3 Tier Technologies Environmental

Using Carboxx ™, an Activated Humic Acid, in the Detoxification of Soils Contaminated with Polychlorinated Biphenyls

The health of existing and future generations depends on the ecological solutions used in their countries. This is the reason why governments, political parties, public organizations, mass media, and most of the people of highly developed industrial countries of the world pay considerable attention to the improvement of their environmental conditions.

It has been recognized during recent years that among the many kinds of xenobiotics there is a group characterized by a very high degree of toxicity that can be qualified as super-toxic substances. This group consists of organic substances such as polychlorinated dioxins, dibenzophurans and biphenyls, pesticides containing chlorine or phosphorus, and polyaromatic hydro carbonates etc.[1] The human body receives super toxicants while breathing, drinking water or eating animal or vegetable food. Super toxicants may have mutagenic, tetragenic, and carcinogenic effects; porphyria, suppression of the immune system, cachexia of the body and otherwise affect the internal organs.[2]

The unique features of polychlorinated biphenyls (PCB) make them a specific kind of toxicant. PCBs also have an extremely high degree of chemical and thermal stability. They were widely used everywhere until 1980. The total amount of PCBs used by the world industry was probably over 1,200 tons. Laws prohibiting the manufacture and use of PCBs are now in force throughout the world. Nevertheless, significant levels of PCB residuals are still found in the environment and in living organisms, including humans.
Highly contaminated soils have been found in most areas where PCBs were recently produced or used. As an example, we can observe the environmental situation in the City of Serpukhov, Russia, where PCBs were used for 25 years as a filling for electrical transformers.

Even though the use of PCBs was halted 10 years ago, both the soil and the produce grown on that soil continue to be severely contaminated by PCBs. The most highly contaminated soils are in the southern part of the city with its private gardens that supply the city markets with fresh vegetables, berries, and fresh greens. Therefore, it was a matter of specific interest to explore the use a technology for in-situ soil detoxification by means of activated humic acids (AHA). It is well known that ecologically toxic substances have an ability to bind to a soil organic substance or to its clay mineral fraction. In the presence of a significant amount of an organic matter in soil, the absorbability of a mineral fraction practically does not exist and the binding to the toxicants is associated only with the organic matter.[3] The main components of soil organic matter are represented by humic substances containing up to 60-70% of the humic acids.

The influence of a natural organic matter on the toxicity and bio-availability of the polychlorinated biphenyls has been considered in detail[5].

It has been shown that the main mechanism of binding of organic xenobiotics represents a hydrophobic interaction of PCB with the humic acids, thus creating PCB-humic acid complexes. These complexes significantly reduce the bio-availability and toxicity of the xenobiotics.

It has been also noted that besides the adsorption of PCB and humic acids, that is similar to the hydrophobic interaction process, there is a possibility of the covalent binding of xenobiotics[6]. The main mechanism of creating the covalent links for organic matter, containing phenol type structures, will represent the acidic binding to humic acids. This process provides the polymerization of xenobiotics with humic acids and creation of polymers that are extremely stable with regard to acidic and alkaline hydrolysis, thermal treatment, and microbiotic decomposition.

Until recently, no one has attempted an in-situ method of detoxification of large areas of soils contaminated with organic xenobiotics by the introduction of various humic acids. One of the main reasons was a lack of an efficient and feasible industrial technology for consistently producing an effective humic acid in sufficient amounts.

Recently an efficient industrial technology for manufacturing a unique Activated Humic Acid (AHA) **(Currently marketed by 3 Tier Technologies as "Carboxx")**, using inexpensive and available materials, has been developed and introduced. The reactive sites of the natural humic acids are blocked by various elements. This is an important distinction between natural humic acids and AHA. AHA has a complex of unique features and represents a complicated organic and mineral compound.

The organic part of AHA contains many functional groups (mainly carboxyl and hydroxyl groups). The inorganic part of AHA contains micromicellious formations consisting of aluminum, silicon and iron oxides. Carboxyl groups are highly reactive and dissoluble in water. Hydrophobic areas of macromolecule absorb the organic xenobiotics. These features allow AHA to detoxify soils contaminated by PCBs.

Table one show the effect of AHA on PCBs in soil.

TABLE 1:

Changes in content of particular groups of PCB congeners after AHA soil treatment

PCB CONGENERS	INITIAL CONTENT OF PCB CONGENERS mg/kg	CONTENT OF PCB CONGENERS AFTER 60 DAYS CONTACT WITH AHA mg/kg	REDUCTION OF PCB CONGENERS CONTENT %
MONO	0.444	0.15	65
Di-	4.545	2.27	50
Tri-	11.472	3.442	69.9
Tetra-	3.738	1.308	65
	20,199	7,175	64,5

As can be seen from Table 1, after 120 hours of contact between the PCB and AHA the congeners concentration is reduced approximately by 65%.

