CO-CONTAMINATION OF SOIL WITH DIOXIN AND ARSENIC AT FORMER MILITARY AIRBASES IN VIETNAM

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Introduction

Vietnam has a few dioxin contaminated hotspots due to the armed conflict in between 1961 and 1971. Former military airbases where chemical defoliants were loaded/stored/handled have elevated level of dioxin in soil and sediment due to the ignorance of toxicity of dioxin at that time. Dioxin existed as impurity of an herbicide commonly called Agent Orange (AO). While two other herbicides namely Agent White and Agent Blue were also extensively used, the environmental impact of these chemicals has not been assessed. Agent Blue is composed of organic arsenic compound (i.e. cacodylic acid salts) and it was sprayed on rice paddy and other croplands to deprive the harvest of opponents' force. As it was handled in the similar manner to AO, mishandling, spillage, wash down, improper disposal and other activities that may have caused the chemicals to be spread over to the airbase is highly expected for Agent Blue.

Vietnamese Government has adopted the National Action Plan to resolve AO/dioxin issue caused by the War and environmental remediation activities that has started since 2009. Two newly introduced technologies that destroy dioxin to detoxify the contaminated soil will soon be implemented at pilot scale and full scale. Yet the effect to the arsenic compound in treating soil has not been studied at all since the concentration level of the arsenic compound has not been surveyed. Arsenic varies its toxicity with the type of compound it forms. Organic arsenic as the Agent Blue is much less toxic than inorganic arsenic. If such soil treatment technology converts organic arsenic into inorganic one, the actual toxicity to human will be greatly increased.

Materials and methods

Vietnamese Government, in collaboration with international donors, has conducted several dioxin surveys at suspected dioxin hotspots. The dioxin concentration level of soil and sediment at Da Nang airbase was conducted in 2006[1] and at Bien Hoa and Phu Cat airbases in 2008[2] and 2011[3]. Soil sampling procedures have been developed by Hatfield Consultants (Canada) and used for above surveys. The samples were analyzed locally with some cross check analysis done by an international laboratory. Analytical methodologies for 2006 and 2008 surveys are explained in respective articles. The analysis of 2011 samples was done in Vietnam with EPA 1613 to determine dioxin and furan congeners with WHO 2005 TEF values (i.e. 17 congeners). Isotopic dilution HRGC/HRMS (Micromass Autospec Ultima) was used for the quantification of these chemicals. The full results of this analysis will be reported elsewhere.

This survey used the archived samples collected in the past 3 surveys described above. Nine (9) locations from three (3) airbases namely Phu Cat, Bien Hoa and Da Nang, were selected for arsenic analysis. 52 samples with known dioxin concentration were selected and the total arsenic concentration was analyzed by two national analytical institutions with 3 duplicating analyses for cross checking purpose.

The samples were preliminarily treated by drying at room temperature and then crushed, sieved with the pore size of 0.25 mm and homogenized. 1.0 g of the sample was put in a test tube and 6 ml of 37% HCl, then another 2 ml 65% HNO_3 were added. Then it was heated under the microwave field in the total time from 20 to 30 minutes. After cooled down to room temperature, the sample was filtered and, insoluble residue on the filter paper was washed with 0.5 M HNO_3. The sample was diluted up to 50ml and 10ml of it was further treated with 4 ml of 37% HCl and 1 ml of 1% KI, then treated with mild heat at 60 ° C for 10 minutes. Let it cool to room

temperature and transfer the entire solution into the flask, whose arsenic content was analyzed by atomic absorption spectrometry (HVG-AAS).

Results and discussion

Dioxin and arsenic contaminations in the samples are plotted on Figure 1. National dioxin and arsenic standards are 1000 pg/g-TEQ and 12 mg/kg, respectively, which are expressed in thick lines that divide the figure into 4 zones. No statistically significant correlation between these parameters is observed on this plot. One of the important findings, however, is that the soil in the hotspot is more contaminated with arsenic than dioxin because many samples fall under lower left zone which indicates dioxin contamination below national standard and arsenic above standard. Arsenic contamination can also occur naturally but the level observed in this survey is abnormally high, as high as 4,500 mg/kg, to conclude it as natural phenomenon.

