



National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

The Dutch Soil Type Correction

An Alternative Approach

RIVM report 607711005/2012

J. Spijker



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and the Environment
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Colophon

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Quality and Risk Assessment

Abstract

The Dutch soil type correction: An Alternative Approach.

The national Institute for Public Health and the Environment (RIVM) developed an alternative method for the so called 'soil type correction' (STC) for metals. Different soil types have varying contents of metals, the so called background values. Using the soil type correction general soil legislative values are recalculated towards the local situation. Last years, a considerable amount of new data and knowledge was published which make it possible to improve this methodology, which is originally based on research of more than 20 years ago. Applying the new data, the alternative method performs equal or better for background values than the current method for soil type correction.

Need for a fundamental discussion about the soil type correction

Following the improved method, the RIVM recommends to discuss for which soil legislative values the soil type correction should be used. This correction works very well at the level of soil background values, but not for values at the level of severe soil contamination. These higher values require another way to normalise for the variability between soil types. From a statistical point of view, the current formula in the Dutch Soil Quality Decree does not correctly describe this variability.

If it is decided to implement the alternative STC into soil policy, then soil legislative values will change. To derive these values it is necessary to have soil background values and risk levels. The RIVM used the alternative soil type correction to calculate new background values. The data used for risk levels must still be calculated.

Insight in uncertainties

To derive the alternative soil type correction, existing datasets were combined. As a consequence, extra uncertainties are introduced. During this research insight in these uncertainties is obtained by comparing the results with independent data.

Keywords:

soil, background concentration, soil type correction

Rapport in het kort

De bodemtypecorrectie: Een alternatieve benadering.

Het RIVM heeft een alternatieve methode ontwikkeld voor de zogenoemde bodemtypecorrectie voor metalen. De verschillende bodemtypen in Nederland bevatten van nature namelijk uiteenlopende concentraties van metalen (achtergrondwaarden). Met de bodemtypecorrectie wordt de algemene bodemnorm voor Nederland omgerekend naar de lokale situatie. De laatste jaren zijn veel nieuwe bodemdata en inzichten gepubliceerd die het mogelijk maken om deze methode, die is gebaseerd op onderzoek van twintig jaar geleden, te verbeteren. Met de nieuwe data presteert de alternatieve methode op hetzelfde niveau of beter dan de huidige bodemtypecorrectie voor achtergrondwaarden.

Fundamentele discussie nodig over bodemtypecorrectie

Voortvloeiend uit de herziene methode beveelt het RIVM aan om een fundamentele discussie te voeren waarvoor een bodemtypecorrectie voor bodemnormen wordt gebruikt. Deze werkt namelijk goed om de diversiteit in achtergrondwaarden te bepalen, maar niet voor verontreinigingen op het niveau van de interventiewaarde, de grens voor ernstige bodemverontreiniging. Hiervoor is een andere manier van corrigeren nodig om de verschillen tussen bodemtypes te kunnen beschrijven. De huidige formule in het Besluit Bodemkwaliteit beschrijft statistisch gezien deze verschillen niet correct.

Als er gekozen wordt om de alternatieve bodemtypecorrectie over te nemen in het bodembeleid, zullen de bodemnormen veranderen. Om de norm te kunnen bepalen zijn de achtergrondwaarden en de risiconiveaus voor mens en milieu nodig. Het RIVM heeft met de alternatieve bodemtypecorrectie de Nederlandse achtergrondwaarden opnieuw berekend. De data waarmee de risico's voor het ecosysteem zijn berekend, moeten nog worden herzien.

Onzekerheden inzichtelijk gemaakt

Voor de alternatieve bodemtypecorrectie zijn bestaande datasets gecombineerd. Hierdoor zijn extra onzekerheden geïntroduceerd. Deze onzekerheden zijn in het onderzoek inzichtelijk gemaakt door de uiteindelijke resultaten te vergelijken met onafhankelijke data.

Trefwoorden:

bodem, achtergrondconcentratie, bodemtypecorrectie

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Summary

In 2006 the first results of an inventory study of ambient soil concentrations in the rural, unpolluted, areas were published (Brus et al., 2009). The data from this study was used to derive 95-percentile values for soil concentrations in the Netherlands, which were used as basis for the current legal threshold levels for soil management in the Dutch Soil Quality Decree. For natural occurring substances, i.e. metals and metalloids, the spatial variability of their concentrations was normalised to a so called *standard soil*. This normalisation procedure is a standard procedure in Dutch soil legislation for many years and it is based on the so called *soil type correction* formula. This formula is based on a set of regression lines originating in the eighties of the last century. During the inventory study and the drafting of the new Dutch Soil Quality Decree, it became apparent that these formulas were in need of an update.

The update of the formula is a rather simple exercise compared with questions about how the formula, and the underlying model, should be implemented in soil management and how it can be used for setting soil quality criteria. While a new model and parameters for the formula can be created using current knowledge and data, the way the soil type correction is implemented, is a matter of science and political choice.

Aim

In this report the question around the feasibility of an alternative, updated, model and formula is addressed. The aim of this report is twofold: first to explain the basic principles behind the current soil type correction and show that the current formula, in a strict sense, is improperly implemented; and second, to provide an alternative formula for normalizing soil concentrations, which reflects current knowledge of Dutch soils and is based on recent and more representative data.

Results

The current implementation of the soil type correction (STC) in the Dutch Soil Quality Decree can be explained by dividing this implementation in four parts:

- 1) a statistical model;
- 2) a formula;
- 3) a background concentration; and
- 4) an added risk level.

Besides a needed update of model parameters, the application of these parameters in the current STC formula leads to two complications. First, legal threshold limits are a sum of the natural background concentration and the added risk level (like a Maximum Permissible Addition, MPA). The current STC also implicitly normalises the added risk level, however, this has no explicit purpose. Although it is often stated that the normalization of the added risk level is a correction for (bio)availability, the underlying model does not incorporate (bio)availability. Secondly, despite that the STC is used to normalise legal values for varying soil types, the current formula only describes soil variability in a proper way at the level of background concentrations. If used for a higher concentration, like a legal limit, the described variability does not reflect reality due to a numerical artefact. Therefore it is needed that besides the model parameters, the formula should be updated also.

As an improvement, an alternative STC is proposed using a robust linear regression model for the estimation of the (spatially varying) natural background concentrations using the clay fraction. A risk level, e.g. the MPA, is added, without normalisation, to this background concentration.

To generate the model parameters, an *engineering solution* was used. Practical usability and suitability prevailed over a proper scientific description of soil variability. For the model the clay size fraction was estimated from the Al_2O_3 concentration from the Dutch Geochemical Atlas using data from literature. The aqua regia based concentration was estimated using unpublished data from the Dutch Soil Monitoring Network containing samples measured with total and aqua regia techniques. From the data of the estimated clay size fraction and element concentrations an alternative model was derived using the same method as for the geochemical baseline models.

To validate the alternative model parameters with field data, the dataset of AW2000 was chosen (Brus et al., 2009). This dataset is the only dataset where the concentrations are determined using commercial aqua regia based methods. These methods are used in the current practice of soil management. When comparing predictions of the alternative model with observed values from AW2000, then for the elements As, Cr, Pb, V, and Zn, the prediction is fairly good ($r \geq 0.80$), for Be, Cu, and Ni the model performs moderate ($r > 0.60$). For Cd and Tl the prediction is poor. This is probably caused by the fact that concentrations for Cd and Tl are below the reported detection limit in the AW2000 dataset.

To see what the effects will be if the alternative model is used within the current STC formula, the data of AW2000 was used. From this data the 95-percentiles, used as threshold values in the current Soil Quality Decree, were recalculated. The 95-percentiles of the current model and the alternative model were compared and the changes are relevant, but within the reported confidence interval of the 95-percentile from AW2000, except for Ba, Mo, and Se. Although the (statistical) significance of implementing the alternative model parameters in the current formula seems limited, in practice the changing values for the 95-percentile, and subsequently the soil quality criteria based on these values, can have a far-reaching impact.

Important to note is that the above comparison between 95-percentiles is hampered. Both models, current and alternative are applied to the current STC formula to generate the 95-percentiles. These 95 percentiles are concentrations which are higher than the background concentrations, hence are sensitive to the aforementioned second problem considering numerical artefacts in the current STC formula. Therefore, the significance of this comparison is limited.

Conclusion

It is concluded that the alternative model parameters implemented in the same way as the current STC, is an improvement compared to the current model. The results indicate that the alternative model performs for all elements, except Ba, better or equal than the current model. For Co no data was available.

It is also shown that with the alternative model an improved formula can be implemented. In this formula a distinction is possible between background variability of soil concentrations and variability in (bio)availability. With such an improved formula a more realistic risk assessment is possible.

Recommendations

Before implementing an alternative soil type correction (STC), or when the one currently used is maintained, we recommend a broad discussion about the role of the STC. Because the current STC is intertwined in many parts of the derivation of legal soil quality criteria, the implementation, of an alternative STC must be part of a general revision of these criteria. Thus, if one decides to change the model of the STC, this also means that many other values in soil legislation will change. For example, the added risk levels, such as the MPA, are based on ecotoxicological test data. These ecotoxicological data are obtained from tests and the soil concentrations from these tests are normalised using the current STC. Only after the normalisation procedure they are submitted to a statistical evaluation, which obtains the risk limits (Spijker et al., 2012). A change in model parameters or formula of the STC also means *sensu stricto* that the toxicological data for each element should be re-calculated. Re-calculation of these data implies a change of risk assessment of trace metals for soils and sediments. This is beyond the scope of this study.

The alternative STC presented in this report is based on soil data from the rural area of the Netherlands and the alternative STC describes the variability of soil concentrations in this area. It is generally known that the variability of trace element concentrations with bulk geochemistry (like Al_2O_3) or clay is distinctively different in urban soils, compared to the rural area. And one can argue if it is even possible to describe this variability in urban soils with a simple formula like the current or alternative STC. The question remains if it is possible to apply a general STC model and formula on natural trace element variability in urban soils. Therefore the role of the STC, both current and alternative, in urban areas should be part of the aforementioned broad discussion.

This work is part of a large evaluation of the current (ecological) soil quality criteria in which such a discussion is pursued.

1 Introduction

In 2006 the first results of an inventory study of ambient soil concentrations in the rural, unpolluted, areas were published (Brus et al., 2009). This study gave an overview of the spatial distribution of concentrations for many compounds, including metals, metalloids, organic substances, PAH, and pesticides.

The data from this study was used to derive 95-percentile values for soil concentrations, which were used as basis for the current legal threshold levels of background concentrations for soil management in the Dutch Soil Quality Decree. For natural occurring substances, i.e. metals and metalloids, the spatial variability of their concentrations was normalised to a so called *standard soil*. This normalisation procedure is a standard procedure in Dutch soil legislation for many years and it is based on the so called *soil type correction* formula. This formula is based on a set of regression lines originating in the eighties of the last century. Although already known among soil scientists and experts, during the inventory study and the drafting of the new Dutch Soil Quality Decree, it became apparent that these formulas were required an update. Along with this knowledge, doubt arose if the formula needed to be used anyway.

The update of the formula is a rather simple exercise compared with the question whether the formula should still be used. While a new model and parameters for the formula can be created using current knowledge and data, the use of the soil type correction is a matter of science and political choice.

In this report the question around the feasibility of an alternative, updated, formula will be addressed. How, and where, this formula should be used within soil legislation is part of a far broader discussion, which is beyond the scope of this report. This work is part of a large evaluation of the current (ecological) soil quality criteria in which such discussion is pursued

1.1 Aim

The aim of this report is twofold: first to explain the basic principles behind the current soil type correction and show that the current formula, in a strict sense, is improperly implemented; and second, to provide an alternative formula for normalizing soil concentrations, which reflects current knowledge and is based on recent and more representative data.

1.2 Outline

In the first place this report gives an in depth technical discussion about the current use of the soil type correction and its role within deriving environmental quality criteria. Secondly, it provides the methodical basis for an alternative soil type correction using current available datasets.

The soil type correction is needed for the use of background concentrations in soil management. Secondly it is used within the so called *added risk approach*. This approach and the role of the soil type correction is discussed in chapter 2. The present-day use and drawbacks of the current soil type correction are discussed in chapter 3, including possible improvements. In chapter 4 it is demonstrated that the data from the Dutch Geochemical Atlas can be used to create an update of the soil type correction and that these data confirm the validity of the added risk approach discussed in chapter 3. Based on the

discussion in previous chapters, a method to obtain an alternative soil correction is presented in chapter 5. This alternative soil type correction, its validity, and its consequences when incorporated in current soil practice is demonstrated in chapter 6. This report ends with a conclusion (chapter 7) and some recommendations (chapter 8).

2 Purpose of the soil type correction

The current soil type correction (STC) was originally derived to obtain an estimate of natural background concentrations of metals and metalloids in soils. The estimation of this natural background concentration is not a fixed value but varies over geographical space, acknowledging the natural variability in soils. A variable natural background concentration is prerequisite for risk based soil management. If a fixed value is used, soils with high natural concentrations might exceed legal risk levels while for soils with low natural concentrations the risk level overestimates the actual risk.

The STC is a series of mathematical relations between the concentrations of elements of interest (such as Pb, Zn, Cr, Cd) with the clay size fraction ($<2 \mu\text{m}$, lutum, in wt-%, weight percentage) and the organic matter content (in wt-%). The current relations are derived about 25 years ago and are based on soil concentrations in 'relatively clean areas' (Crommentuin et al., 2000).

In the following sections we will explain 1) why the natural background concentration is of importance for risk assessment of concentrations of metals and metalloids and 2) why this natural background concentration is a geographically variable value.

2.1 Added risk approach

Distinguishing between natural and anthropogenically enhanced levels of chemical elements is a necessity for the proper execution of the Dutch environmental legislation. This legislation is based on the stand still principle of (background) concentrations and the so-called *added risk approach*. This principle and the added risk approach are used for setting risk limits for chemical soil quality (Struijs et al., 1997). In the added risk approach only risks resulting from anthropogenic addition are considered, the natural concentration does by definition not add to the perceived risk, the local ecosystem is considered to be adapted to the local circumstances.

The separation of the metal concentration in a soil sample is illustrated in Figure 2.1. This figure also shows these concentrations (natural, C_b and anthropogenic, C_a) can differ in availability (inactive and active part). The concentrations can be split into two fractions, an available fraction (φ and γ) and a non-available fraction ($1-\varphi$, $1-\gamma$). Within the added risk approach it is assumed that only the available anthropogenic concentrations result in negative effects on soil organisms.

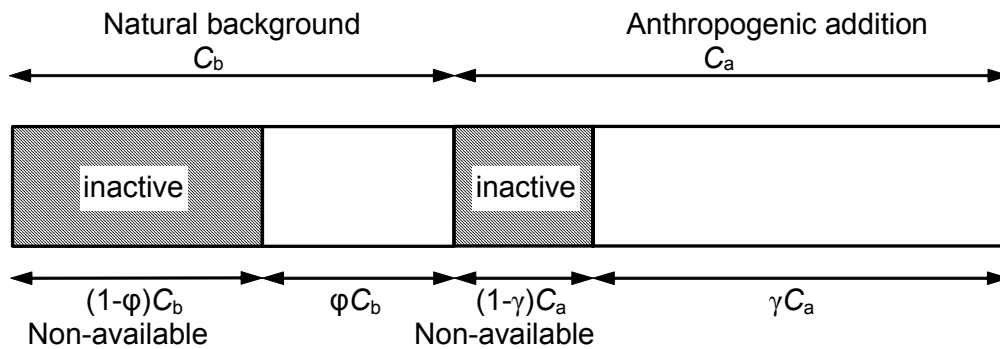


Figure 2.1: Illustration of differences in availability between natural background and anthropogenic concentrations (figure from Struijs et al., 1997).

