; and lately deer, rabbits, and wild turkey have been attracted to this stop(Pace, 2004). It almost seems funny to think how nature goes and goes and seems to end up right back where it started.

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