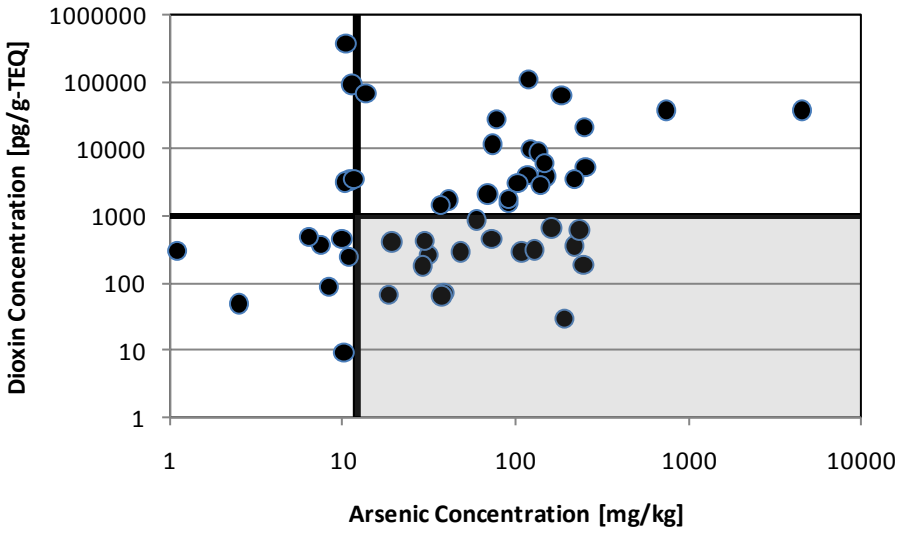

Figure 1: Dioxin and arsenic contamination at 3 former US military airbases

The dioxin concentration and arsenic concentration in soil are scientifically not related because they came from different defoliants used for different purposes. However, the similar handling/mishandling during the war-time military operations may have resulted in the similar leakages happened for both chemicals. Figure 2 plots the same dataset used for the Figure 1 with the distinctive symbols by sampling locations. There are weak but certain level of correlation between these parameters for soil samples in Bien Hoa while such relation is invisible for the data in Da Nang. If the arsenic contamination happened purely naturally, the correlation would not have observed at all. Therefore it is premature to conclude that the arsenic came from war-time defoliant, but still it is potential source of contamination in these 3 dioxin hotspots.

The spatial distribution of the dioxin and arsenic in Phu Cat (one of dioxin hotspot) is presented in Figure 3. There are 3 sub-sites in the airbase where elevated level of dioxin has been identified. The area noted as “B” in the Figure 3 is the largest contamination site in Phu Cat. Northern half of the area where chemical storage tanks were installed during war time is commonly called Z3 area. The highest level of the dioxin contamination (238,000 pg-TEQ/g) was observed at the Z3 area. The area noted as “A” which is located at approx. 500m north to the Z3 area has just been identified in 2010 (the highest concentration of 89,900 pg-TEQ/g). The area noted as “C” is a lowland (seasonal wetland) which receives storm water from area “B”. The dioxin contamination level is much lower than the other two areas (maximum concentration of 420 pg-TEQ/g) but it still exceeds national limit of sediment (i.e. 150 pg-TEQ/g).