Figure 2.1 is a simplification of reality. For example the aspects of aging, sometimes resulting in lower availability, are not taken into account. Also, the aspect weathering, resulting in higher availability, is also neglected. By definition, the toxic effects of the natural background concentrations are not considered a risk.

Struijs et al. (1997) further simplified Figure 2.1 by assuming that the available fraction in the natural background concentration is zero (i.e. $\phi=0$) and that the anthropogenic addition is fully available (i.e. $\gamma=1$). These simplifications can be regarded as a worst case approach towards the availability of the anthropogenic addition. Figure 2.2 depicts how the added risk approach is used during the derivation of soil quality criteria. The added concentration (C_a) is now assumed to be fully available. From toxicity experiments a Maximum Permissible Addition (MPA) for metals is derived. This is a criterion where no adverse effects are to be expected. The environmental risk limit is the sum of the MPA and the natural background concentration (C_b).

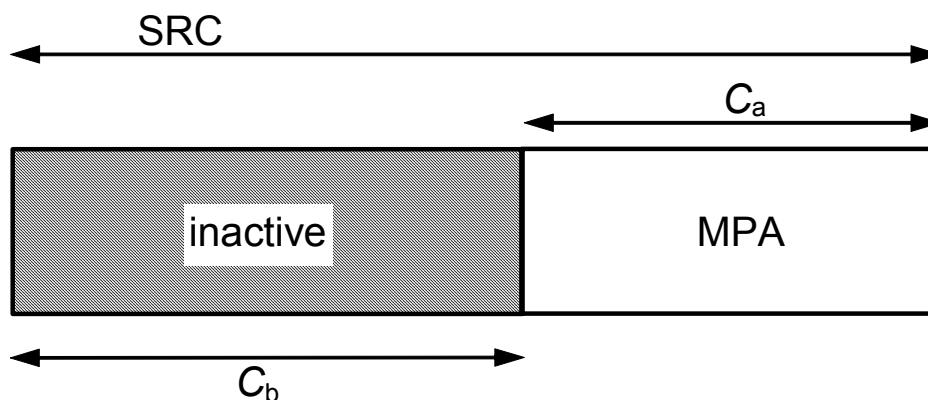


Figure 2.2: Illustration of differences in presumed availability used in the added risk approach.

2.2 Natural background concentration

The natural background concentration varies for the different soil types occurring in the Netherlands. In general Dutch soils comprise four major lithologies: sand, peat, marine and fluvial clays. These lithologies are depicted in Figure 2.3.

X-Ray Fluorescence Al₂O₃ top soil

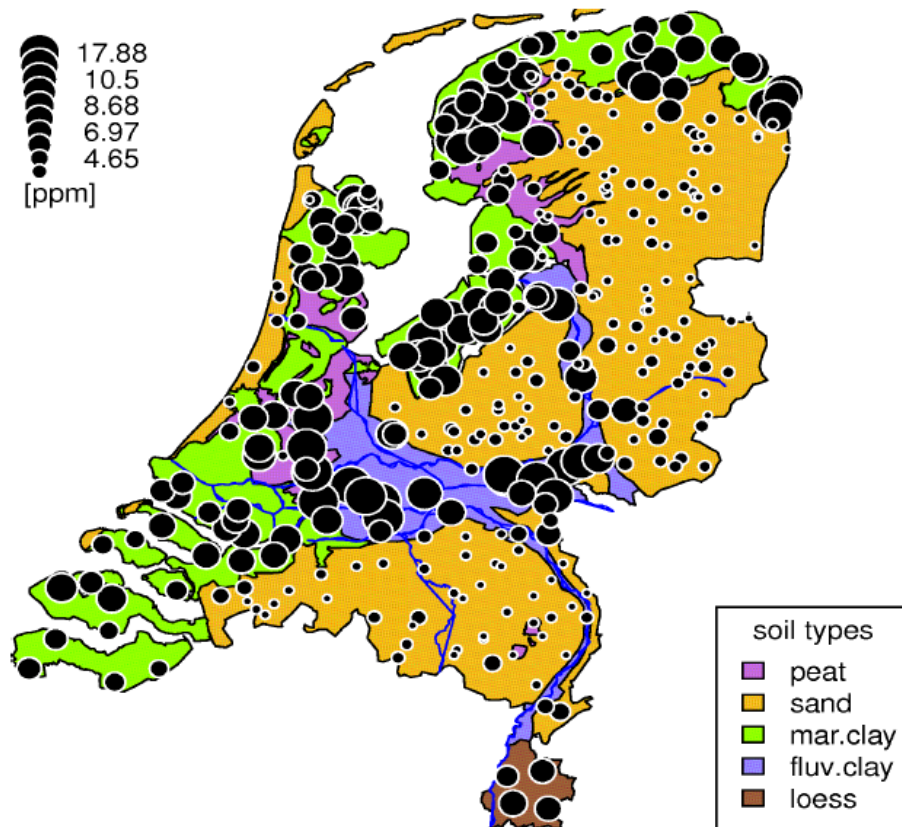


Figure 2.3: Map showing the spatial distribution of Al₂O₃ in the Netherlands in relation with the four major soil lithologies and loess.

These lithologies differ both in mineralogy and structural characteristics. For the Netherlands the variability in soils is for the largest part explained by the variability in clay content. Figure 2.3 also shows the spatial variance of clay content, expressed as weight percent Al₂O₃. The similarity with the soil lithology map is apparent, sandy areas with low Al₂O₃ concentrations can be easily discerned from clay areas with high Al₂O₃. Spijker (2005) and Van Helvoort (2003) showed that there is a good relation between the clay size fraction ('lutum') and Al₂O₃.

Concentrations of natural occurring metals and metalloids vary with this mineralogy and these characteristics of soils, as can be seen in Figures 2.4 and 2.5. Here the spatial variability of Cr is shown (Figure 2.4) and the variability of Cr with Al₂O₃ (Figure 2.5).

The original STC was thus derived as a regression model using the clay fraction and organic matter as predictors of the natural background concentration. These two parameters were regarded representative for the soil lithology and variability within the lithology for the area of the Netherlands (de Bruijn et al., 1992).

With the spatial variable STC it was possible to generate an estimate of the background concentration for a sample from a specific geographical location.

X-Ray Fluorescence Cr top soil

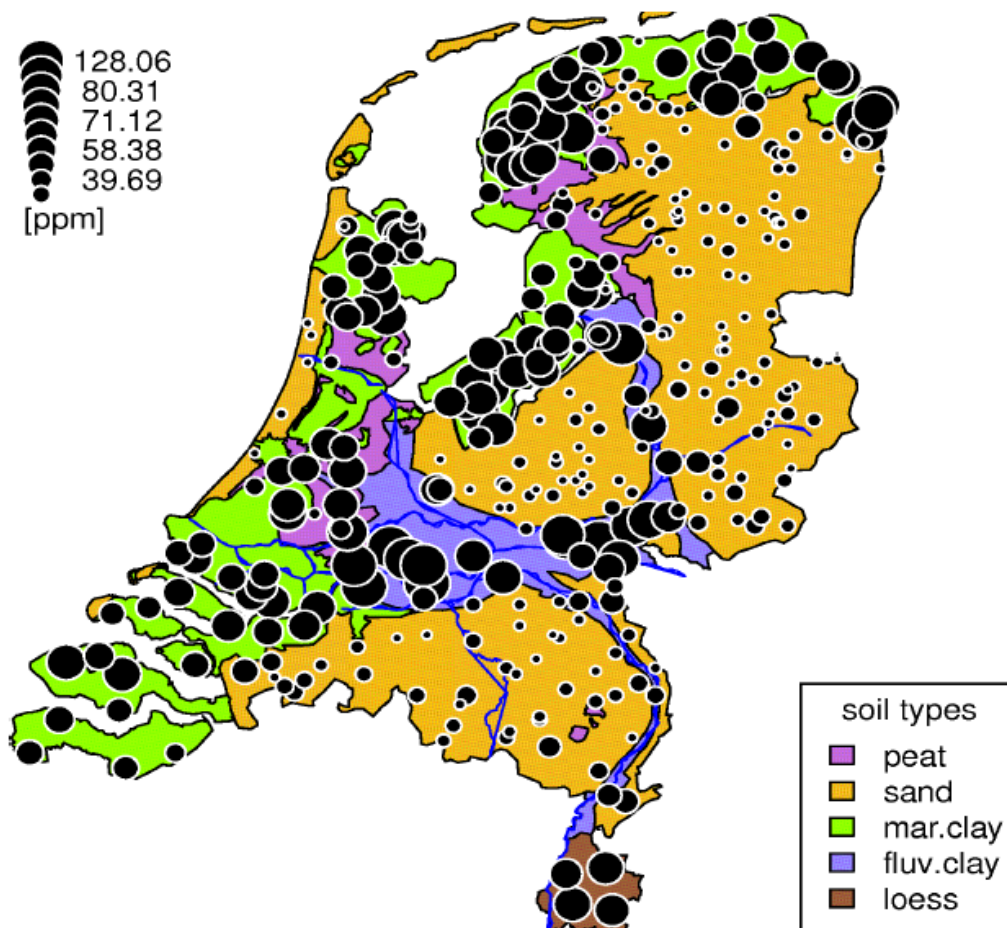


Figure 2.4: Map showing the spatial distribution of Cr in the Netherlands in relation with the four major soil lithologies and loess.

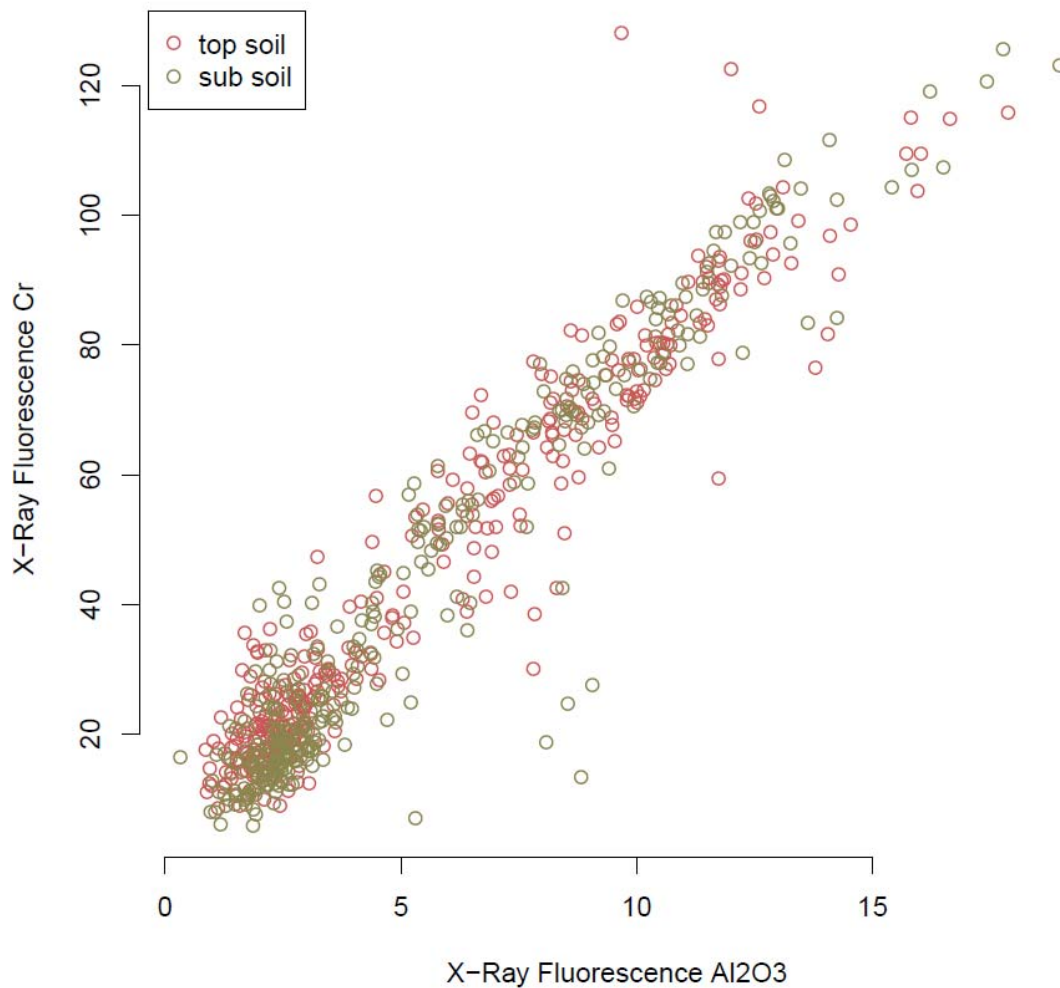


Figure 2.5: Scatterplot of the top- and sub soil concentration of Al_2O_3 [wt-%] against total concentration of Cr [mg/kg].

3 Current problem and possible improvements

As mentioned in chapter 2 the background concentrations are playing a vital role in the Dutch soil legislation. However these data were derived from small areas in the Netherlands, in general sandy soils, using non-current analytical methodology (Edelman, 1984). In the year 2000 the Ministry of Environment commissioned an update of these data. Now, the prevailing Dutch legislation on soil pollution is based on normative or reference values that are taken from an inventory study, the so called AW2000 study, in which the concentrations of many substances including organic compounds and inorganic elements were determined (Brus et al., 2009). The sampling area consisted of the natural and agricultural areas on the four major soil groups (sand, peat, marine- and fluviatile clay). The resulting background concentrations are actually ambient concentrations as they include diffuse anthropogenic pollution. (For more details on this inventory see Brus et al. (2009)). Despite the update of the data, the current STC is still the same and based on the former inventory from the nineties of last century (Van den Hoop, 1995, Crommentuijn et al., 2000).

Legally, soils are considered clean when measured concentrations do not exceed the legal threshold values based on the AW2000 inventory study. Although this approach is apparently effective for addressing legal issues, it does not necessarily reflect reality. Particularly not because the threshold values that have been determined are based on the 95-percentiles of the distributions found in the inventory study. To calculate these 95-percentiles the sample were statistically weighted based on the spatial surface area of the sample stratum (See Brus et al., 2009). The 95-percentiles guarantee that the reference values will not be exceeded very often (on average in 5% of the cases), but, foremost, it means that these values for many soils are (much) higher than the *natural* background values which will lead to data-artefacts when the original STC is used. These artefacts are demonstrated in the next section.

3.1 Current Soil Type Correction and risk

The STC normalizes soil concentrations to a concentration in so called 'standard soil'. This standard soil is arbitrarily defined as a soil with a clay fraction (lutum) of 25 wt-% and 10 wt-% organic matter, although soil with these characteristics can only be expected in a very small area in the Netherlands. Soil concentrations are expressed as concentrations in this standard soil. Both concentrations as measured in field samples and soil concentrations used during the derivation of soil quality criteria are expressed as a concentration in standard soil. When soil quality criteria are derived from toxicity experiments, the concentrations in these experiments are also recalculated as a concentration in standard soil.

