Scientific Basis for Risk-Based Acceptable Concentrations of Metals in Fertilizers and Their Applicability as Standards

Introduction

The fertilizer industry, the U.S. EPA, the California Department of Food and Agriculture (CDFA), the American Association of Plant Food Control Officials (AAPFCO) and other stakeholders are working to address the issue of safe levels of metals in inorganic fertilizers. This includes both primary nutrient (NPK) fertilizers as well as micronutrient fertilizers. To this end, several of the stakeholders (specifically the USEPA, CDFA and The Fertilizer Institute [TFI]) have undertaken evaluations of potential human health risks as a result of exposure to metals in fertilizers. The three risk assessments share much of the same methodology and underlying science. All three conclude that, in nearly all cases, the metal levels found in fertilizers do not pose a risk to the applicators, to farm families or to the general public[1].

The widely utilized risk paradigm emphasizes use of current scientific thinking and modeling to regulate and/or otherwise sensibly manage chemicals in a health protective manner. While it is commonly acknowledged that an excess of exposure to any substance, including metals in fertilizer, can conceivably result in a health risk, it is also an established fact that chemical exposure can occur without risk to health. The establishment of 'safe exposure levels' and 'safe levels of chemicals in products' is done using risk assessment techniques that take into account the inherent toxicity of a substance as well as the type and degree of exposure. These risk models are designed to assure the outcome is protective of health, that is, they incorporate assumptions that will nearly always overpredict, but rarely if ever underpredict, health risks.

For fertilizers, a generalized risk model for establishing safe levels of metals includes the following components:

fertilizer product (NPK or micros)	→	application rates (vary by crop and soil)	→	metal level in soil at 50-100 years (K_d range)	→	metal uptake into plants (PUF range)	→	food ingestion rates for crops (FDA, USDA)	→	established acceptable metal level in diet (toxicity)

→ back calculate to an acceptable upper limit of a specific metal in the fertilizer product (i.e., a RBC)

In the interest of assuring the public that fertilizers are safe and also to prevent the use of what could be unsafe materials in fertilizers, some stakeholders have called for standards for metals in inorganic fertilizers. A risk assessment can serve as a scientifically sound basis for setting health protective standards (i.e., safe levels) as part of the risk management process.

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[1] A screening evaluation conducted by USEPA and CDFA identified the farm family as the group having the highest potential for exposure and risk among those groups that come in contact with fertilizers. A risk-based protective level for metals based on the farm family would also be protective for other exposure scenarios including, for example, home owners who have a vegetable garden and who apply turf products.

Risk-Based Acceptable Concentrations (the Proposed AAPFCO Standards)

Collaborations among the consultants working on behalf of TFI and CDFA resulted in the following risk-based acceptable concentrations (RBCs) for 9 metals in inorganic fertilizers:

Metal	ppm per 1% P_2O_5 in NPK products	ppm per 1% micronutrient in micronutrient products
arsenic	13	112
cadmium	10	83
cobalt	3,100	23,000
lead	61	463
mercury	1	6
molybdenum	42	300
nickel	250	1,900
selenium	26	180
zinc	420	2,900

The RBC is the estimated maximum 'safe level' of that particular metal in that type of fertilizer product at one percent (1%) of the nutrient level (e.g., P_2O_5 or iron, manganese, zinc). These numerical values were recommended by AAPFCO's Board of Directors at its February 18, 2001 meeting in Albuquerque to be incorporated into SUIP #25, the fertilizer adulteration clause.

The Chronology and Science Behind the RBC Values and Proposed AAPFCO Standards

The chronology and scientific basis for the development of these 'safe levels', which have become the proposed AAPFCO standards, are described below.

CDFA was the first to develop RBCs for arsenic, cadmium and lead in micronutrient and phosphate fertilizers. Risks were evaluated using standard CDFA and USEPA risk models and acceptable risk levels. The evaluation is detailed in their 1998 report entitled *Development of Risk-based Concentrations for Arsenic, Cadmium and Lead in Inorganic Commercial Fertilizers.*

Shortly thereafter, USEPA conducted what is called a 'forward risk assessment' of phosphate and micronutrient fertilizers in commerce and concluded in their 1999 draft report *Estimating Risk from Contaminants Contained in Agricultural Fertilizers* that "hazardous constituents in fertilizers generally do not pose harm to human health or the environment." USEPA evaluated exposure and risks for 9 metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, vanadium and zinc) plus dioxins using their standard models and acceptable risk levels.