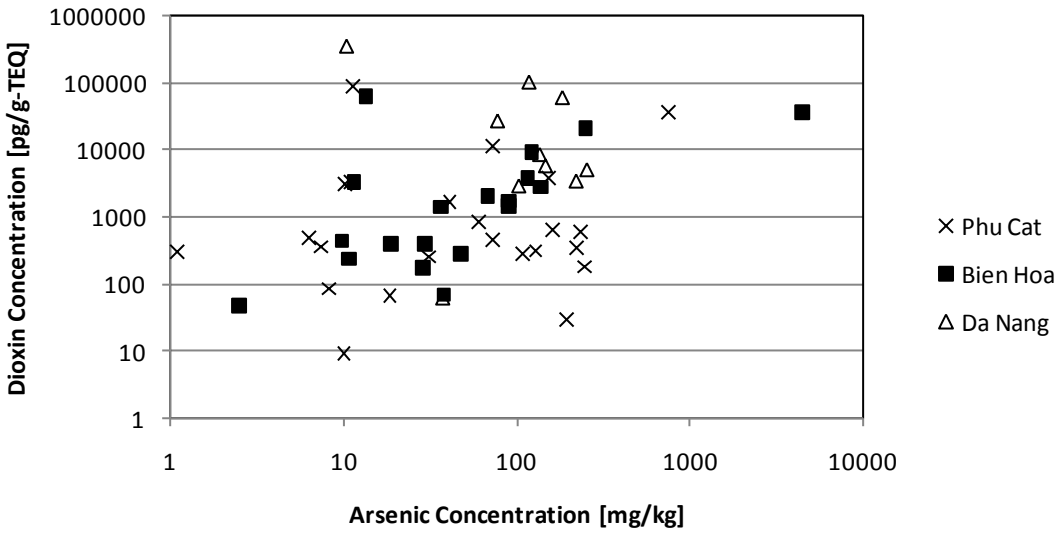

Figure 2 Correlation of dioxin and arsenic contamination per airbase

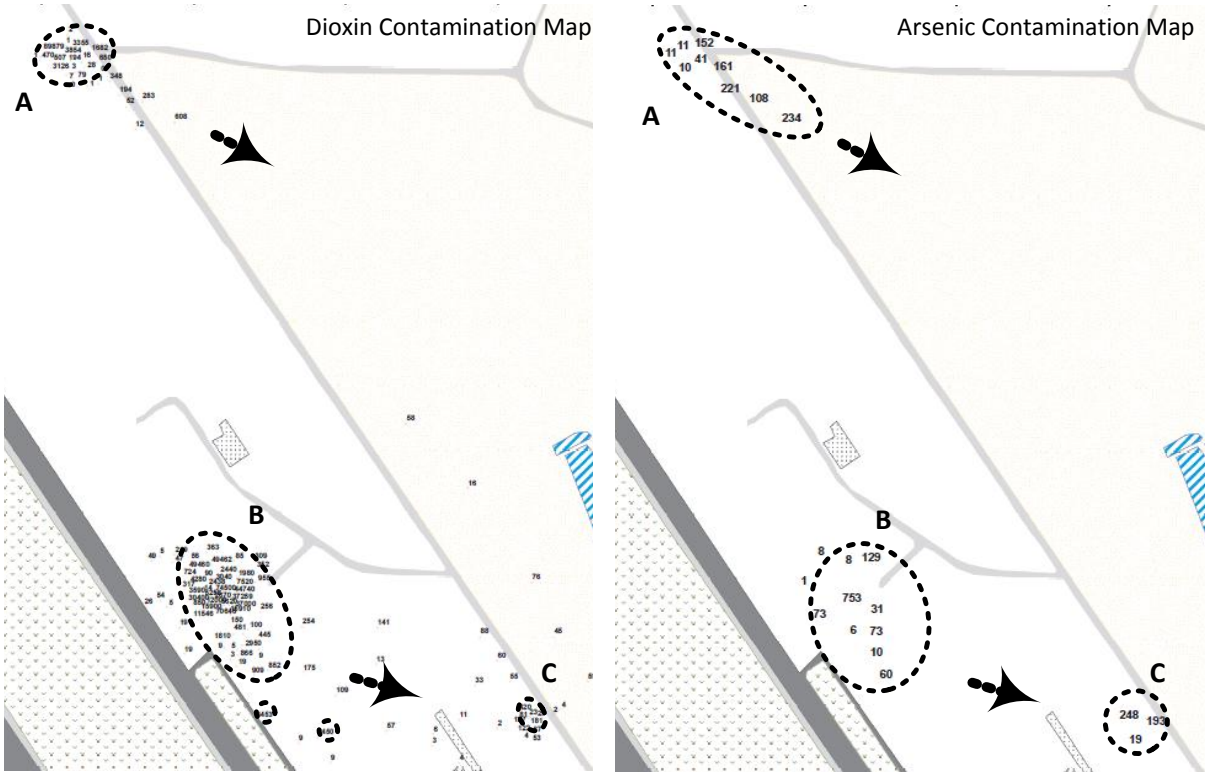

Figure 3 Geographical extensions of dioxin and arsenic contamination at Phu Cat airbase

The arrow signs in the Figure 3 indicate general water flow direction at these areas. The maps indicate that the arsenic contamination boundaries are stretched to the way following the water flow. Although actual contamination boundary of arsenic has not been surveyed, the contamination areas seem to be larger than the areas of dioxin. It is also notable that the arsenic levels at downstream are higher than those at upstream. All

arsenic contamination at area “B” except the highest (753 mg/kg) is lower than two out of three results at area “C”. This is significant difference of contamination status of dioxin that area “B” is much higher than area “C”.

This is the very first survey on arsenic contamination at dioxin hotspots in Vietnam. Following hypotheses have been drawn:

- The arsenic contamination happened together with dioxin contamination during war time, which came from Agent Blue
- The contamination of arsenic is wider than that of dioxin especially stretching out to downstream
- The form of arsenic has not been surveyed so the actual toxicity and exposure risk to human are not known
- The existence of arsenic in soil may impact technology selection of dioxin remediation

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