Figure 3.1 shows the hypothetical effect of the current STC. The bars indicate the concentration in soil with a specific clay size fraction, for the sake of simplicity the variation of the fraction of organic matter is neglected in this example. This soil concentration is the sum of the natural background concentration and an added part, either being a Maximum Permissible Addition, conform the legal soil limits, or enrichment in the field sample due to human activity. This represents the added risk approach as depicted in Figure 2.2. Two soil concentrations are depicted, one in the so called standard soil with a clay

Current situation

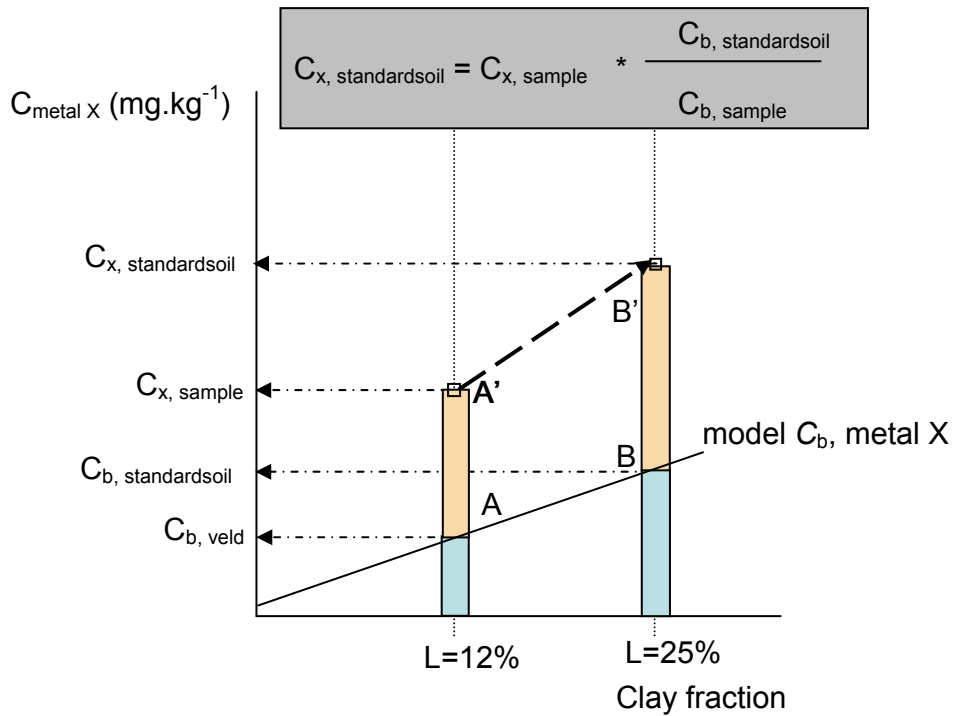


Figure 3.1: Current situation as used in the derivation of the environmental quality criteria. Bars indicate hypothetical soil concentration in standard soil (right) and an arbitrarily chosen soil (left), the blue part of the bars indicate the natural background concentration, orange is the added part. Lines indicate the current STC model without variability in organic matter (see equation 3.1).

size fraction of 25 wt-% and another in an arbitrarily chosen soil with a clay size fraction of 12 wt-%.

The line AB depicts the model which estimates the natural background concentration, following the equation (Van den Hoop, 1995):

$$(3.1) \quad C_b = \beta_0 + \beta_1 L + \beta_2 O + \varepsilon$$

In which C_b is the natural background concentration, L is the clay size fraction in wt-% (lutum) and O is the organic matter fraction in wt-%. The regression parameters of this bivariate regression are given as $\beta_{0,1,2}$ with β_0 as intercept. The ε is the regression error.

The final regression line used in the current STC is adjusted, by increasing the intercept, until 90% of the observed values were below the line. The rationale of this step is that the line now presents the upper limit of the variation of the background concentration.

Table 3.1: Model parameters (see eq. 3,2) and $C_{b,s}$ for the current soil type correction.

Element	β_0	β_1	β_2	$C_{b,s}$
As	14	0.4	0.4	29
Ba	30	5	0	160
Be	8	0.9	0	31
Cd	0.4	0.007	0.021	0.8
Cr	50	2	0	100
Co	2	0.28	0	9
Cu	15	0.6	0.6	36
Hg	0.2	0.0034	0.0017	0.3
Pb	50	1	0	85
Ni	10	1	0	35
Sn	4	0.6	0	19
V	12	1.2	0	42
Zn	50	3	1.5	140

The background value for standard soil ($C_{b,s}$) with 25 wt-% clay and 10 wt-% organic matter is thus given as

$$(3.2) \quad C_{b,s} = \beta_0 + 25\beta_1 + 10\beta_2$$

Where $C_{b,s}$ is the background concentration in standard soil. Model parameters for equation 3.2 are given in Table 3.1.

Normative values, e.g. from the Dutch Soil Quality Decree (VROM, 2007), are expressed as concentrations in standard soil (i.e. 25 wt-% clay and 10wt-% organic matter). To assess if soil concentrations measured in the field comply to a normative value, either the normative value should be expressed as a soil type specific value (i.e. left bar in Figure 3.1) or the measured soil concentration should be expressed as concentration in standard soil (i.e. right bar in Figure 3.1). By decree the formula to relate standard soil concentrations with soil type specific concentrations is (Anonymous, 2007):

$$(3.3) \quad C = C_{b,s} \cdot \frac{\beta_0 + \beta_1 L + \beta_2 O}{\beta_0 + 25\beta_1 + 10\beta_2}$$

Where $C_{b,s}$ is the concentration in standard soil and C the concentration in a specific soil, L and O are the clay and organic matter fractions for this specific soil.

Looking at Figure 3.1, the line A'B' depicts the correction of a legislative value (B') in standard soil into a soil type specific value (A'). It is immediately clear that the slope of the line differs from the slope of the model, i.e. line AB. Despite the use of the added risk approach, the current use of the STC does not only result in correction for the background concentration, but also the added part is implicitly corrected. This can be numerically demonstrated: let us assume that the organic matter content in the specific soil is 10 wt-%, with this choice we neglect the variability in organic matter; then let $10\beta_2 + \beta_0 = k$, thus:

$$(3.4) \quad C = C_{b,s} \cdot \frac{\beta_1 L + k}{25L + k}$$

Which can be rewritten as:

$$(3.5) \quad C = L \cdot \frac{\beta_1 C_{b,s}}{25\beta_1 + k} + \frac{kC_{b,s}}{25\beta_1 + k}$$

Equation (3.5) can be regarded as a linear function in the form $y=ax+b$, with x as the independent variable and a and b respectively the slope and intercept of the line described by this function. This line is depicted in Figure 3.1 as line $A'B'$ and it is clear that both slope and intercept depend on the choice of $C_{b,s}$, hence each normative value has its own line $A'B'$ with a slope and intercept different from AB .

The implication is as follows: the line AB and equation (3.1) depict the variability of a natural background concentration in a geographical area, or for differences in lithology, which spatially varies. It is this variability for which the STC is used and the relation underlying the STC is derived as a regression model based on field data. However, from equation (3.3) to (3.5), it is clear that the current STC formula describes a model ($A'B'$) with a different slope and intercept than equation (3.1), hence a model which is not representative for the observed variation in the field. This defies the original purpose of the STC.

So, if a soil quality criterion, a normative value, is recalculated from a standard soil into a concentration for the specific soil, then both background concentration (C_b) and the MPA are normalized. The implicit normalization of the MPA has no explicit purpose. It will be shown in section 4.3 that the anthropogenic addition is independent of soil variability, so there is no need to correct the MPA for background variability.

Sometimes it is stated that the correction of the MPA can be considered as a implicit correction for bioavailability, but this is not proper reasoning since the underlying model, equation (3.3), does not include bioavailability. Even more, the underlying model for the background concentrations (see Figure 2.2) assumes no adverse concentration by definition.

In summary, the STC formula from equation (3.3) only reflects reality when the natural background concentration is used. Any other value for $C_{s,b}$ leads to a numerical artefact, and as a result the explained variability does not reflect reality. For these other values of $C_{s,b}$, the formula can be improved.

3.2 Improvements

To understand the improvements, one must understand the building blocks of the use of a soil type correction within soil management and their function in the creation of soil quality guidelines.

Table 3.2 shows the different parts, the building blocks, of the soil type correction. There are four parts:

1. The *model* is the statistical model, which describes the soil variability and gives the parameters (β_x) for the soil type correction formula.
2. The *formula* is the equation to normalise the soil concentration using the model parameters.

3. In the added risk approach the background concentration and the added concentration are needed. The *background concentration* (C_b) is the third part. This background concentration can be derived by normalising field data using the STC formula or it can be calculated directly from the model and STC formula.
4. The *added risk* can be normalised using the STC formula. But it is also possible to use actual data from literature, without normalisation.

Table 3.2 contains options for each part. The options of the current STC are given and explained in section 3.1. In this section an alternative is proposed and its options are also given.

Figure 3.2 graphically represents the alternative from Table 3.2. In this scenario only the background concentration (C_b , blue) is normalised. The MPA is kept constant. This reflects the option that the background concentration varies while the risk associated with the added concentration will not vary. This risk is regarded independent of soil type. This alternative neglects variability in availability as the concentration of many elements is only partial available for certain (bio)chemical reactions in soils. These partial concentrations include so called bio-available or potential (chemical) available concentrations

Table 3.2: The four parts for a soil type correction. For both the current STC and the proposed alternative STC the content of each part is given. For further explanation, see text.

Part	Current	Alternative
1 Model	Linear regression model, based on lutum and organic matter	Robust linear regression model, based on lutum
2 STC formula	Ratio, eq. 3.3	Linear, eq. 3.6
3 Background concentration	Fielddata, normalised 95-percentile using above part 1 and 2	Fielddata, using above part 1 and 2
4 Added risk	Literature data, normalised using above part 1 and 2	Actual (non-normalised) data

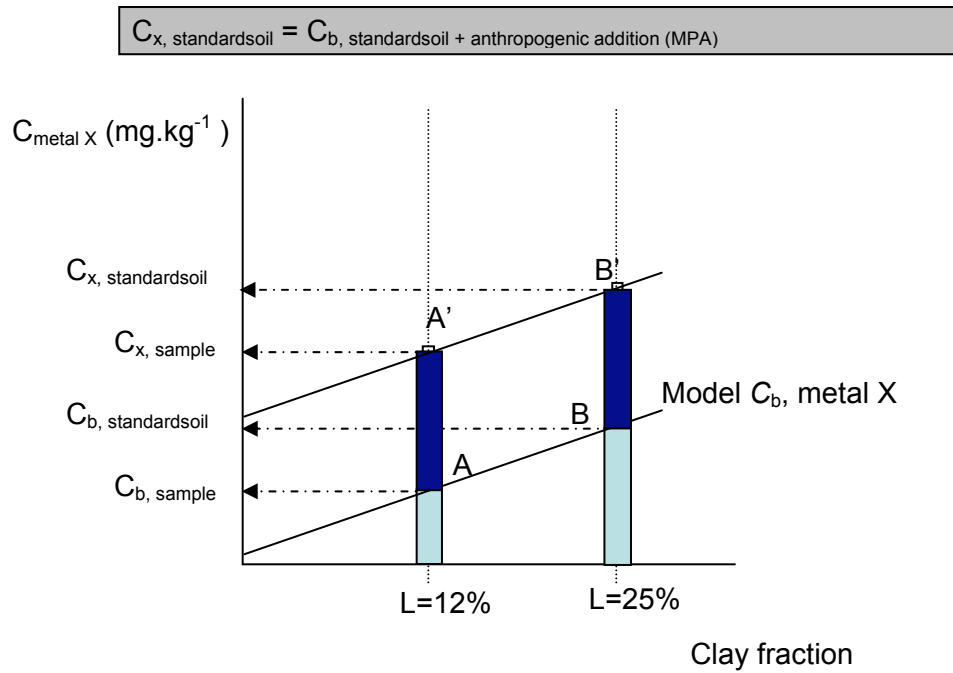


Figure 3.2: scenario were only a correction is applied on the natural background variation.

From Figure 3.2 it is clear that a model for the variability in the background concentration is needed, like the current model as described in equation (3.1). Only the intercept of line A'B' changes with changing the value for the MPA, in formula:

$$(3.6) C = \beta_0 + \beta_1 L + C_a$$

Where L is the clay size fraction, C_a is the added concentration (see Figure 2.2) and $\beta_{0,1}$ are respectively the intercept and the slope. This formula reflects the situation depicted in Figure 3.2, where $\beta_0 + C_a$ form the intercept of line A'B'.

In the next chapters of this report the model parameters for the model in equation 3.6 will be derived and discussed. Using equation 3.6 as soil type correction formula for the background concentration, together with the derived parameters, it provides the data for the options in part 1 to 3 of the alternative STC in Table 3.2.

4 Geochemical baseline model for Dutch soils

In the previous chapter it was explained that the soil type correction (STC) is based on a model which predicts (natural) background concentrations in soil. This model was derived about 20 years ago. More recently, the Geochemical Atlas of the Netherlands was published (Mol et al., 2012) and based on the original work of Van der Veer (2006). This is a study into the geochemical composition of Dutch soils. One of the objectives of the study was to reduce variability as a result of sampling and analytical procedures. With this reduction subtle patterns in the geochemical composition of Dutch soils can be discerned, like spatial variability of natural trace element concentrations with the major soil composition.

While the first edition of the Geochemical Atlas aimed at presenting total concentrations (Van der Veer, 2006), as measured by X-ray Fluorescence (XRF) and HF-digested soil samples analysed with Inductive Coupled Plasma-Mass Spectrometry (ICP-MS), the latest edition also contained reactive concentrations (0.43 M HNO₃ extracted soil samples analysed with ICP-MS and ICP-OES, Optical Emission Spectrometry) and available concentrations based on 0.01 M CaCl₂ extractions of the soil samples. This means that the dataset of the Geochemical Atlas provides a nation wide overview of total, reactive and exchangeable concentrations of major and trace elements which gives information about soil composition, soil reactivity and (bio)availability. By using this dataset, the derived models can be related to other soil processes than soil composition alone. For example relations with soil leaching or risks for the ecosystem.

From the data of the Geochemical Atlas a relation between soil composition and trace element concentrations is derived. This relation, a geochemical baseline model, was developed to estimate the natural background concentration in a diffusely polluted soil (Spijker et al., 2012). This model is applicable for the whole area of the Netherlands. Since the natural background concentration is the basis of the normalization of soil concentrations (like the STC) and because the baseline model describes the spatial variability of the natural background concentration, it was chosen to use this model as an alternative for the STC. In the next sections we will explain some details about this geochemical baseline model and how this model can be used to 1) obtain the natural concentrations as needed for the scenario in Figure 3.2 and 2) to confirm the added risk approach mentioned in chapter 2.

4.1 Aim of the baseline model

The aim of the baseline model is to describe the natural variability between the bulk geochemistry and trace elements in a simple statistical manner. Like the relations currently used in the STC. However, the model is not based on clay size fraction but on Al₂O₃. Some authors already pointed out that there is a close relation between trace elements and this bulk geochemistry. Spijker (2005) and Van Gaans et al. (2007) have shown that for the marine clayey soils in the South-West of the Netherlands a strong relation exists between trace element geochemistry and Al₂O₃ as measured by XRF. Spijker (2005) used a relation where the trace element content was expressed as function of Al₂O₃, using an ordinary least square linear regression model. Van der Veer (2006) showed that the same method of regression as used by Spijker (2005) applies to all major

soil types in the Netherlands. It is therefore that Al_2O_3 was chosen as predicting variable for the baseline model.