The Weinberg Group, on behalf of TFI, developed RBCs for 12 metals (arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, vanadium and zinc) plus radium in phosphate and micronutrient fertilizers. The risk evaluation followed the standard USEPA risk methodology and acceptable risk levels. The evaluation is detailed in a January 2000 draft report entitled *Health Risk Evaluation of Select Metals in Inorganic Fertilizers Post Application.*

In mid-2000 CDFA performed a reevaluation of its original RBC values in response to comments received from outside reviewers. In particular, the soil:water partitioning coefficients (called "K_d values") that were used in CDFA's original assessment were challenged as being too low.[2,3,4] By using higher K_d values, the CDFA reevaluation resulted in lower RBC values.[5]

In late 2000 The Weinberg Group, working in collaboration with the CDFA consultant (New Fields), recalculated RBC values using the K_d values reported in the 1999 USEPA fertilizer risk assessment. The USEPA K_d values include a wide range of field measurements and are consistent with those K_d values reported by Sauve et al. which are relevant to agriculture conditions.[6] These recalculations also took into account the correlation between K_d and the plant uptake factor (PUF) for any given metal. This important aspect had not been taken into account in any of the previous evaluations.[7] No other changes were made in the reevaluation of RBCs.

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[2] CDFA and The Weinberg Group used identical K_d values in their original evaluations of RBCs. These K_d values were from a 1983 article entitled *A Proposal for Estimation of Soil Leaching and Leaching Constants for Use in Assessment Models [J. Environmental Quality 12:17-28]*. The authors (Baes and Sharp) reported K_d values that were measured in the laboratory but under conditions intended to mimic agricultural soil conditions.

[3] A 'low' K_d value equates to: less metal found sorbed to the soil, more found soluble in the pore water surrounding the soil particles and therefore relatively more metal is available to be taken up into plants as well as to leach toward groundwater. Conversely, a 'high' K_d value equates to: more metal sorbed to soil, less in the pore water and therefore relatively less metal is available to be taken up into plants but relatively more metal is likely to accumulate in the surface soil.

[4] The reviewer pointed out that 'if the same K_d values used to predict soil accumulation and metal RBCs were used in soil-to-groundwater-leaching models, the prediction would be high metal levels in groundwater. And since 'high levels' are not observed, the K_d values that were used are unrealistically low.' At about the same time, an article entitled *Solid-Solution Partitioning of Metals in Contaminated Soils: Dependence on pH, Total Metal Burden, and Organic Matter* was published in the journal *Environmental Science and Technology [ES&T 34:7,1125-1131]*. In this article, Dr. Sauve and colleagues reported a very wide range of K_d values taken from the literature and based on numerous soil conditions, both agricultural conditions and non-agricultural conditions.

[5] In its first re-evaluation, CDFA used the entire range of 'Sauve K_d values' without consideration of the source of the data. That is, both agriculture-relevant and non-agriculture-relevant data were combined. Subsequently it was recognized that only the agriculture-relevant K_d values should be used to establish fertilizer RBCs. Since higher K_d values lead to a prediction of higher soil accumulation levels, they in turn result in a lower acceptable limit in fertilizer (that is, a lower RBC) for a given application rate.

[6] K_d values are derived in either laboratory or field studies and vary by orders of magnitude (for a single metal) depending upon the form of the metal applied and environmental conditions such as soil type, pH, and organic matter content. Some of the K_d values reported by Sauve et.al. are not relevant for agricultural settings. For example, the data include contaminated waste sites and soils at pH levels well outside agricultural ranges. USEPA reviewed the currently available literature on field studies, as did Sauve et.al., but rather than reporting all of the K_d values, USEPA selected "only K_d values derived for settings that most closely approximate the conditions found in agricultural soil..." [USEPA 1999, Appendix D].

[7] The PUF is a measure of how much metal is taken up by a plant. PUFs are reported in the literature and vary depending upon the local conditions. As reported previously, a high K_d means that less of the metal would be available in the pore water for plant uptake, and visa versa. That is, there is a strong negative correlation between K_d and PUF; when K_d is high, PUF is low and when K_d is low, PUF is high. This correlation is widely acknowledged and reported in the published literature.

The results, both the original risk estimates using the Baes and Sharp K_d values and the re-evaluation using the USEPA K_d values and paired PUF values, are presented as six figures (attached), one each for arsenic, cadmium and lead for both phosphate fertilizers and micronutrient fertilizers. Each figure represents the exposure scenario (farm adult or child), with the highest potential risk from being exposed to that particular metal and fertilizer product. The 'x' axis is the risk-based concentration (RBC) in parts per million (ppm). The 'y' axis is the acceptable risk percentile, for example the 90^{th} percentile risk level.