The effect of AHA on PCBs, with respect to soil restructuring and detoxification, was tested by introducing AHA into the contaminated soil. All the work was done in 1995 in an area adjacent to a transformer manufacturing factory in the City of Serpukhov. The content of PCBs in the soil before and after treatment was determined. The macro flora of the soil was also studied. The determination of PCB content in soil before and after the treatment by activated humic acids was performed by a gas chromatography method using a Hewlett-Packard chromatograph, supplied with an electronic detector having a capillary tube 25 m in length and 0.25 micron diameter with the phase HP-1. *A mixture of 62 percent synthetic of PCB in isooctane was used as a calibrating standard.*

Table 2 shows the changes of PCB content before and after the AHA soil treatment in natural conditions in soils, having different content of PCB. It appears that there is a stable reduction of PCB soil concentration. In highly contaminated soil, after 60 days, it reaches 20-35%. In soils having 0.5- 3.7 mg/kg of contaminants, it goes up to 52-56%.

Table one shows the effect of AHA on PCB’s in water.

TABLE 2;

Reduction of PCB content in natural conditions after AHA water treatment.

Initial Content of PCB mg/kg	**Content of PCB after 120 hours contact with AHA mg/kg**	**Reduction of PCB Content %**
89.1	17.2	80.6
12.3	4.5	63.4
12.9	4.54	64.8
3.7	1.95	47.3
0.5	0.28	44.0

Tables 1 and 2 show the changes of concentration of the particular congeners after AHA treatment. The dichlorinated biphenyls and several kinds of trichlorinated biphenyls have not been found in soil after 60 days of contact with AHA (#6, #8, #15-18, #17). The concentration of several types of tri- and tetrachlorinated biphenyls proved to be ten times lower. As was found for pentachlorinated and other groups of highly chlorinated biphenyls, the reduction of PCB concentration after AHA soil treatment was considerably lower. It is also well known that the low chlorinated biphenyls have a higher degree of absorption, dissolubility, and steam elasticity, than highly chlorinated ones.

Basically, the soils of the City of Serpukhov were contaminated by low chlorinated biphenyls (up to 70% of soils) because electrical transformers had been filled by Arochhlorine - 1242. The main part of this substance contained low chlorinated biphenyls and only 2.5% of highly chlorinated biphenyls.

The growth of azotobacter culture (nitrogen fixing bacteria) in contaminated soils is very sensitive to the influence of various kinds of toxicants and represents a very clear index of the reduction of soil contamination. The results of this bio-test are shown in Table 3.

TABLE 3:

Changes in AZOTOBACTER after AHA soil treatment

Variant	Accumulation of Azotobacter on the Surface of Soil Particles–%
Initial Soil, Untreated by AHA	58
Soil After 25 days of AHA Treatment	80
Soil After 60 Days of AHA Treatment	91
Soil after 25 days of treatment by AHA and by Microorganisms	99
Soil after 60 Days of Treatment by AHA and by Microorganisms	99

* Every figure has been obtained from the results of two separate tests

Table 3 shows that the insertion of AHA into a soil provides an efficient soil detoxification in a short period of time. An additional insertion of native microorganisms increases this effect. It has been found that native microorganisms, represented basically by the group of pseudomonas, develop very quickly in the presence of AHA. Their concentration in the soil treated only by AHA after 25 days and in the soil treated by AHA and by microorganisms also after 25 days, remains just the same and equals to 10^8 CCU/g.

The testing area has been used for farming, and that was the reason to conduct the additional PCB concentration tests on the samples of vegetables produced in this region. Three vegetables: White cabbage (Slava), the carrot type (Shantane), and beet type (Bordo) were chosen for testing.

Table 4 shows the averaged figures of the total PCB concentration in the above mentioned vegetables at the end of a farming season.

TABLE 4

Changes of PCB concentration in vegetables after AHA soil treatment

PCB concentrations, mg/liter

VARIANT	CARROTS (ROOTS)	BEETS (ROOTS)	CABBAGES (LEAVES)
Untreated Soil	9.4	1.53	6.7
Soil Treated by AHA	1	0.07	3.6

Table 4 shows the averaged figures of the total PCB concentration in the above mentioned vegetables at the end of a farming season.

Table 4 demonstrates that the decontamination of a soil by AHA reduces the PCB content in carrot by 89%, more than by 95% in beet, and approximately by 46% in cabbage.
Related tests also showed a significant improvement in several agrochemical characteristics of soils treated by AHA. Among these improvements are: an increase moisture holding capacity, an improvement of soil structure, an increase in the availability of plant nutrients, etc. In addition, the productivity of the treated soils was increased by 30-40%.

SUMMARY CONCLUSIONS:

High efficiency, low costs, simple technology, feasibility, the possibility of cultivating ecologically clean produce on previously contaminated lands, a significant improvement in soil agrochemical characteristics, and increases in soil productivity are the specific beneficial features of this new soil detoxification technology. All this permits us to recommend this technology for introduction into a much wider practice for the remediation of PCB contaminated soils.

POSTSCRIPT:

This report covered a field test lasting only 60 days. However a "follow-on" study was conducted 12 months later. The same test procedures were used in order to detect any residual PCB in the treated soils. This "follow-on" test found that the residual levels of PCB were undetectable at the 1 part per million levels.

PRESENTER'S NOTE:

Carboxx ™ has been found valuable in the remediation of heavy metal contamination of soil and water as well as the remediation of hydrocarbon contaminations of soil. We can supply small quantities of Carboxx ™, together with some guidance and suggestions for exploring additional uses. For additional information contact: dburdette@3tiertech.com