Organic matter is not part of the model. Van der Veer (2006) showed that organic matter content is partly related to mineral organoclay aggregates in soil. This means that a part of the variability of trace elements with organic matter is explained by the variability in clay content, which is covered by the variability in Al_2O_3 . Spijker et al. (2008, 2012) showed that adding organic matter as variable to the baseline model does not improve the estimation of the natural background concentration, hence organic matter was excluded from the model.

4.2 Regression model

The baseline model is, like the STC, a regression model using Al_2O_3 as predicting variable. This regression model is described in Spijker et al., (2012). It is a robust regression model using the Least Quantiles of Squares (LQS) algorithm (Leroy and Rousseeuw, 1986) Based on the results of Spijker (2005) and Van der Veer (2006), the following linear model was used for the LQS regression:

$$(4.1) \quad C = \beta_0 + \beta_1 C_{Al} + \varepsilon$$

Where C is the estimated total trace element concentration, using C_{Al} expressed as Al_2O_3 in wt-%. The regression parameters $\beta_{0,1}$ are calculated using the LQS method mentioned above. The regression error ε gives the deviation of the residuals, which represents the variation not explained by the variability in Al content.

According to Leroy and Rousseeuw (1986) the linear interval of 2.5ε compares to the range of the normal distributed residuals. Since the LQS method does not assume normality of the data, no values determining significance of the regression are derived.

Spijker et al. (2012) showed that the baseline model gives a good prediction of the variability in natural background concentrations. These baseline models were created for As, Ba, Be, Cd, Cr, Cu, Pb, V, Zn, Ni, Sb, Sn and are shown in Figure 4.1. From this figure the good prediction of the baselines is clear. For each distinct soil lithology in the Netherlands (peat, sand, fluvial clays, and marine clays) a model was created and also a generic model for all soil types together. This generic model, the lines depicted in Figure 4.1, complies to the wish for a simple model to describe the Dutch soil geochemistry, and can be used as an alternative normalization procedure. From Figure 4.1 it is apparent that this generic model describes the soil variability very well, with Ba being an exception.

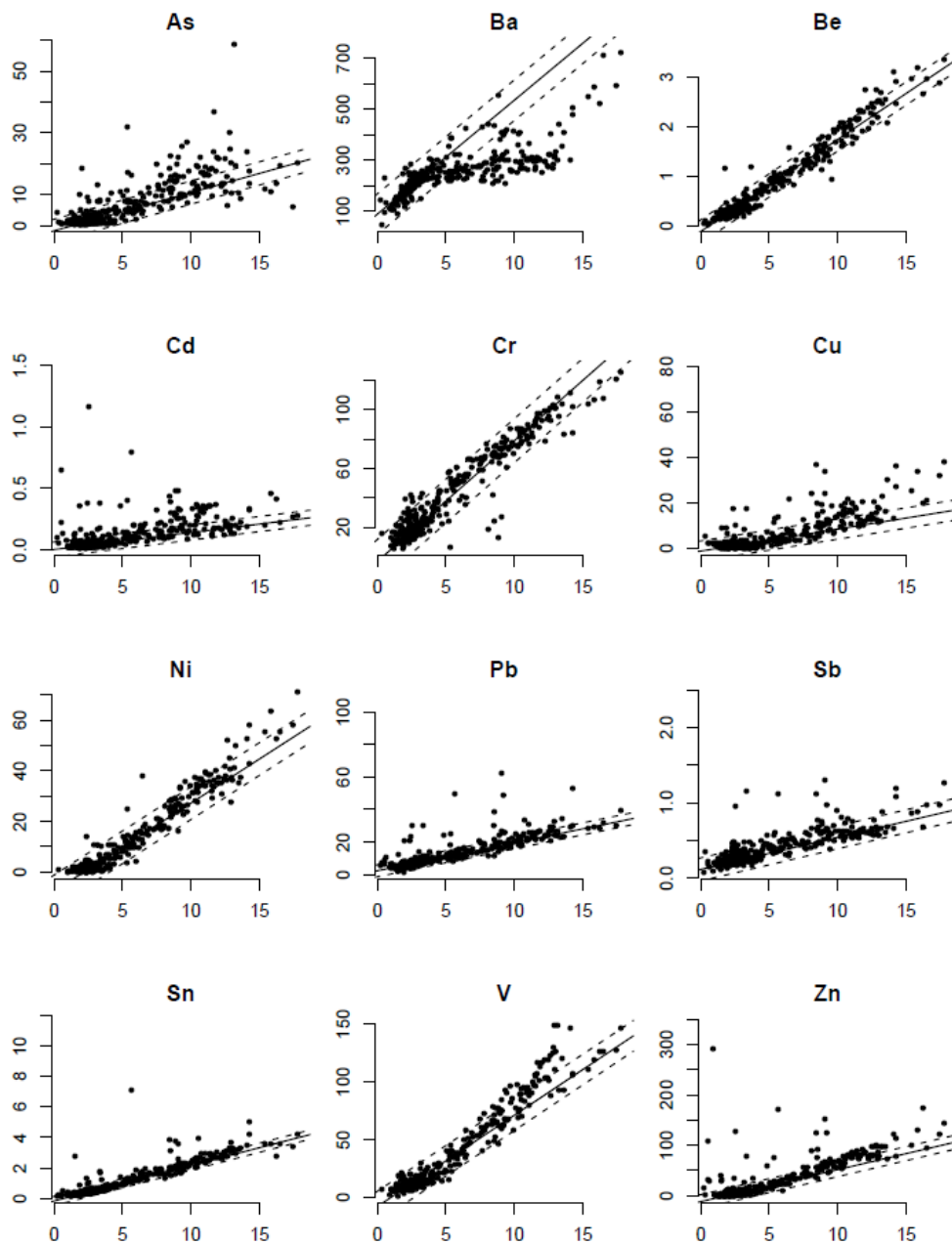


Figure 4.1: plots of each element (y-axis) against Al_2O_3 (x-axis). Element concentrations are in mg/kg, Al_2O_3 concentrations is in wt-%. The black dots are sub soil concentrations. The lines denote the generic regression model, solid line is the LQS regression line, dashed lines are the regression error (2.5ϵ). From Spijker et al., 2012

From the study of Spijker et al. (2012) it was apparent that the covariability of trace elements with Al_2O_3 in sandy soils (i.e. soils with low Al_2O_3) was far less than the covariability in clayey and peaty soils (see Figure 4.1). Although the generic baseline model described the overall variation very well, if one is interested in trace element concentrations in sandy soils, a sandy soil specific baseline model seems more appropriate. Geochemical baseline models for specific soil lithologies (e.g. sand, peat and clay) are available from Spijker et al.

(2012) but deriving a lithology specific STC model is beyond the scope of this study.

4.3 Confirmation of added risk approach

Using these baseline models the estimated concentration can be compared with the actual measured concentration; this gives the enrichment of elements compared to the baseline. Based on the ratio between estimated baseline concentrations and enrichment, the elements Cd, Pb, Sb, Zn and Cu are in general considered as enriched.

Figure 4.2 gives four examples of the baseline models of Cd, Cu, Pb and Zn (Spijker et al., 2011.). In the left part of the figure it can be seen that the top soil concentrations (black circles) are enriched compared to the sub soil concentrations (green crosses). Considering that the baseline model gives the natural background concentration, C_b within the added risk approach (see Figure 2.2), the enrichment then compares with the soil concentrations associated with risk. An assumption in the added risk approach is that this added fraction, the enrichment, is fully reactive while the background is inert. In the right part of Figure 4.2 the relation between reactivity (i.e. potential availability) and enrichment is depicted. The 1:1 line is shown for comparison. From the figure it is apparent that the reactivity of these four metals is indeed comparable with the enrichment. This agrees with the assumption behind the added risk approach, see Figure 2.2. Hence, the principles behind the baseline model are suitable to predict the C_b .

Remarkably, organic matter is not part of the geochemical baseline model. As Spijker et al. (2008) and Spijker et al. (2012) explained, organic matter has limited value in the prediction of background concentrations. Adding organic matter to the model does not improve the prediction compared with a model without organic matter as variable.

Unfortunately the model of Spijker et al. (2012) is based on a relation of Al_2O_3 and total metal content, while the soil type correction and normative values are based on a regression model based on clay fraction, organic matter and concentrations based on aqua regia digestions. Therefore, it can not directly be applied as replacement of the soil type correction, despite the fact that it is very suitable, see Mol and Spijker (2009) for a more detailed explanation. In the next chapters we will show how the model can be adapted so it can be used as an alternative for the STC.

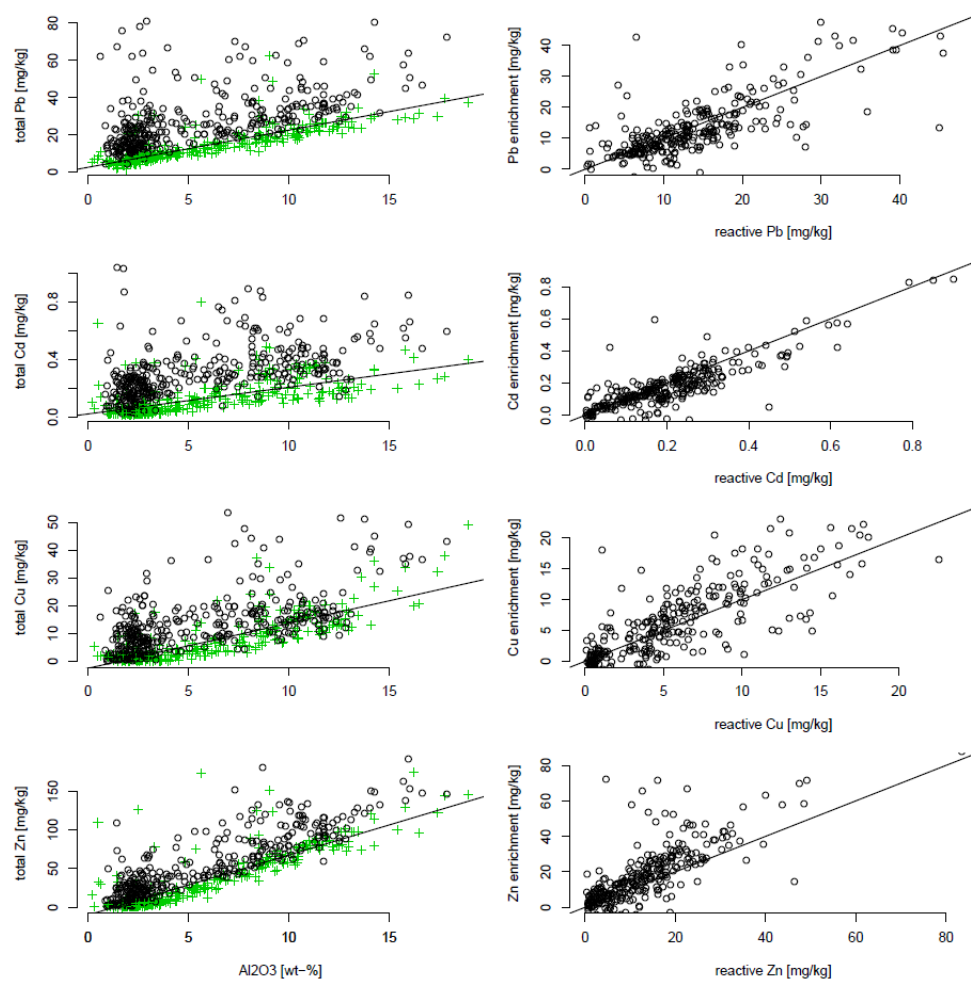


Figure 4.2: (Left) Scatter plots depicting the way in which metal enrichments in the topsoil are estimated with a geochemical baseline model; green crosses subsoil sample metal concentrations; lines Al₂O₃ baseline models; black circles topsoil sample metal concentrations. (Right) Linear relationships between reactive metal concentrations (0.43 M HNO₃ extractable metal concentrations) and enrichments (topsoil concentrations minus baseline-estimate concentrations). The line depicts the 1:1 relation. From Spijker et al. (2011).

5 Method for an alternative model for background concentrations.

One of the aims of this study is to obtain a practical and uncomplicated method to predict the C_b of a field sample. This C_b is the basis of the Added Risk Approach, discussed in chapter 2. The results presented in chapter 4, based on Spijker et al. (2012), indicate that it is indeed possible to get an estimate of the natural background.

An alternative method should be based on variables and measurements that are currently used in the field of soil management and sanitation, like the digestion of soil samples with aqua regia. Although there are state of the art techniques, like the geochemical baseline model of chapter 4, they are not widely used due to reasons related to laboratory infrastructure, safe working conditions, and costs. The alternative method or model should be simple and easy to apply to soil concentrations as well. This means for example that the method preferably should be relevant to the whole area of the Netherlands, instead of having several methods for different areas or lithologies.

With the geochemical baseline model it is possible to predict the background concentration of a field sample, likewise the current STC. However, this geochemical baseline model is based on variables not used in common practice, i.e. total metal content and Al_2O_3 . There are similarities though: the Al_2O_3 content is related to the clay content while the total metal content is related to the aqua regia digested concentrations used within the current practice.

Considering that 1) the geochemical baseline model is based on the total area of the Netherlands, 2) the sampling and analytical variance provide sufficient accuracy to describe the relations between major and trace elements, 3) the data can be related to not only composition but also to soil processes, and 4) the data is publicly available through the Dutch Geochemical Atlas, it was chosen to use this dataset for the alternative STC.

From literature and unpublished data it is possible to derive regression models of the relations between clay fraction and Al_2O_3 . Also models can be derived for the relation of total metal content and aqua regia digested concentrations. By combining these models a model which relates clay content to trace element variability can be created. However, this means that by combining different regression models, the variability of some variables is explained solely based on these models rather than on data. From a statistical point of view this is questionable, but from a pragmatic viewpoint it is sensible to base the new method on existing data and models. By combining these existing data and models one must be aware of the consequences. The resulting model should only be used, if used at all, as an *engineering solution* that just fits the current problem, and not as a scientific model to explain variability and significance. The resulting model will be validated against a fully independent dataset to see if it proper fits its purpose or that it results in a biased assessment.

This chapter shows the methodology behind an alternative STC model. This method is applied to the data of the Dutch Geochemical Atlas and the results are given in chapter 6.

5.1 Approach for using data from the Geochemical Atlas

As explained above, to derive a STC model from the geochemical baseline model, based on data from the Geochemical Atlas, three steps are necessary:

1. Create a model to express Al_2O_3 as clay fraction (i.e. lutum).
2. Create a model to express total concentrations as concentrations based on aqua regia.
3. Combine both models to create a model in which the background concentration is expressed as function of clay fraction.

After creating the final model, the model should be validated to see if the model does explain the natural variability of trace element concentrations in a satisfying way. In the next sections these steps will be discussed.