The two curved lines on each figure represent the output of the RBC model across a range of risk distribution percentiles from 85% to 95%. The curved line on the right represents the results using the Baes and Sharp K_d values (referred to on the figure as the 'upper bound conditions'). The curve on the left represents the results using the USEPA K_d and paired PUF values (referred to on the figure as the 'lower bound conditions'). A RBC value is selected by choosing the desired level of protection for the exposures modeled, that is, the acceptable risk level. The typical acceptable risk level (and that used by USEPA in their risk evaluation of fertilizers) is the 90^{th} percentile as shown on the 'y' axis.[8] The next step is to read across to where the 90^{th} percentile intersects with the results curve, and then reading down to find the corresponding RBC value. For example, consider arsenic in phosphate fertilizers as depicted in Figure 1. The 90^{th} percentile line intersects the results curve on the left side of the graph at seven (7) and intersects the results curve on the right side of the graph at nineteen (19). Therefore, the EPA K_d data predict a RBC (i.e., safe level in product) of 7 ppm arsenic (for each 1% P_2O_5) while the Baes and Sharp K_d data predict a RBC of 19 ppm arsenic.

Interpretation and Use of the RBC Results

The most accurate method of establishing exposures and related risks would be using actual measured soil concentrations and measured crop concentrations in place of the model estimates. This would however necessitate getting measurements from a wide range of fertilizer types, use patterns, soil types and other field conditions. These data are generally not available and certainly not on a nationwide basis. It is therefore typical to use modeled estimates in place of measurements and it is critical to use the most relevant input parameters and data in the models.[9] Because the risk estimates for metals in fertilizers are so highly dependent upon the K_d value, exposures estimated using the Baes and Sharp K_d data and those estimated using the USEPA K_d data serve to bound what is likely happening in agricultural settings. Both data sets include agriculture-relevant K_d measurements and combined they cover a very wide range of likely field conditions. RBCs derived from either set of data are therefore going to be health protective. In the example just presented above, this means that 7 ppm arsenic, 19 ppm arsenic, and all values in between are "health protective" levels in phosphate fertilizers.

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[8] Because the modeling was done using a probabilistic technique, this 90^{th} percentile covers ninety percent of the possible exposure scenarios given the variability in the input parameters. And because the standard risk equations and models are designed to be health protective (that is, they are much more likely to overpredict the actual risk than to underpredict the actual risk) it is not necessary to select a higher percentile in order to assure the resulting RBC will be health protective.

[9] UC Riverside has undertaken a soil and crop monitoring study to 'validate' the model parameters used in the fertilizer risk assessment. This is expected to be a two-year program with results coming in 2001 and 2002.

This type of ‘bounding exercise’ is an often-used risk assessment technique that takes into account the wide range of possible and anticipated exposure scenarios. For example, a ‘nationwide standard’ would take into account the variability in fertilizers, their use patterns and soil/farm conditions. The risk assessment models used by TFI’s and CDFA’s consultants and by USEPA are designed to protect health even at the high end of the range of exposures. The models accomplish this by using health-protective assumptions for both toxicity and exposure along with a probabilistic analysis of risk.

The outputs from the risk models, while acknowledged to be health protective, can be further interpreted based on the available observations and trends in the levels of metals in soils and in crops. After all, models are just estimators and conservative models are just conservative estimators. As stated earlier in this paper, the RBC values have been shown to be highly dependent upon the K_d values used in the risk model. It was also noted that if relatively low, agriculture-relevant K_d values (e.g., Baes and Sharp values) are put into a standard soil-leaching-to-ground-water model, the model predicts considerable metal leaching from fertilizers into ground water. We know from ground water measurements that this is not happening, and thus we can conclude that the Baes and Sharp K_d values may actually underpredict soil and crop levels under some conditions. Likewise, if relatively high, agriculture-relevant K_d values (e.g., USEPA values) are put into a standard soil accumulation model, the model predicts metal buildup in soils to levels that are significantly higher than what has actually been measured in agricultural settings, and thus we conclude that the USEPA K_d values may actually overpredict soil and crop levels under some conditions.[10]

<u>Selection of Numerical Standards</u>

The science needed to support risk-based numerical standards includes both the exposure and risk modeling described above plus the ‘reality check’, that is, taking into account real-world data on the trends of metal levels in agricultural soils and in food crops. If standards are deemed necessary, they should reflect the science as well as the economic and practicality aspects of implementing standards for agricultural fertilizers. Based on the science, TFI and CDFA consultants agreed that the midpoint between the 90th percentile RBC values for the upper and lower bounds (i.e., the left and right curves) can be defended as a ‘health protective standard’ for

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[10] For example, the more than 100+year agricultural field monitoring study in Rothamsted, UK [Johnston and Jones, *Origin and fate of cadmium in soil; The Fertilizer Society 1995]*, and the 50+ year Columbia River Basin Irrigation Project demonstrate limited metal concentration buildup in agricultural soils. In addition, the 30-year ongoing US Food and Drug Administration’s Total Diet Study (also known as the Market Basket Study) shows the dietary consumption of arsenic, cadmium and lead are declining. If metals from fertilizers were building up in agricultural soils and being taken up in larger and larger amounts by crops, the metal concentration in food basket items would be going up, not down.