5.2 Relation between Al_2O_3 and lutum

Clay size fraction in the Netherlands is measured as 'lutum', the clay fraction with grain size $<2 \mu\text{m}$. Two methods are currently in use, one is the pipette method, the other is based on laser diffraction. Both methods are described in Buurman et al. (2001). Buurman et al. (2001) have noted that the methods are not comparable. Although measurements of the clay fraction in both methods are highly correlated ($R^2 > 0.95$), the absolute clay fractions differ by a factor up to 2. Both methods are also dependent on the exact laboratory procedure. To our knowledge there is no good dataset available, which relates lutum with Al_2O_3 . For this study the data of Edelman (1984) and the National Soil Monitoring Network were available and contained both total Al concentrations and clay size fractions. However, they did not contain sufficient information about the method used for measuring lutum. Therefore the relation between Al_2O_3 and clay size fraction in these datasets were hard to interpret. As a result, it was chosen to select a relation of Al_2O_3 and clay size fraction from literature. In Spijker (2005) a relation is described between Al_2O_3 and clay size using the same method for Al_2O_3 as the Geochemical Atlas and a method applied in commercial laboratory, using pipettes, for the clay size fraction. The latter method reflects the common method as used in Dutch practice. This relation is given as:

$$(5.1) \text{Clay} = 4.76 \text{Al}_2\text{O}_3 - 15.47$$

Equation (5.1) does not apply for sandy soils, which contain approximate 2 to 3 wt% Al_2O_3 (Mol et al., 2012). Using equation (5.1) the Al_2O_3 concentrations for other soils are expressed as wt-% clay (see section 6.1).

5.3 Relation between total concentration and aqua regia

Common practice requires that soil concentrations of metals and metalloids within the frame work of the Dutch Soil Quality Decree are expressed as concentration after an aqua regia extraction, an extraction with a hot mixture of three parts hydrochloric acid and one part concentrated nitric acid. With this extraction only partial concentrations are obtained. The data of the Geochemical Atlas was analysed using so called total methods, either using X-Ray fluorescence or digestion in a hydrofluoric acid mixture. These latter concentrations are generally higher than the aqua regia extracted concentrations. Hence, for the alternative STC the total concentrations of the atlas should be expressed as concentrations measured by aqua regia extractions.

We selected unpublished data from the Dutch Soil Monitoring Network in which samples of Dutch soil were analysed using both total and aqua regia methods. The total method uses the same analytical procedure as for the data from the Geochemical Atlas. The aqua regia method is an in house method of the laboratory of the Dutch Geological Survey/TNO, comparable with commercial methods.

For each element, a robust LQS regression model was created where the aqua regia concentration (C_{ar}) was expressed as function of the total concentration (C_t), according to:

$$(5.2) \quad C_{ar} = \beta_0 + \beta_1 C_t + \varepsilon$$

In equation (5.2) $\beta_{0,1}$ are respectively the intercept and slope of the regression and ε is the regression error. The statistical method, the LQS regression, was the same as for the geochemical baseline (see chapter 4).

Using the model in equation (5.2) the total concentrations of the Geochemical Atlas are expressed as aqua regia concentrations (see chapter 6.2).

5.4 Relation between lutum and trace element concentrations

In the two steps described above the data of the Geochemical Atlas are expressed in concentrations which are comparable with concentrations as demanded in de Soil Quality Decree. Metals and metalloids are expressed as concentrations measured using an aqua regia extraction, and Al_2O_3 is expressed as clay size fraction. These data are now suitable to create a relation of clay size with trace element concentrations. This is likewise the estimation of the background concentration in the current STC (see chapter 2).

Again a regression model was created based on the sub soil data of the Geochemical Atlas, using the same method and LQS regression model as Spijker (2012). Clay size (lutum) was used as independent variable. However, as discussed in section 4.2 the covariation of Al_2O_3 with trace elements is low in sandy soils and, discussed in section 5.2, there is no suitable model available for the relation between Al_2O_3 and lutum for small lutum values (<5 wt-%). Therefore the model is assumed to be variable for clayey and peaty soils, and constant for sandy soils. In the model soils with a clay size fraction lower than 5 wt-% are defined as sandy soils. This results in the following formula:

$$(5.3) \quad C = \begin{cases} \beta_0 + \beta_1 L + 2.5\varepsilon \wedge L > 5 \\ \beta_0 + 5\beta_1 + 2.5\varepsilon \wedge L \leq 5 \end{cases}$$

Where C is the concentration of the metal or metalloid and L is the clay size fraction. The parameters $\beta_{0,1}$ are respectively the intercept and slope, and ε is the regression error. By using 2.5ε the upper limit of the error interval is chosen and 90% of the values fall below this level (see Leroy and Rousseeuw 1986)

5.5 Model error

Ideally, the fitted model of equation (5.3) is validated against an independent dataset. Unfortunately, for this study there are no datasets available which use the same method for measuring trace element concentrations and grain size as used with the datasets for which the above model was derived. To get an

impression of the residual variability of the model compared with field data, three datasets were selected for comparison.

The first dataset is the dataset of the inventory study of Brus et al. (2009), this is the so called 'AW2000' dataset. This dataset was chosen for two reasons. First, these data are based on metal and metalloid concentrations measured after an aqua regia extraction using commercial available methods. Clay size fractions were also measured using commercial methods. Secondly, legislative threshold values of the Dutch Soil Quality Decree are based on this dataset.

The second study is the dataset of the Dutch Soil Monitoring Network, this dataset has a slightly different analytical procedure based on extraction with fleischman acid (a mixture of concentrated sulphuric and nitric acid) and clay size fraction using the pipette method. This dataset is, like the dataset of Brus et al. (2009), based on a nationwide sampling and in comparison with AW2000 gives an indication of analytical variability.

Additionally an unpublished dataset from the area of Zuid-Holland is used. This dataset was chosen because it was sampled from peaty soils, containing high organic matter. This dataset is more representative for soils with high organic matter than the other two datasets.

All three datasets contain trace element concentrations and grain size fractions. However, the methodology for measuring trace elements concentrations can differ between the studies.

In chapter 6 the alternative STC is compared with the field data in two ways. First the trace element concentrations are plotted against the clay size fraction. This gives an indication of the covariability between clay size fractions and trace elements as obtained by the different analytical techniques. Second the natural trace element background concentration is estimated by 1) the alternative STC (see equation (5.3)) and 2) the original STC (see equation (3.5)) and plotted against the observed concentrations. Data used for this step are the sub soil concentrations from the inventory study of Brus et al. (2009). This gives an indication of how the alternative STC perform in comparison with the original STC. Since the intercept of the regression model of the original STC was increased to an upper level, the 90-percentile, of the residual variance of the regression, it is expected that in comparison with observed values the predicted values are an overestimation. The covariance between observed and predicted however, should be comparable.

Although this method is not a validation common in statistical analysis, it gives an impression of the fit of the model for the chosen datasets.

5.6 Consequences

The current normative values for metals and metalloids, as defined in the Soil Quality Decree (VROM, 2007), are based on the 95-percentile from the inventory study (Brus et al., 2009) together with an ecological risk level, as explained in chapter 2. These 95-percentiles are derived after normalising the measured top soil concentrations in the field using the current STC. Again, a change in model of the STC means that the data of the inventory study also should be re-evaluated. Luckily, normalising the data of the inventory study using the alternative STC and calculating the 95-percentile, using the same weights as Brus et al. (2009), can be easily performed. So, to obtain an

impression of the consequences when the alternative STC model parameters are used, the resulting weighted 95-percentiles are calculated based on normalised data. For this normalisation the following formula is used (see equation (3.3)):

$$(5.4) \quad C_s = C_f \frac{C_b}{C_{b,f}}$$

Where C_s is the normalised concentration, C_f is the measured concentration, C_b is the concentration calculated with equation (5.2) using $L=25$ wt-%. $C_{b,f}$ is the concentration calculated with the same equation (5.2) but then with L being the measured grain size fraction of the field sample.

The method of equation (5.4) is equal to the current formula of the STC (see equation (3.3)) and shows what happens if the current STC model parameters are exchanged by the alternative parameters. This ignores the fact the 95-percentile is a different property than the natural background concentration and is subject to the problem presented in equation (3.5). Both current and the alternative STC of equation (5.4) are, *senso stricto*, not representative for the soil concentrations in the range of the 95-percentile. However, it will give an indication of the consequences.

6 Results and discussion of the alternative model

6.1 Relation between lutum and Al_2O_3

For the relation between the clay size fraction ('lutum', grain size $<2\mu\text{m}$) a fixed relation was used (see equation 5.1). This relation is plotted in Figure 6.1 together with data from two independent datasets as comparison. The first dataset is the one from Edelman (1984), where lutum was measured with the pipette method and Al using Instrumental Neutron Activation Analyses (INAA). The other dataset is unpublished data from the National Soil Monitoring Network (Landelijk Meetnet Bodem, LMB). In this dataset lutum was measured using laser diffraction and Al was determined using X-Ray Fluorescence.

In Figure 6.1 the line of the used relation of lutum vs. Al seems to fit the Edelman data better than the LMB data, the latter showing lower values for lutum (or higher values for Al_2O_3) and less variance in Al_2O_3 .

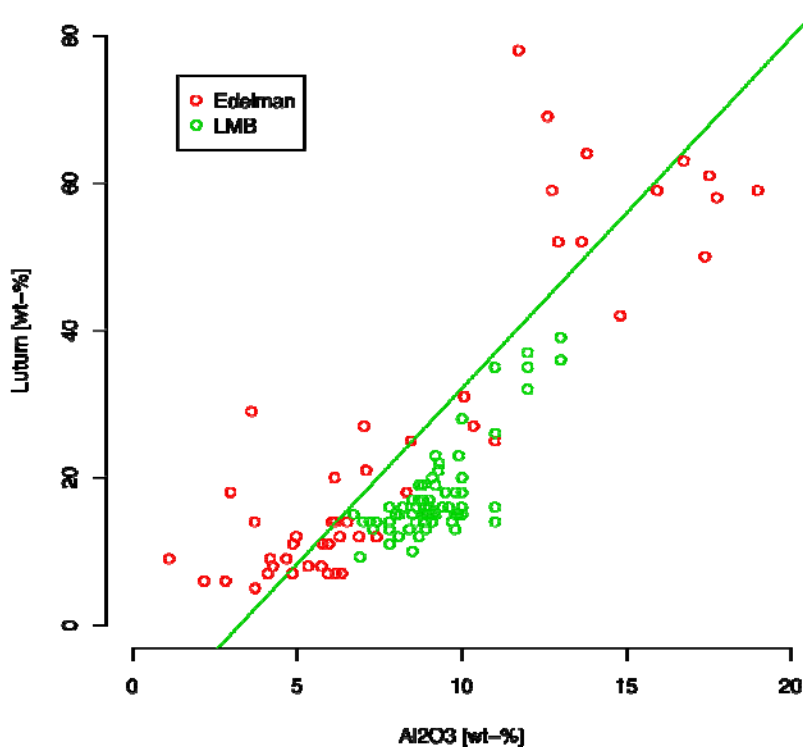


Figure 6.1: The relation of Al_2O_3 with lutum (line) together depicted with data from two independent datasets (Edelman and LMB). For explanation, see text.

Figure 6.1 also shows no apparent relation between Al_2O_3 and clay size for clay size fractions lower than 5 wt-%. This confirms the choice not to derive a alternative STC for soil with clay size fractions below 5 wt-%.

6.2 Relation between total concentration and aqua regia

From the unpublished dataset of the National Soil Monitoring Network 22 data points were selected where each element was both analysed using aqua regia and total methods. The relation between total and aqua regia method is depicted in Figure 6.2. The regression parameters are given in Table 6.1.

Opposite page: Figure 6.2: Relation between total concentrations (x-axis) and aqua regia extracted concentrations (y-axis) for 15 trace elements. The dashed lines indicate the 1:1 line, the solid line is the regression model, dotted lines indicate the 2.5ϵ range.

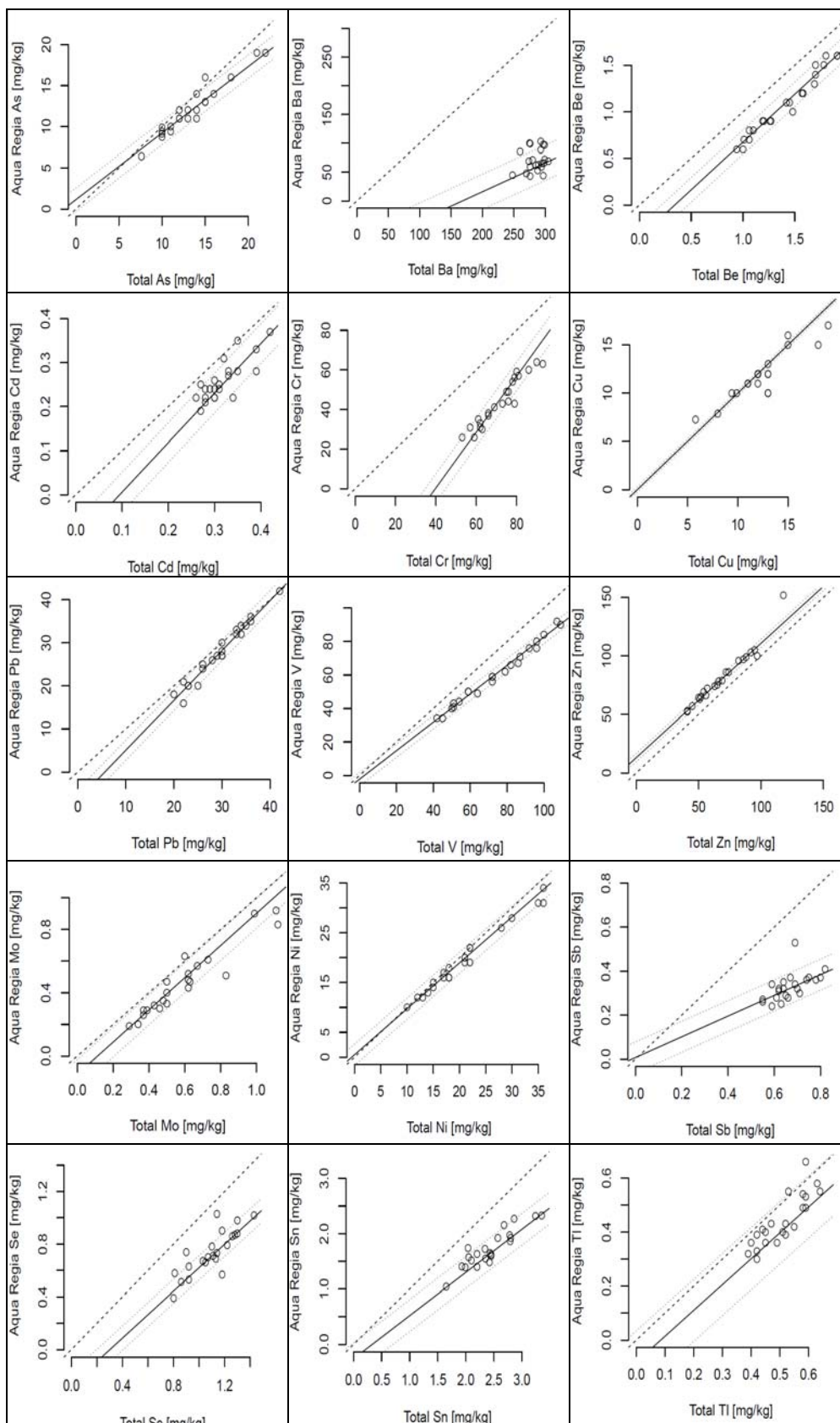


Table 6.1 Regression parameter ($\beta_{0,1}$), regression error (ε) and robust correlation coefficient (r) of the relation between total metal concentrations and aqua regia extraction (see equation (5.2)).