There are also two recent publications in the journal *Environmental Science and Technology.* The first *[Hodson et al 2000, Bonemeal Additions as a Remediation Treatment for Metal Contaminated Soil]* reports the presence of bonemeal (akin to superphosphate fertilizer) reduces the solubility and bioavailability of metals (cadmium, copper, lead and zinc) in soil. The second *[Hettiarchchi et al 2000, In Situ Stabilization of Soil Lead Using Phosphorus and Manganese Oxide]* reports that the addition of phosphate rock or triple superphosphate reduces the solubility and bioavailability of lead compounds. The formation of metal phosphates following phosphate fertilizer additions could provide an explanation for why higher concentrations of metals are not being measured in crops.

the given metal in agricultural fertilizers. The midpoint is marked as an ‘X’ on each of the six figures.[11] Again, using the example of arsenic in phosphate fertilizers, the midpoint between 7 ppm and 19 ppm is 13 ppm. This value, along with midpoints for the other eight metals (for both phosphate and micronutrient fertilizers) are the values listed in the RBC table on the first page and are the values recommended by AAPFCO’s Board of Directors for SUIP #25, the fertilizer adulteration clause.

Further Support for the Proposed AAPFCO Standards

These same nine metals have been the subjects of risk-based health assessments conducted by numerous regulatory bodies. As mentioned above, USEPA has conducted its own risk assessment for fertilizers and concluded that the levels of metals in products in commerce today are generally safe. The World Health Organization (WHO) has also developed risk-based standards for ingestion of a number of these metals. The WHO Acceptable Daily Intakes (ADIs) are health protective targets for certain substances in the diet. For example, the ADI for arsenic is 0.002 mg As per kilogram body weight per day. There are WHO ADIs for most of the metals covered by the proposed SUIP #25 standards. By using the generalized risk model for metals in agricultural fertilizers (depicted on page 1 of this paper) and assuming that a fertilizer product contained the metal of interest at the maximum level allowed under the proposed AAPFCO standard, an estimate of the corresponding dietary intake can be calculated and then compared to the WHO ADI value. Plugging in high fertilizer application rates (e.g., 160 pounds P_2O_5 per acre per year) and the highest plant uptake factors used by USEPA, the resulting ‘high end’ estimates of dietary intake are in line with the WHO ADI target levels for metals including arsenic, cadmium, lead and mercury. Basically, this exercise confirms that if the levels of metals in fertilizers are kept at or below the proposed AAPFCO standard levels, the actual dietary exposures for farm families and for the general public would not exceed the targets established by WHO.

Conclusion

The RBC values derived for the nine metals in inorganic fertilizers are considered to be health protective and applicable at a nationwide level. Products with levels of metals at or below the proposed AAPFCO standards are considered safe for professional applicators, farm families, home gardeners and the general public. The values in the table on page 2 of this paper are scientifically defensible for use as ‘standards’ to protect human health in the context of risk management.

Note: 6 figures accompany the text (attached)

[11] While figures are provided for only three of the nine metals, the same approach was applied to all nine metals; that is, the recommended RBC values are the midpoint between the RBC values from the original and re-evaluated assessments where the only changes are the K_d values. The re-calculated RBCs for cobalt, mercury, molybdenum, nickel, selenium and zinc are based on USEPA K_d values in combination with the original PUF values reported in The Weinberg Group 2000 draft report. USEPA’s risk assessment for metals did not include PUFs for all six of these metals. There is no consistent pattern of USEPA’s PUFs being higher or lower than The Weinberg Group’s original PUFs for those metals where both exist. Both sets of PUFs were taken from reviews of the published literature.

Figure 1. Arsenic in phosphate fertilizer @ 1% P2O5 [farm family adult]

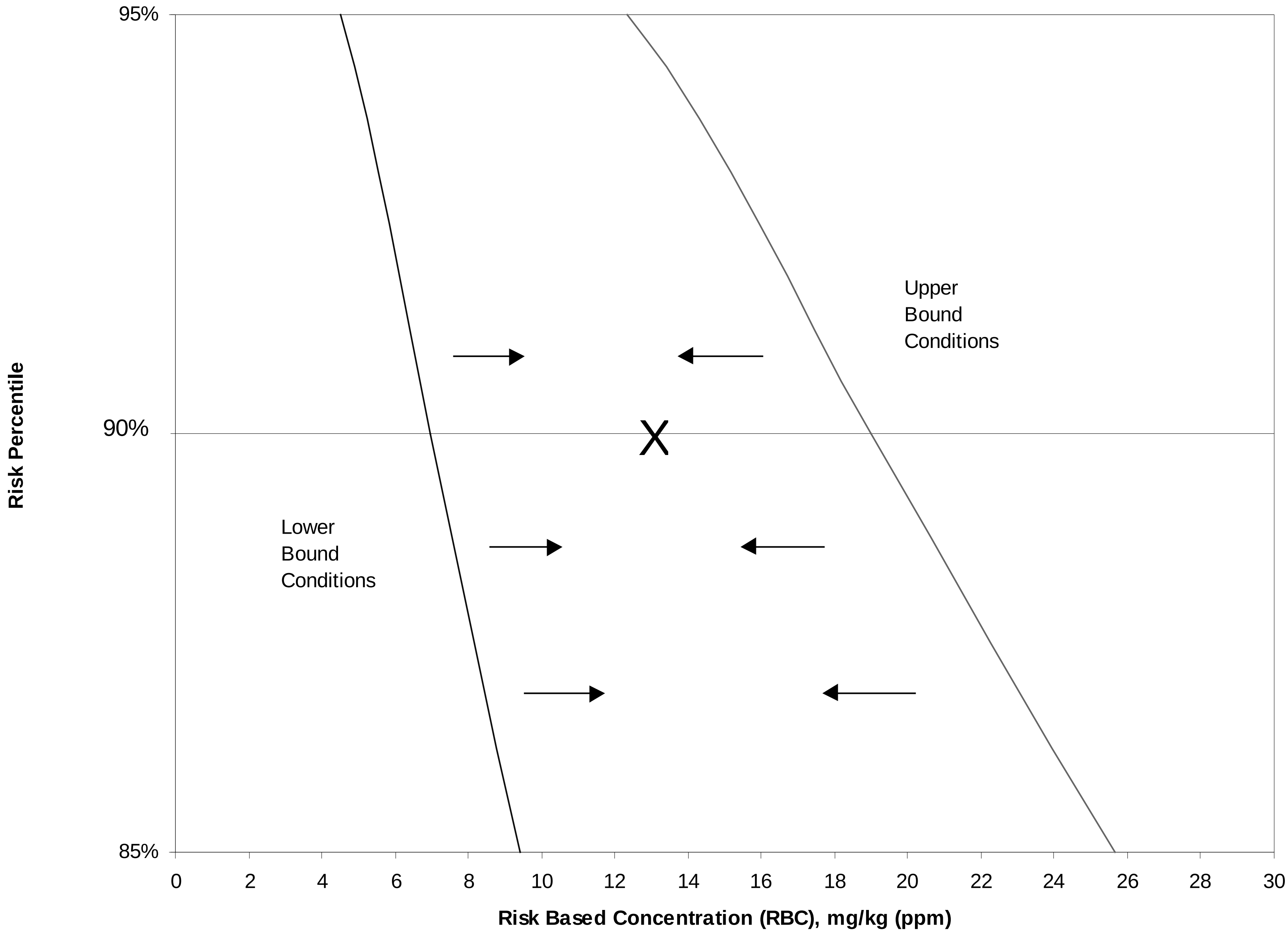

Figure 2. Arsenic in micronutrient fertilizer @ 1% iron, manganese or zinc [farm family adult]