Element	β_1	β_0	ε	r
As	0.81	1.15	0.57	0.98
Ba	0.50	-84.0	12	0.52
Be	1.0	-0.350	0.052	0.99
Cd	1.1	-0.107	0.018	0.74
Cr	1.4	-56.0	2.9	0.99
Cu	1.00	-0.00167	0.11	0.91
Pb	1.2	-6.52	0.93	0.98
V	0.85	-2.25	1.6	0.99
Zn	0.98	13.1	1.4	1.00
Mo	1.0	-0.115	0.038	0.97
Ni	0.92	0.486	0.85	0.98
Sb	0.47	0.00730	0.028	0.82
Se	0.89	-0.268	0.037	0.97
Sn	0.78	-0.260	0.12	0.84
Tl	0.96	-0.081	0.046	0.82

Figure 6.2 shows in general a good relation between the aqua regia and the total methods. The robust correlation coefficient confirms these good relations, in general $r > 0.90$. Exceptions are Ba, Cd, Sb, Sn and Tl. For Ba $r = 0.52$, for Cd $r = 0.74$ and for Sb, Sn and Tl $r > 0.80$.

For Ba it is generally known that the total concentration of this element can not be properly measured using an aqua regia extraction. For Cd, Sn, Tl and Sb it is known that the reproducibility is relatively large, i.e. less accurate, for both the aqua regia extraction and the HF digestion (see Mol and Spijker, 2009, for a detailed discussion about the analytical methods).

6.3 Relation between lutum and aqua regia

In the above two sections regression models were derived which express aqua regia concentrations and grain size fraction as function of total concentrations and Al_2O_3 respectively. With these regression models the metal and metalloid concentrations of the Dutch Geochemical Atlas were recalculated as data expressed in aqua regia concentrations and Al_2O_3 was expressed as lutum. The trace element concentration can be expressed as function of lutum using a regression model cf. equation (5.3). These results are shown in Figure 6.3 and Table 6.2.

Table 6.2: constants for the STC regression, including regression error, see equation (5.3). R is the robust correlation coefficient based on the Minimum Volume Ellipsoid. The range of predicted concentrations is given in Table 6.3.

Element	β_0	β_1	error	r
As	3.72	0.207	2.93	0.81
Ba	36.6	0.779	17.21	0.60
Be	0.142	0.0439	0.137	0.96
Cd	-0.0390	0.00317	0.0607	0.65
Cr	-9.05	2.10	7.30	0.97
Cu	0.679	0.256	3.21	0.88
Pb	2.45	0.417	2.52	0.94
V	9.59	1.80	6.64	0.96
Zn	17.66	1.99	6.70	0.97
Mo	-0.00683	0.0146	0.225	0.69
Ni	2.363	0.773	3.01	0.97
Sb	0.149	0.00347	0.0349	0.84
Se	0.099	0.0214	0.226	0.77
Sn	0.145	0.0442	0.133	0.98
Tl	0.0931	0.0108	0.0454	0.95

Table 6.2 shows that the correlation between the clay size fraction and the trace element concentration is good ($R > 0.9$). The elements As, Cu, Sb, Se have somewhat lesser correlation coefficients ($0.77 < R < 0.88$). Barium, Cd, and Mo have a R of respectively 0.60, 0.65 and 0.69. For Ba it is already stated that this element is difficult to analyse using aqua regia. For Cd and Mo relatively large values for duplicate precision are reported (Van der Veer, 2006).

In Figure 6.3 the model prediction is shown graphically. The robustness of the model is clear when, for example, if one looks at Cd and Cu. Higher, more outlying values, have minor impact on the direction of the regression line.

Barium clearly shows that a generic model is in some cases not favourable. Figure 6.3 shows that for Ba the generic model follows the variability in clayey soils which is distinctively different from sandy soils (i.e. the grey dots).

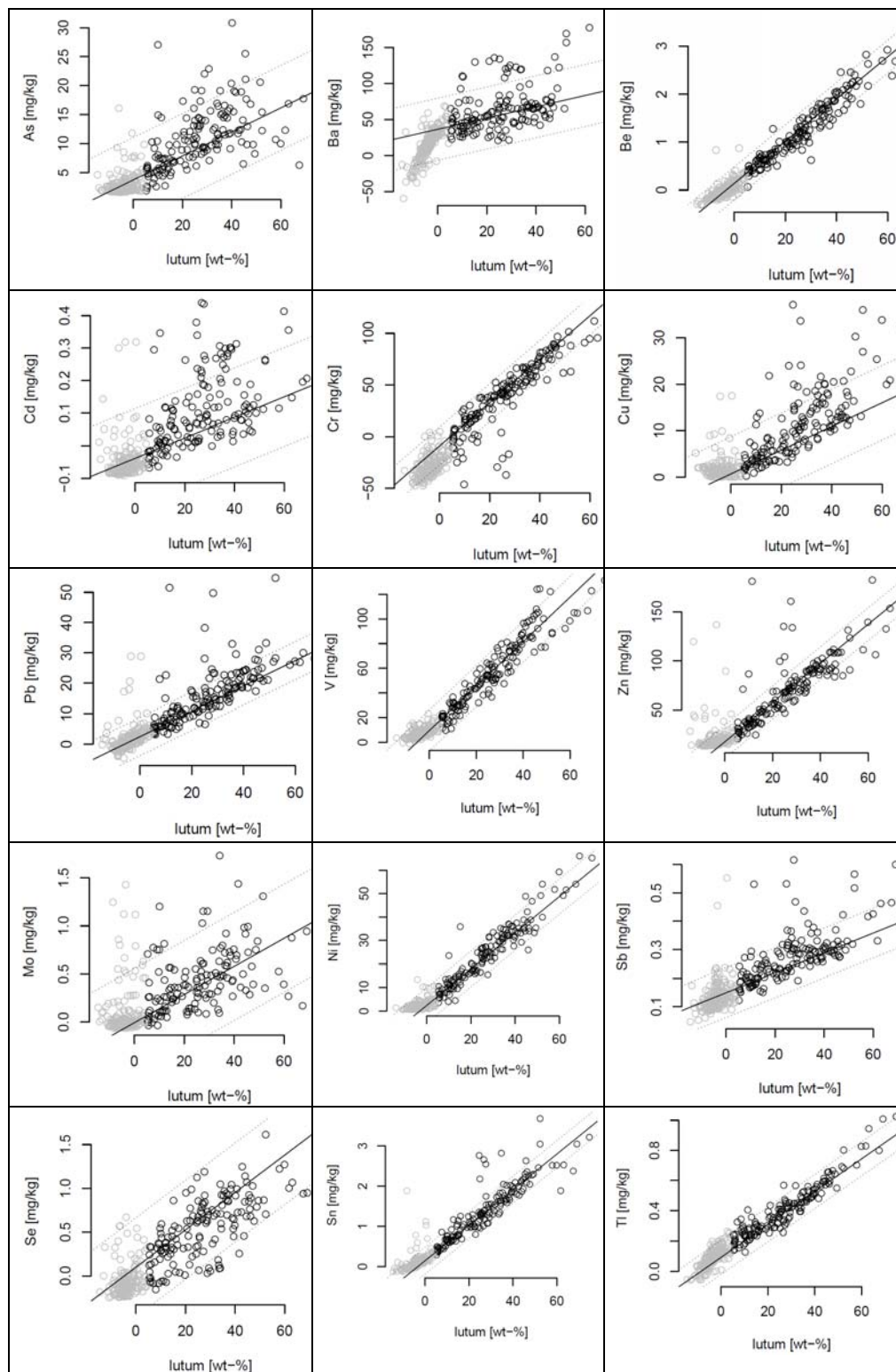


Figure 6.3: Regression models of lutum, recalculated from Al_2O_3 , and trace element concentration, recalculated from total concentrations. Regression parameters are given in Table 6.3.

6.4 Validation

Figure 6.4 shows how the alternative STC perform compared to actual measured data from independent datasets. The figure is divided in three panes. The left pane is the comparison with the three chosen datasets (see section 5.5). The alternative STC (equation (5.3), with parameters from Table 6.2 and using 1ϵ for the regression error) is depicted as a gray line. The range of the model, defined as 2.5ϵ , is also shown. The black line gives the upper limit, the gray dashed line the lower limit. In the current STC the regression model was altered, by increasing the intercepts, in such way that 90% of the values were below the model prediction. The range of 2.5ϵ gives the interval where roughly 98% of the normal distributed residuals of the model fall within (Leroy and Rouseeuw, 1986), which can be used to give the upper limit of the natural variation.

From the left panes of Figure 6.4 the large variability of soil concentrations and the distinct groups related to the distinct datasets are clear. Some elements, like Se and Mo, are dominated by censored data due to relatively high limits of analytical quantification. Other elements indicate that slight differences in analytical methodology can result in differences in measured concentrations. For example Cr, for each dataset a different variance with lutum is shown.

The middle panes of Figure 6.4 give the observed and predicted values of the model applied to the data from the AW2000 dataset. Here the estimated background concentration is compared with concentrations as found in the Dutch sub soils. Ideally the variation between observed and predicted values should be oriented around the 1:1 line (the black line) and with a good correlation.

For the elements As, Cr, Pb, V, Zn the prediction is fairly good ($r \geq 0.80$), for Be, Cu, and Ni the model performs moderate ($r > 0.60$) compared to field data. For Cd and Tl the prediction is poor. This is probably caused by the fact the concentrations for Cd and Tl in the AW2000 study are below the reported detection limit of respectively 0.1 and 0.5 mg/kg, which results in a higher uncertainty of the measurements. For comparison, the regression model is derived using data from the Dutch Geochemical Atlas with a 'detection limit', i.c. limit of quantification, of 0.02 mg/kg for Cd (Van der Veer, 2006). It is expected that the model performs well in the range of these lower concentrations of AW2000, despite the fact that they are hard to measure using common commercial available methods.

For Ba the prediction of the background values is also poor. It is known that for Ba no proper general baseline model exists for all the Dutch soil lithologies together. The variability of Ba concentrations vary widely for each soil lithologie, making it difficult to create one model covering all lithologies together. Also, there is a poor relation between total concentration and aqua regia determined concentrations (see Figure 6.2) These two arguments make that the alternative STC for Ba is highly uncertain.

For Mo, Sb, and Sn no comparison between field concentrations and STC prediction is possible. The field data from AW2000 is dominated by censored data due to values which are too low to determine analytically by the used analytical methods.

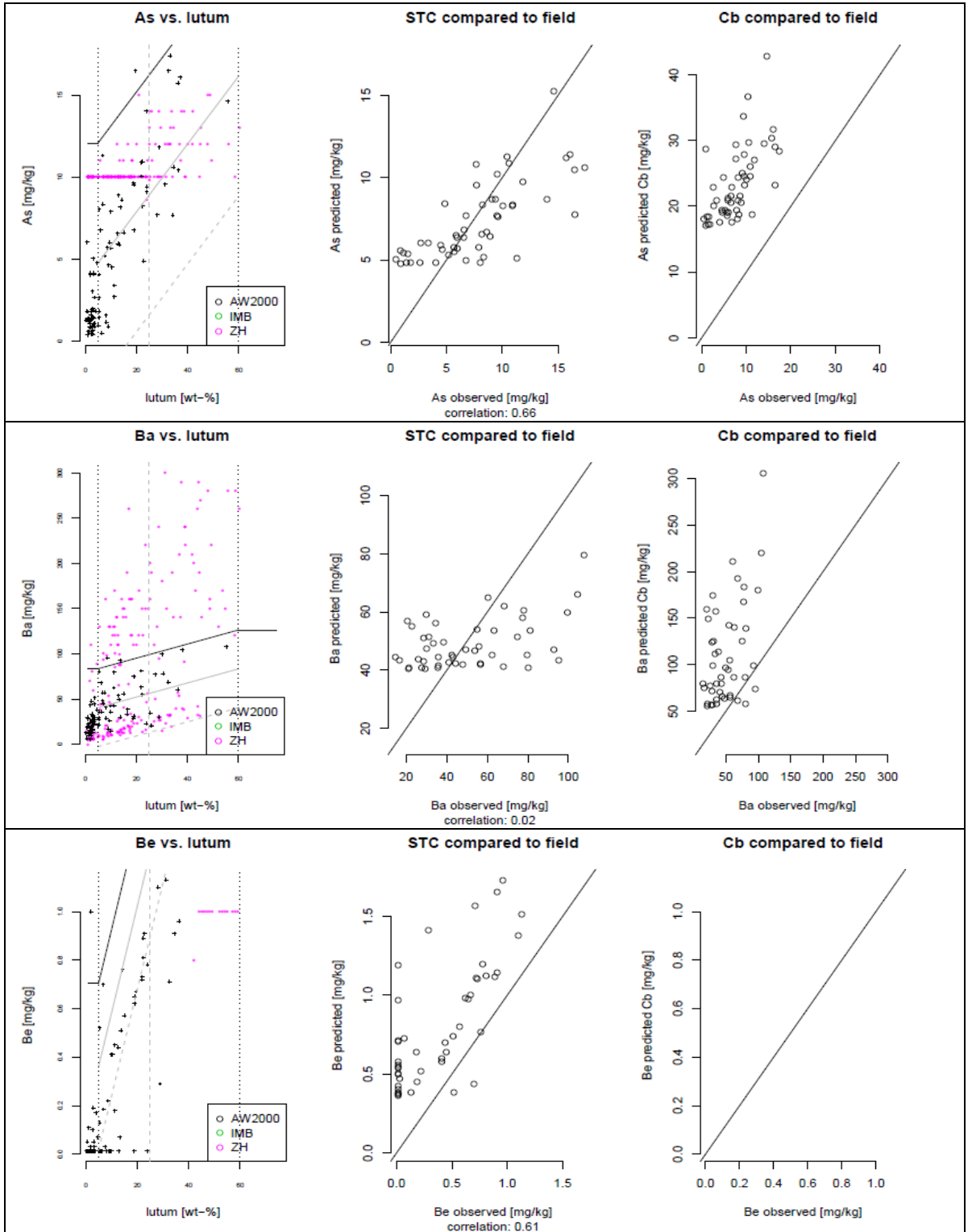
In general by comparing both models (middle and right panes in Figure 6.4), the alternative STC perform equal or better compared to the current STC, though Ba