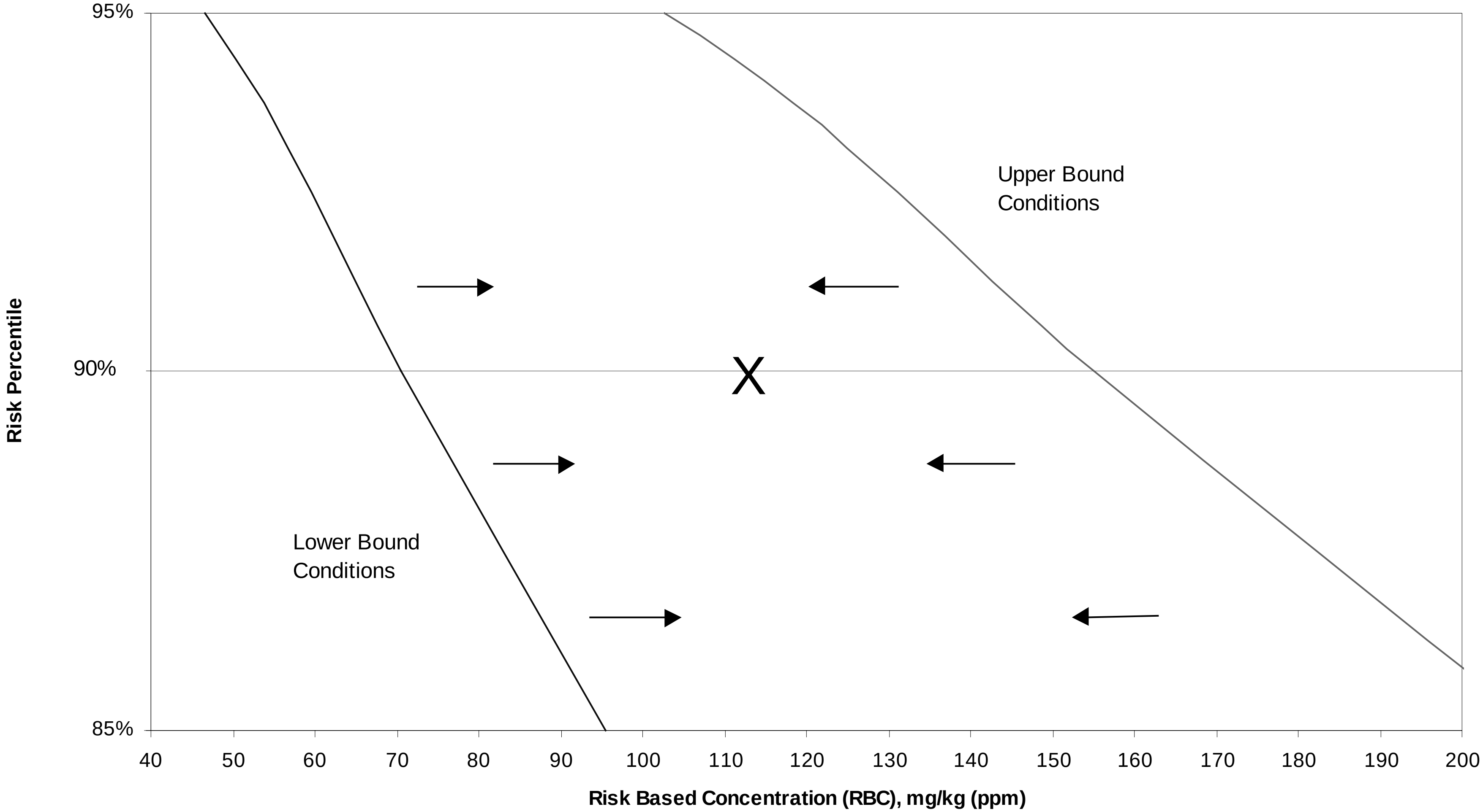

Figure 3. Cadmium in phosphate fertilizer @ 1% P2O5 [farm family child]