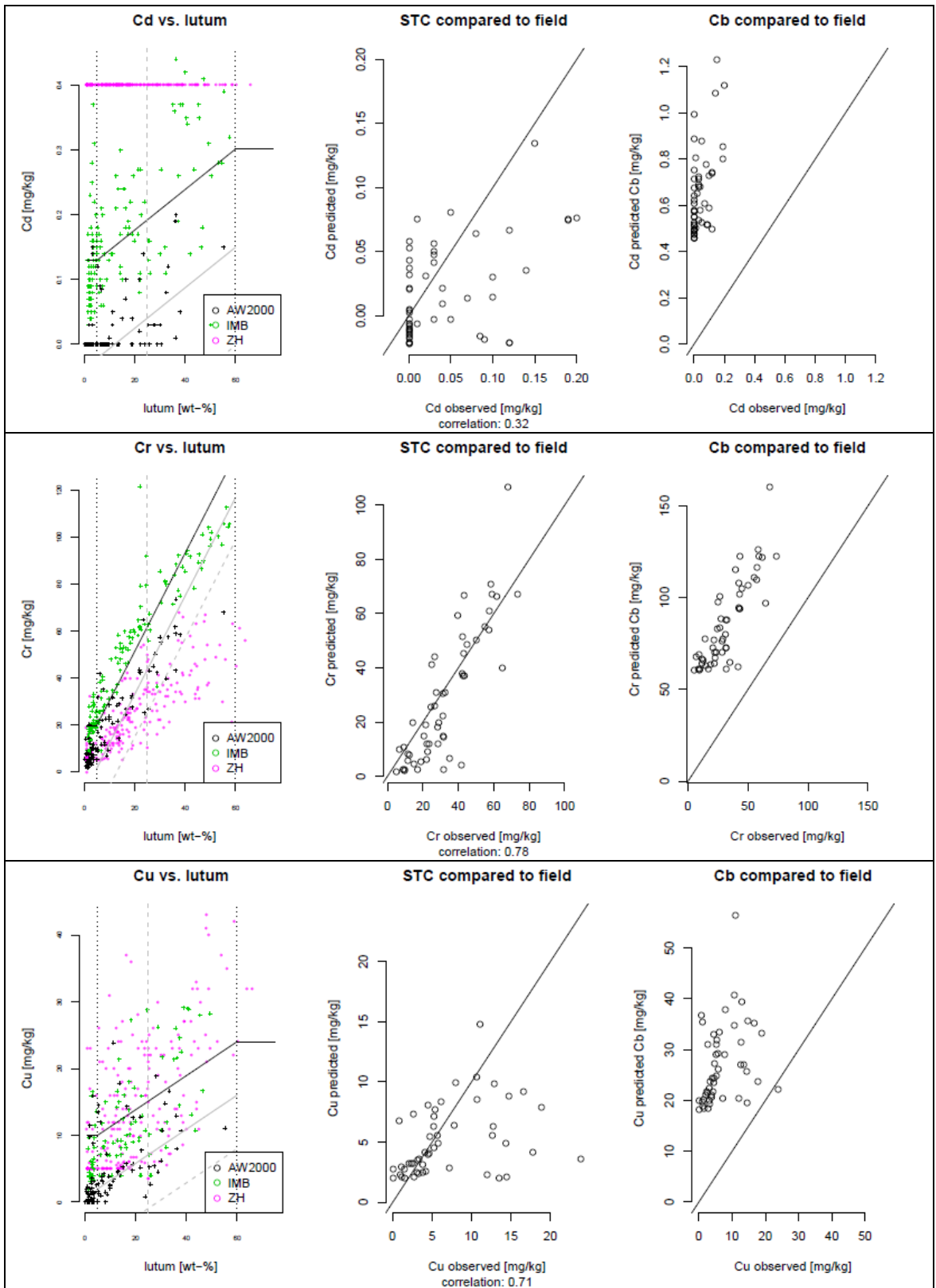
being an exception. The current model seems to predict Ba soil concentrations better than the alternative model.

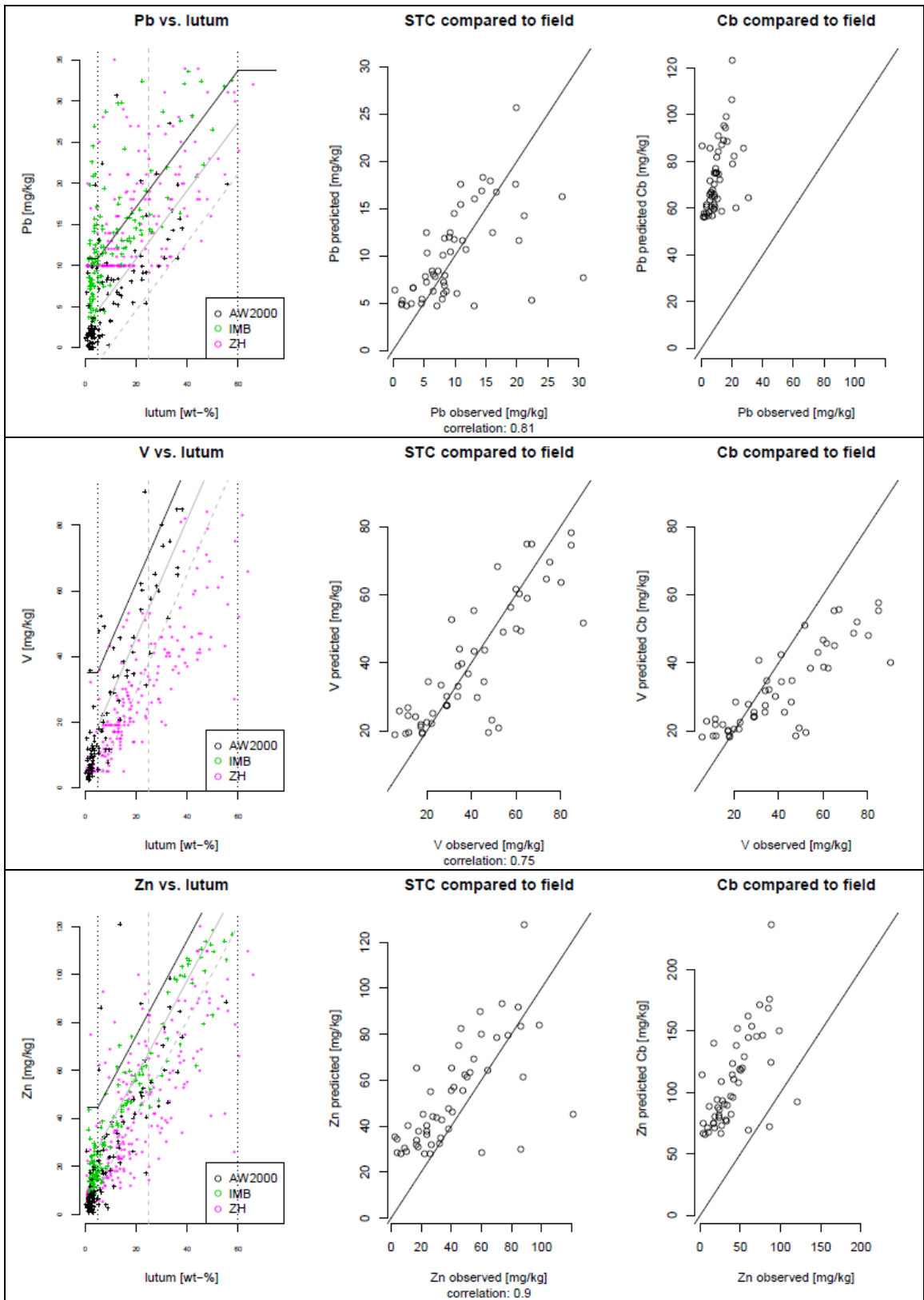
The right panes give the predicted concentration using the current STC model and are given for reference. The intercept of this model lies at the 90-percentile of the residual variation of the regression, hence the predicted values are in general higher than the observed values. Ideally the predicted concentration should lie above and in parallel with the 1:1 line.

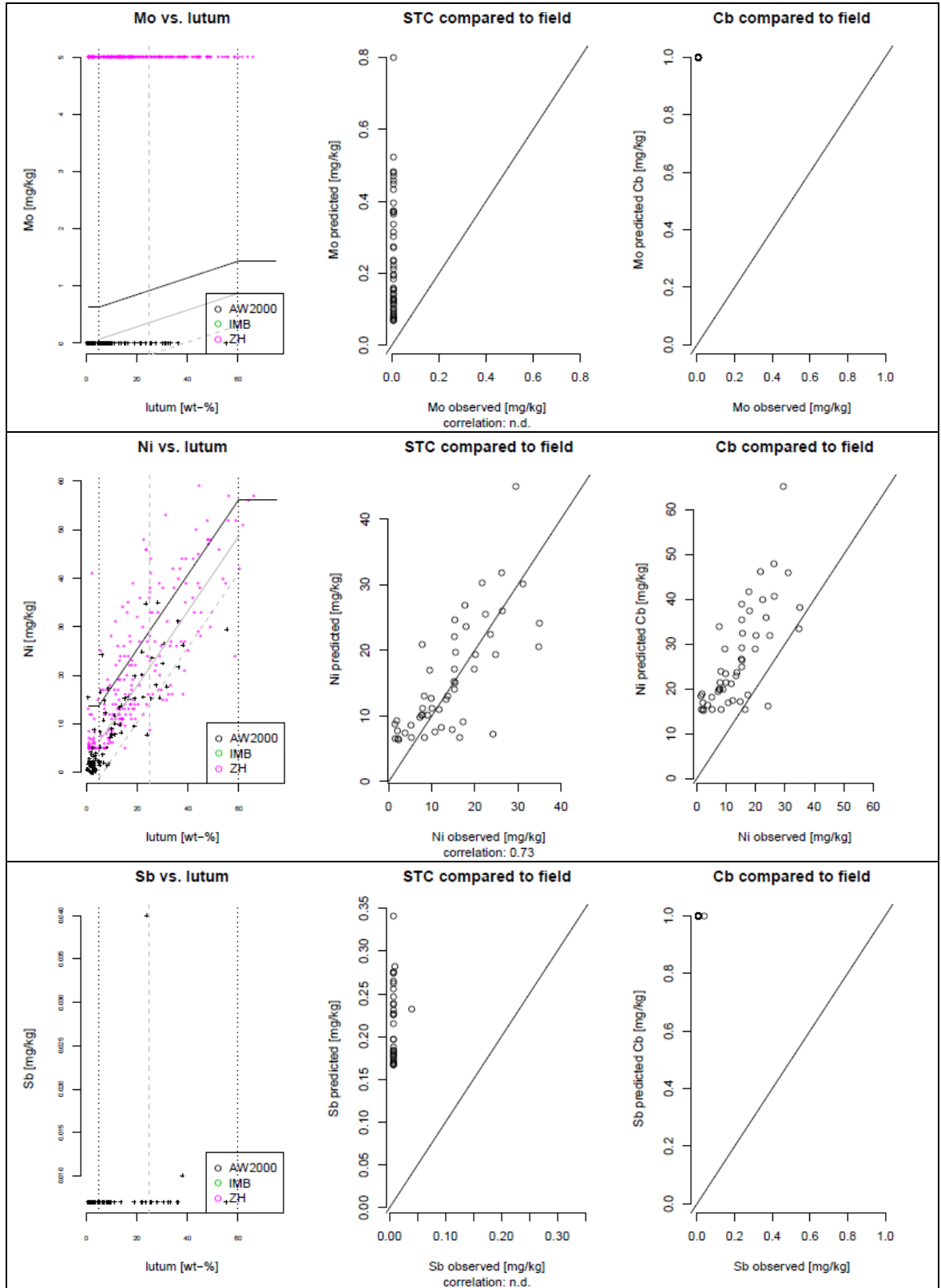
Figure 6.4 (next pages): Results of the alternative STC.

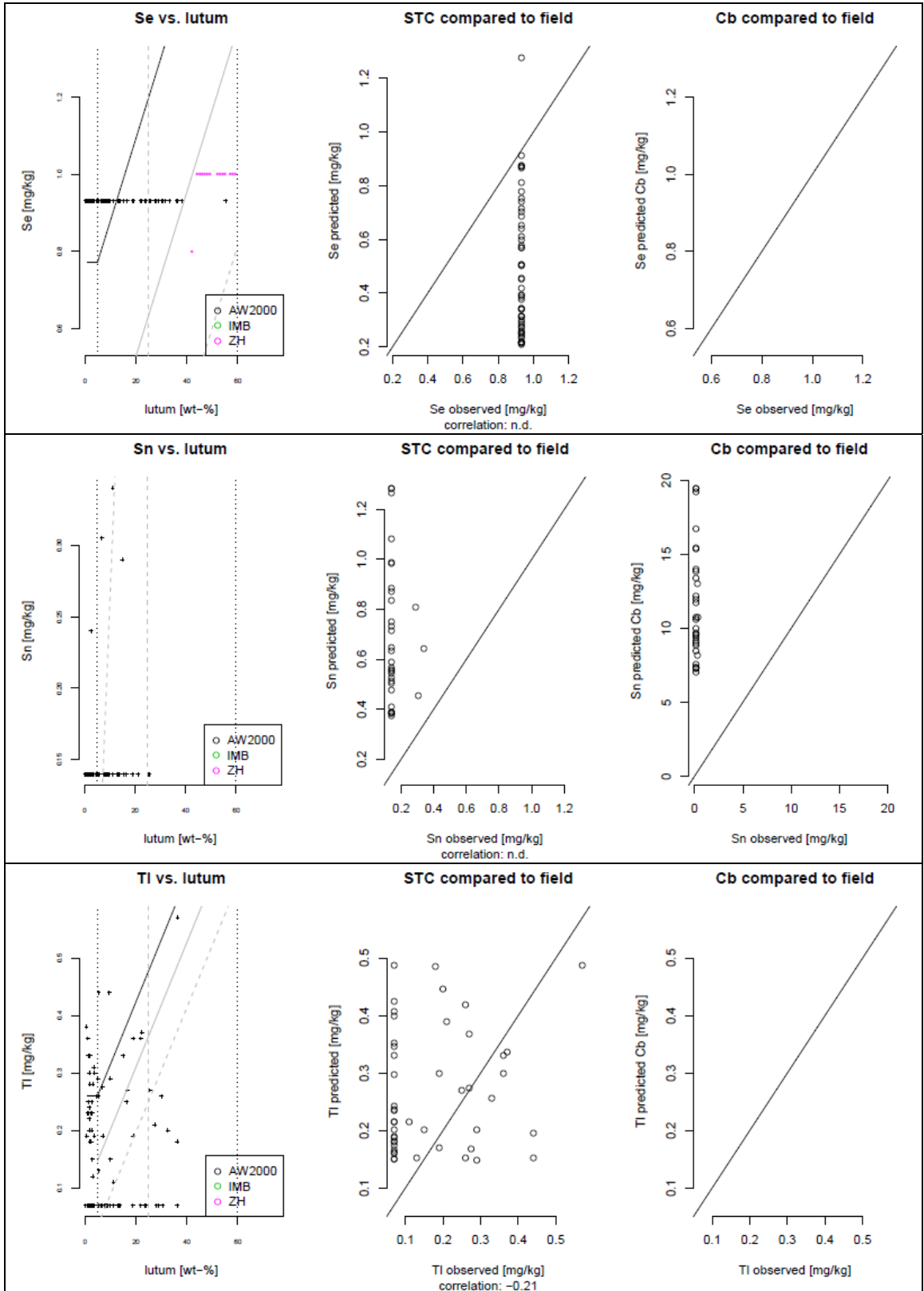
On the left, the metal or metalloid concentration is depicted against clay size fraction (lutum) for samples from three independent datasets, some elements are not available in each dataset. The gray line is the alternative baseline, the black line is the upper limit of the baseline variance (2.5ϵ), the dashed gray line is the lower limit. The vertical dashed lines depict from left to right respectively 5, 25 and 45 wt-% lutum. The middle and right figure show the predicted concentration (y-axis) for the alternative STC (middle) and current STC (right) against the observed concentration (x-axis). If no current STC is available, the right plot is empty.