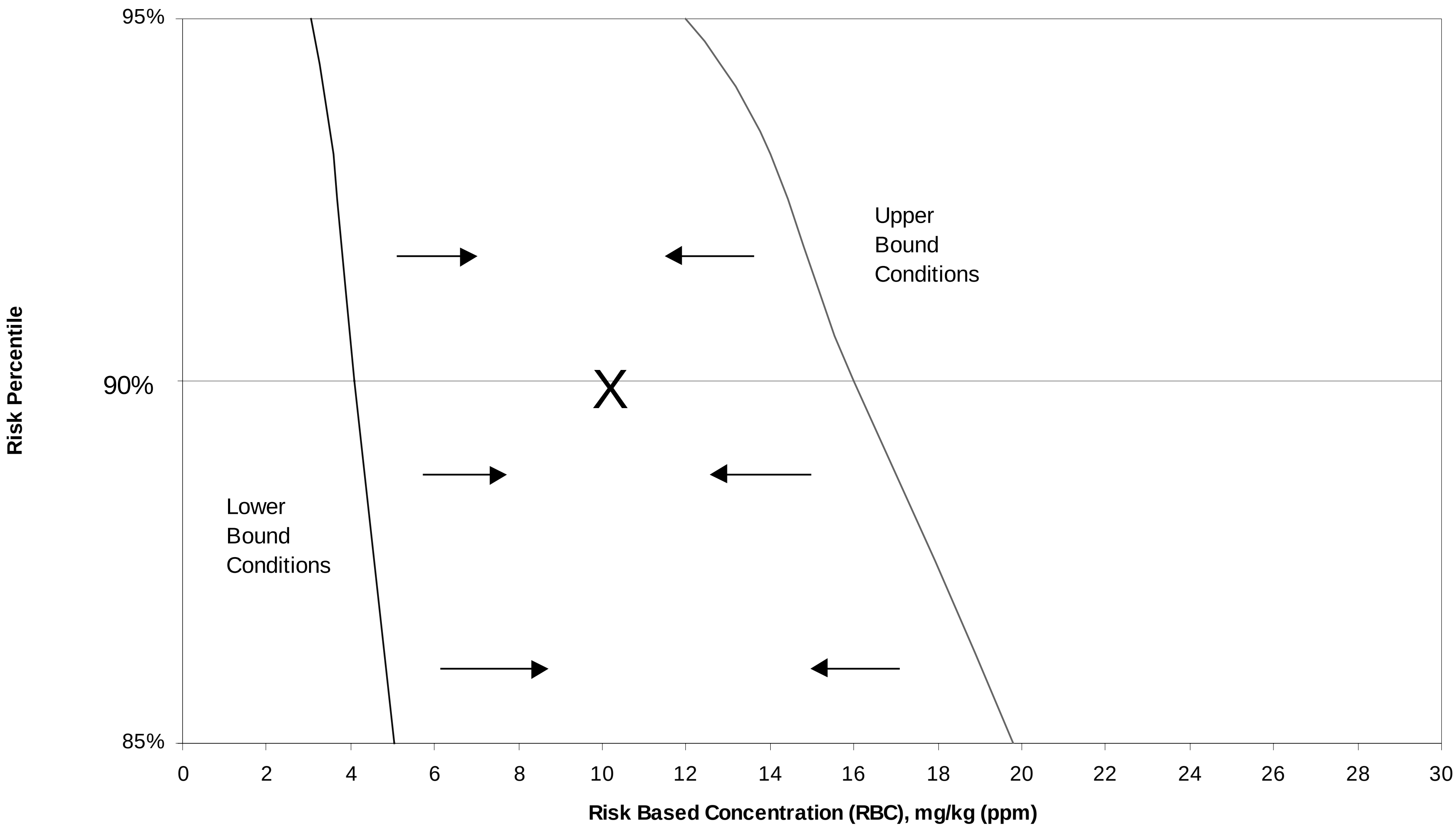

Figure 4. Cadmium in micronutrient fertilizer @ 1% iron, manganese or zinc [farm family child]