6.5 Consequences for background values (C_b) and the 95-percentile

The choice of model parameters and formula (see Table 3.2) is an important factor considering the estimation or normalisation of background concentrations. Table 6.3 lists the ranges for each element for three different options of the STC. The first model, option I in Table 6.3, is the current STC, using the model parameters derived roughly twenty years ago and the current STC formula (see equation (3.3)). These are parts 1, 2, and 3 from the current STC from Table 3.2. For option II the model parameters of the alternative model (see Table 3.2, part 1 alternative model) are used in the current formula (i.e. part 2 of the current STC in Table 3.2). This gives an indication of the change in background concentrations when the alternative model parameters are applied in the current STC formula. This formula is more representative for modal values than for higher values like the 95-percentile, as will be discussed further on. The third option, option III, is the range of background concentrations as estimated by the alternative model parameters (see Table 6.2) and alternative formula of equation (5.3) (part 1 and 2 of the alternative model in Table 3.2). For option III the minimum and maximum concentrations are calculated and the concentration in so called 'standard soil' containing 25 wt-% lutum.

In general, when the median concentrations in Table 6.3 are compared, there are no big differences between the first and the second option. Comparing with the standard values of the third option is somewhat difficult; the median lutum concentration in the AW2000 dataset is 6.1 wt-%, which is closer to the minimum value of the model of equation (5.3) (i.e. 5 wt-%) than to the lutum concentration in standard soil (i.e. 25 wt-%). Comparing the standard concentration of option III with the minimum values of option I en II gives a better indication of the differences between the three options. This shows, in general, that for Cr, Mo, Pb, Sb, and Sn, and to a somewhat lesser extent V and Zn, the differences are significant.

If the standard soil concentrations of option III are compared with the background concentration $C_{b,s}$ of current STC (see Table 3.1), then in general the alternative model gives lower values for the background values than the current model.

Looking at Table 6.3 (and 3.1) the alternative model prevalently gives lower estimates of the natural background concentration. This is probably due to the fact that the current model parameters are derived based on soil data of 'relatively clean areas', which appear not so clean after all compared to the alternative model. The latter model is based on a geochemical model which defines natural background in terms of geochemical composition instead of concentrations from a spatial defined area.

Table 6.3: Calculated ranges for the background concentrations (C_b) when normalising the AW2000 data using three different options, see text. Min, P25, P75, and max are respectively the minimum, 25-percentile, 75-percentile and maximum concentration. Median/standard is for option I en II the median concentration, for option III it is the concentration in a 'standard soil' containing 25 wt-% lutum. All concentrations are in mg/kg.

Element	Option	Min	P25	Median/ Standard	P75	Max
As	I	0.40	4.0	8.1	13	33
	II	0.40	3.6	7.4	12	29
	III	12		16		20
Ba	I	17	52	74	100	278
	II	6.42	23	37	66	381
	III	83		99		115
Be	I	0.014	0.014	0.035	0.53	2.13
	II	0.019	0.031	0.079	0.71	1.47
	III	0.70		2.6		2.5
Cd	I	0.00066	0.011	0.19	0.29	1.39
	II	0.00062	0.011	0.17	0.29	2.59
	III	0.13		0.19		0.26
Cr	I	4.2	14	26	41	65
	II	6.7	23	37	47	102
	III	20		62		104
Cu	I	0.11	8.3	13	20	86
	II	0.10	7.6	13	18	76
	III	10		15		20
Mo	I	0.0070	0.0070	0.0070	0.0070	2.7
	II	0.005	0.008	0.010	0.010	2.13
	III	0.63		0.92		1.2
Ni	I	0.088	4.0	12	19	38
	II	0.07	3.2	11	19	38
	III	14		29		45
Pb	I	1.3	15	20	29	239
	II	2.1	17	21	33	287
	III	11		19		28
Sb	I	0.0070	0.0070	0.0070	0.020	1.9
	II	0.0058	0.0081	0.0089	0.026	2.17
	III	0.25		0.32		0.39
Se	I	0.93	0.93	0.93	0.93	0.93
	II	0.69	1.1	1.4	1.4	1.4
	III	0.77		1.2		1.6
Sn	I	0.15	0.45	0.83	1.8	20
	II	0.15	0.32	0.78	1.5	17.93
	III	0.70		1.6		2.5
Tl	I	0.070	0.070	0.22	0.40	1.2
	II	0.048	0.13	0.34	0.51	1.6
	III	0.26		0.48		0.69
V	I	5.7	38	52	64	200
	II	3.8	28	48	60	186
	III	35		71		107
Zn	I	9.52	44	63	79	167
	II	8.0	43	59	81	167
	III	44		84		124

The consequences of using an alternative STC for the 95-percentile of the AW2000 dataset (Brus et al., 2009) are given in Table 6.4. Arsenic, Ba, Be, Cu, and Sn have higher concentrations for the 95-percentile derived using the alternative STC. Lead, Sb, Se and TI will have lower concentrations. For Cd, Cr, V, Zn, and Ni the differences are less relevant.

If the changes are compared in relation with the reported confidence interval (see Lame et al., 2004), only Ba, V, and Sn show relevant changes. For Be, Mo, and Se no confidence interval is reported.

Due to the, sometimes high, uncertainty in derived 95-percentiles, the effect of using the alternative STC model parameters in the current STC formula is limited in relation to this uncertainty. However, relative changes compared to the current value of the 95-percentile can be as large as 20% to almost 60%.

Table 6.4: Calculation of 95-percentiles of the AW2000 dataset normalized with the original soil type correction and with the baseline model. The first three columns give respectively the lower confidence limit of the 95-percentile, the 95-percentile and the upper confidence limit of the 95-percentile as reported in *Lame et al., (2006)*. The three middle columns give the absolute 95-percentile of the uncorrected data, the 95-percentile of the data normalised using the current STC and the 95 percentile using the alternative STC. The last three columns show if the 95 percentile derived using the alternative STC is within the confidence limit of the current 95-percentile, and the absolute and relative difference with the current 95-percentile. All numbers are in mg/kg unless stated otherwise.

Element	95 percentiles			AW2000		Change		
	AW2000 Reported			AW2000 Calculated		within conf. limit	absolute	relative [%]
	lower conf. limit	p95	upper conf. limit	standard soil	p95, baseline			
As	16.6	19.6	32.8	19.61	17.032	yes	-2.57	-13
Ba	148	184.4	278	184.41	141.596	no	-42.81	-23
Be	n.a.	n.a.	n.a.	1.30	1.047	n.a.	-0.25	-19
Cd	0.46	0.57	1.3	0.59	0.635	yes	0.04	7
Cr	50.3	52.71	65.3	52.71	55.110	yes	2.40	5
Cu	30.2	36.18	86.2	36.18	30.211	yes	-5.97	-17
Mo	n.d.	0.5	n.d.	0.01	0.010	n.a.	0.00	46
Ni	24.7	28.44	31.4	28.43	27.393	yes	-1.04	-4
Pb	37.4	48.35	239	48.39	76.389	yes	28.00	58
Sb	0.43	1.3	1.70	0.78	0.994	yes	0.21	27
Se	n.a.	n.a.	n.a.	0.93	1.446	n.a.	0.52	55
Sn	4.37	6.05	17.2	6.05	4.055	no	-2.00	-33
Tl	n.a.	n.a.	n.a.	0.75	0.915	n.a.	0.17	22
V	72.2	75.53	200	75.55	70.924	no	-4.63	-6
Zn	121	133.79	167	133.85	126.621	yes	-7.23	-5

7 Discussion and conclusion

7.1 Importance of background concentration and a soil type correction

Distinguishing between natural background and anthropogenically enhanced levels of elements is a necessity for the proper execution of the current Dutch environmental legislation. Setting risk limits within Dutch soil policy is based on the so called added risk approach. This means that the legal threshold value is determined by the risk of the anthropogenically enhanced levels. The subsequent threshold limit is determined by the allowed risk (e.g. the Maximum Permissible Addition (MPA)), plus the natural background.

To estimate the natural background concentrations of elements, metals, and metalloids, in soils, a statistical model was derived in the eighties of last century, using lutum (grain size fraction <2µm) and organic matter as predictors. This model used samples from relatively clean areas. The estimate of the background concentration is needed, because these concentrations are not fixed values but vary in geographical space, acknowledging the natural variability in soils.

The Soil type correction (STC) is a normalisation procedure in which legal threshold limits can be normalised for the varying natural background concentrations. In this normalisation procedure, a formula, the model parameters from the statistical model for the background concentrations are applied. With this normalisation formula both the natural concentration and the added risk level are normalised. The current implementation of the STC in the Dutch Soil Quality Decree can be explained by dividing this implementation in four parts: 1) a statistical model, 2) a formula, 3) a background concentration, and 4) an added risk level (see section 3.2, Table 3.2).

The current STC also implicitly normalises the added part. However, this has no explicit purpose. Although it is often stated that the normalization of the added part is a correction for (bio)availability, the underlying model does not incorporate (bio)availability. The current formula only describes soil variability in a proper way at the level of background concentrations. If used for a higher concentration, like a legal limit including an added part, the described variability does not reflect reality due to a numerical artefact. Therefore it is needed that besides the model parameters, the formula should be update too.

7.2 Improvement of the soil type correction

As an improvement a model is proposed using a robust linear regression model for the estimation of the natural background concentrations using the clay fraction. This also results in an estimation of the spatially variable background concentration. A risk level, e.g. the MPA, is added, without normalisation, to this background concentration (see section 3.2). Instead of the risk level, a value corrected for (bio)availability can also be used, but such a correction is not yet available.

Currently no single coherent dataset exists which is suitable to create the statistical regression model for the estimation of the background values. This model must be based on the same parameter as the current STC, i.e. clay fraction, organic matter and aqua regia based element concentrations. However, from the Dutch Geochemical Atlas a geochemical baseline model is available

which estimates the natural background concentration using Al_2O_3 . In this study it was shown that this model can be transformed into a model based on the clay size fraction.

For this transformation of the model an *engineering solution* was used. Practical usability and suitability prevailed over a proper scientific description of soil variability. For this transformation the clay size fraction was estimated from the Al_2O_3 concentration from the Dutch Geochemical Atlas using data from literature. The aqua regia based concentration was estimated using unpublished data from the Dutch Soil Monitoring Network. From the data of the estimated clay size fraction and element concentrations an alternative model was derived using the same method as for the geochemical baseline models.

The correlation in the final regression model between clay size fraction (lutum) and element concentration is in general good. ($R > 0.9$). The elements As, Cu, Sb, Se have somewhat lesser correlation coefficients ($0.77 < R < 0.88$). Barium, Cd, and Mo have a R of respectively 0.60, 0.65 and 0.69. For Ba the lower correlation is expected. The variation of this element with soil bulk geochemistry, like Al_2O_3 , varies widely among soil lithologies. This makes a general model for Ba covering all soil lithologies less favourable. The current STC predicts background concentrations for Ba better than the alternative STC. For Cd and Mo relatively large values for duplicate precision are reported (Van der Veer, 2006), which might explain the lower covariance in the regression model.

7.3 Model validation

To compare the model with field data, the dataset of AW2000 was chosen (Brus et al., 2009). This dataset is the only dataset where the concentrations are determined using commercial methods. For the elements As, Cr, Pb, V, Zn the prediction is fairly good ($r \geq 0.80$), for Be, Cu, and Ni the model performs moderate ($r > 0.60$) compared to field data. For Cd and Tl the prediction is poor. This is probably caused by the fact that concentrations for Cd and Tl are below the reported detection limit in the AW2000 dataset.

The regression model also provides relations for Mo, Sb, and Se. For these elements no relations exist in the current STC. There are no model parameters for Co, since for this element no data was available in the datasets used.

To see what the effects will be if the alternative model is used within the current STC formula, the data of AW2000 were used. From these data the 95-percentiles, used as threshold values in the current Soil Quality Decree, were recalculated. The 95-percentiles of the current model and the alternative model were compared. The changes are very relevant and for most elements they are within the reported confidence interval, except for Ba, Mo, and Se. Although the (statistical) significance of implementing the alternative model parameters in the current formula seems limited, in practice the changing values for the 95-percentile, and subsequently the soil quality criteria based on these values, can have a far-reaching impact.

Important to note is that the above comparison between 95-percentiles is hampered. Both models, current and alternative are applied to the current STC formula to calculate normalised soil concentrations for which the 95-percentiles are derived. However, these models describe variability at the level of natural background concentrations, which are distinctly differ from concentrations at the

level of the 95-percentile. Therefore, the significance of this comparison is limited (see section 3.1).

7.4 Conclusion

It is concluded that the alternative model for the STC is an improvement compared to the current model. The results indicate that the alternative model performs for all elements, except Ba, better or equal than the current model.

The model parameters are used within a formula. The current formula only describes soil variability in a proper way at the level of background concentrations. If used for any other, higher, concentrations the described variability does not reflect reality. Therefore not only the model, but also the formula should be updated. An improved formula is proposed in section 3.2. In this formula only the variability of the background concentrations is incorporated. The added part is not corrected. For the correction of the added part, e.g. a correction for (bio)availability, further research is required.

8 Recommendations

Before implementing an alternative soil type correction (STC), or maintaining the current one, we recommend a broad discussion about the role of the STC first. Because the current STC is intertwined in many parts of the derivation of legal soil quality criteria, the implementation of an alternative STC must be part of a general revision of these criteria. Thus, if one decides to change the model and/or the formula of the STC, this also means that many other values in soil legislation will change. A change in model parameters or formula (see Table 3.2) of the STC also means *senso stricto* that the toxicological data for each element should be re-calculated. Re-calculation of these data means also a change of risk assessment of trace metals for soils and sediments.

The alternative STC presented in this report is based on soil data from the rural area of the Netherlands and the alternative STC describes the variability of soil concentrations in this area. It is generally known that the variability of trace element concentrations with bulk geochemistry (like Al_2O_3) or clay is distinctively different in urban soils, compared to the rural area. One can argue if it is even possible to describe this variability in urban soils with a simple formula like the current or alternative STC. The question remains if it is possible to apply a general STC model and formula on natural trace element variability in urban soils. For soil management in urban areas insight is needed in, for example, the consequences of maintaining the current STC, using the alternative STC, or deriving an urban soil specific STC.

One step further than normalising the natural background concentrations is the normalisation of the added concentration C_a . The background concentration is normalised using a model for background variability while the added concentration can be normalised using a model for variability in (bio-) availability. This scenario is closest to reality. Therefore it is recommended that the possibilities for such a model is studied.

The current soil quality criteria are based on the added risk approach and in this approach the natural background concentration plays a vital role, thus requiring a method for estimating this, variable, background concentration. On the other hand, if one wants to base soil quality criteria on other soil concentrations like the nowadays discussed chemical- or bioavailable fraction, instead of the currently used total concentrations, the natural background concentration becomes less relevant. When considering the use of other soil concentrations, one must also consider the role of the STC.

The alternative STC presented in this report is an *engineering solution* using current data. Since no proper coherent single dataset is available, relations from different datasets are combined to obtain the alternative, resulting in, yet unknown, uncertainties. A cost effective solution to obtain a proper, single, dataset with the needed parameters is to perform extra analyses on the archived samples of the Dutch Geochemical Atlas. These analyses give further insight in the relation of total, reactive, and (bio)available concentrations with concentrations derived using aqua regia based methods. Combining these extra analyses with the already available data might also create information needed for a future correction for (bio)availability. Finally, these analyses also generate data for Co, which is now currently missing.

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