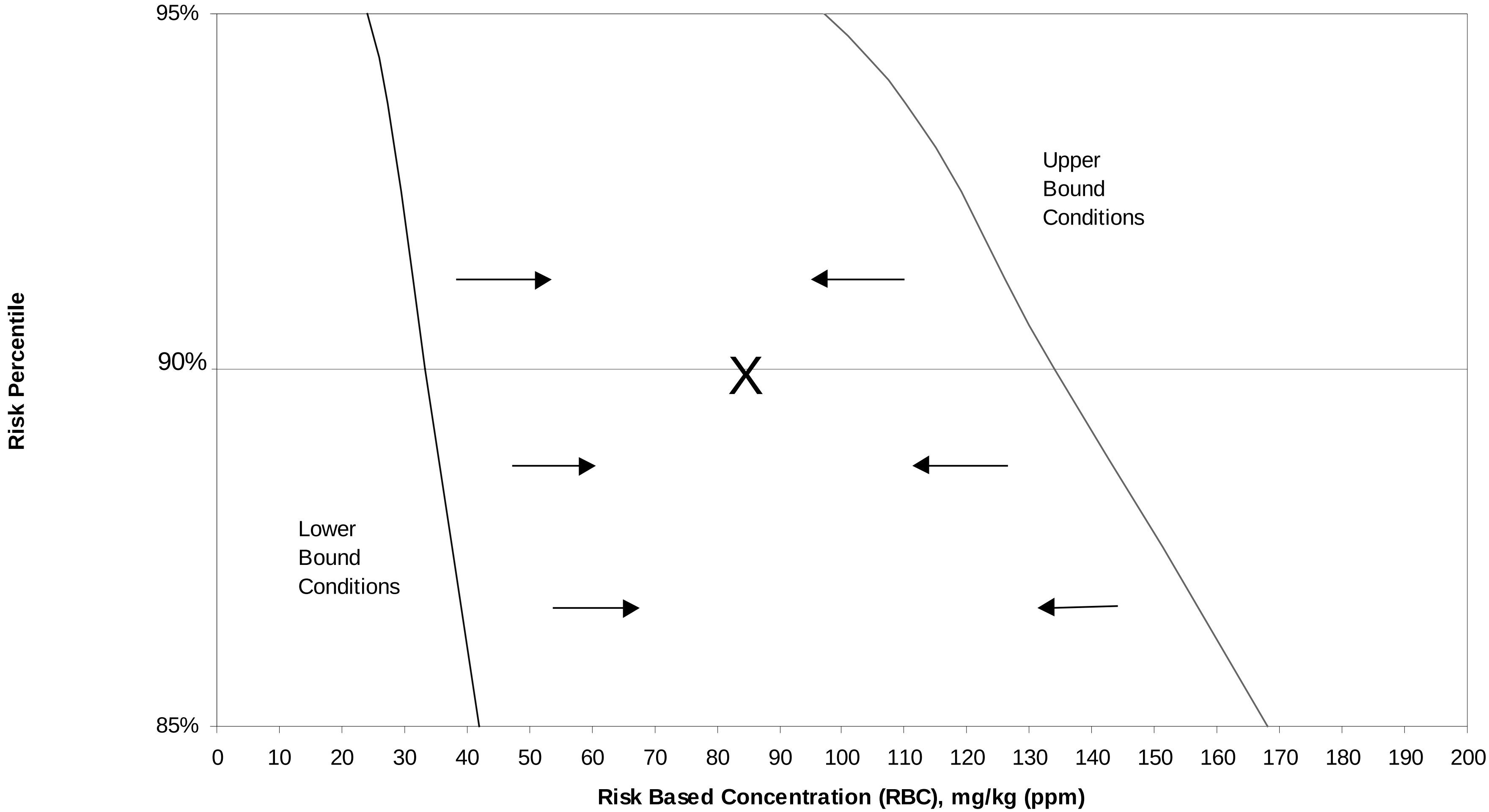

Figure 5. Lead in phosphate fertilizer @ 1% P2O5 [farm family child]

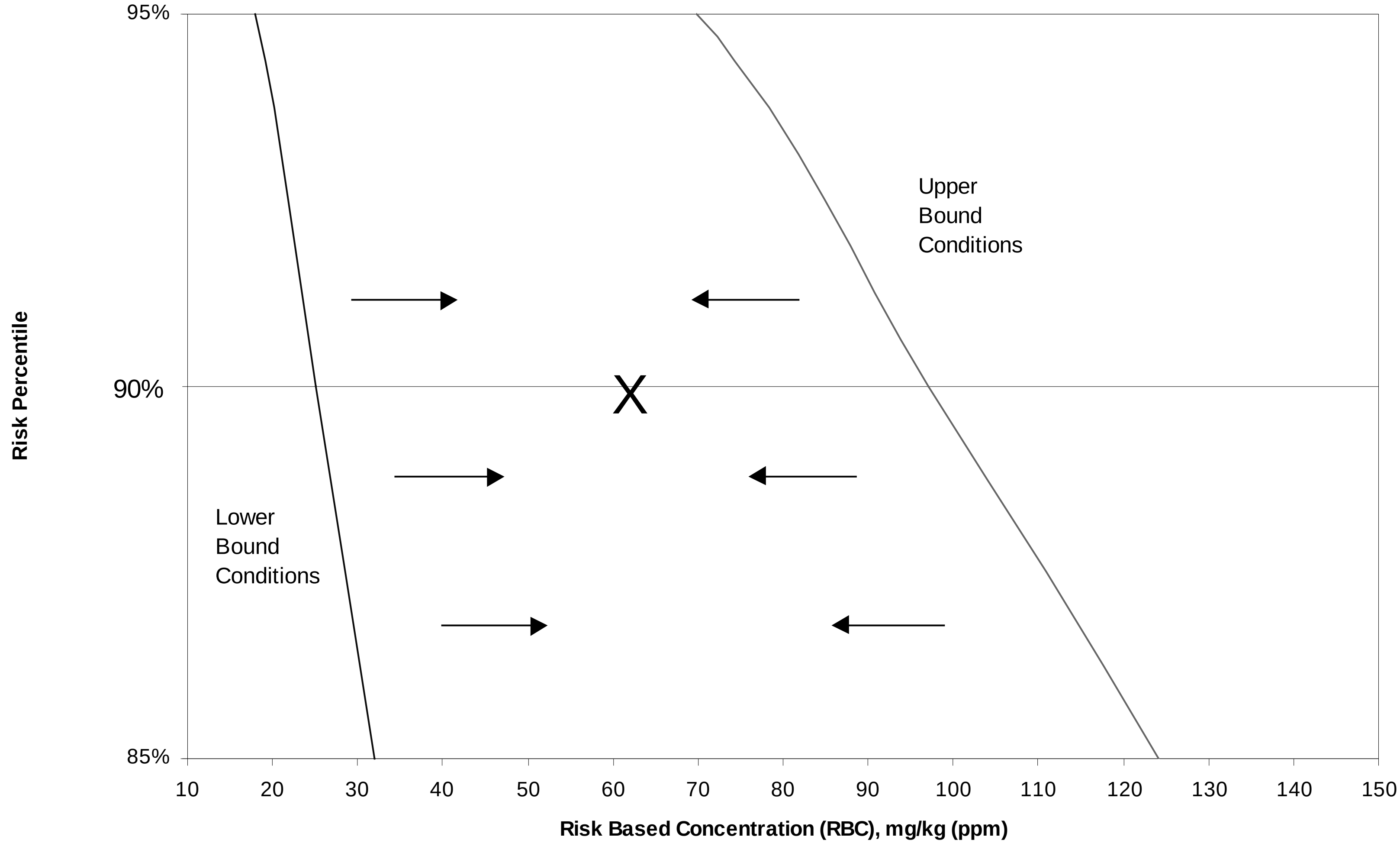

Figure 6. Lead in micronutrient fertilizer @ 1% iron, manganese or zinc [farm family child]