



## **Eindrapportage-formulier TRIAS projecten Final report format for TRIAS projects.**

When a TRIAS project has finished, or is about to finish, a Final Report is required. This report serves several goals simultaneously:

- it enables the program commission to check whether the project has met its goals,
- it enables NWO-ALW to finalize the project administratively, e.g. pay the final part of the personnel costs of the project,
- it provides some of the information needed for evaluation purposes,
- it provides information which can be publicized, e.g. via a web site.

We have integrated the questionnaires from TRIAS and ALW into one, in order to prevent the need to fill in the same answers twice.

Please send in the filled out forms within a month after the project is completed to:

Netherlands Organisation for Scientific Research  
Earth and Life Sciences  
Carmen van Meerkerk and/or Theo Saat  
P.O. Box 93510  
2509 AM The Hague



Part I

General information, also intended for publication through the TRIAS website

- 01 Project Title.  
**Solubility and mobility of arsenic under changing redox conditions as affected by multi-component transport part I**
- 02 TRIAS/ALW project number or file number  
**Trias project 835.80.006/DelftCluster 5.17**
- 03 Research period, at what date did the project start, at what date did it end.  
**April 15th 2002 -April 15th 2006 extended to August 31st 2006 by the Department of Soil Quality, Wageningen University.**
- 04 Names of the researchers involved, the names and addresses of the institutes where the research work was carried out.  
**Part I Prof. Dr. W.H. van Riemsdijk, M. Stachowicz, Ir. T Hiemstra, Department of Soil Quality, Wageningen University. Dreijenplein 10 6700 HB Wageningen, The Netherlands.**  
**Part II Dr J. Bruining, Dr.M.I.M Darwish, Department of Civil Engineering en Geosciences, Delft University, Mijnbouwstraat 120 2628 RX Delft, The Netherlands.**
- 05 Short scientific summary (500 words) in English of: main research objective, research methods, results and conclusion.  
***Introduction***  
**Worldwide, arsenic is a major natural contaminant in many aquifers that are used for drinking water production. Groundwater aeration, induced by either injection of water or withdrawal in irrigation practices, may reduce the As concentration, due to interaction with in particular iron oxides. These interactions take place in multi-component environments, which are very heterogeneous. The natural variation restricts generalization of empirically obtained results. However, the chemical interaction on the microscopic scale can be considered as a constant factor, but the microscopic processes require up-scaling and transformation to the macroscopic scale of the measurements to allow interpretation.**  
***Main Objectives***  
**The main objectives of this research are:**  
**1) Characterization of the adsorption behavior of As(III) and As(V) in well-defined (goethite) as well as in ill-defined (HFO) iron oxide systems with a variable solution chemistry focusing on the influence of ions relevant for groundwater systems, e.g. carbonate, phosphate, calcium, magnesium and silicate.**

- 2) Description and prediction of the experimental results with surface complexation models (SCM) based on a mechanistic approach, including information from the microscopic scale.
- 3) To contribute to the understanding of the main factors ruling the binding and release of arsenic under field conditions, and to develop simplified chemistry that can be used in transport models for aeration of ground water.

#### *Research methods*

Experimentally, the adsorption of arsenic by goethite particles was studied as function of pH and loading with batch experiments using single component systems with As(III) and As(V) separately and in its combination. Multi-component systems of As-(H)CO<sub>3</sub>, As-PO<sub>4</sub>, As-Mg, and As-Ca and some combinations were also studied.

Theoretically, the geometries of the microscopic surface complexes of As(III) and As(V) were studied with quantum chemical methods and theory was developed to transform this information to parameters that can be implemented in modern SCM as used in this project, i.e. the charge distribution (CD) model.

#### *Results*

Electrostatic interactions are a dominant factor in the adsorption behavior of arsenic. Location of the ion charge in the interface is found to be crucial. This project shows that the interfacial charge distribution (CD) is directly related to the structure of the surface complexes, in particular the bond lengths. The bond lengths have been assessed with quantum calculations and transformed into an ionic CD value. As shown with new theory, this CD parameter can be used in surface complexation modeling if corrected for orientation of water molecules that are present near the surface. The theoretical results suggest that a calculated CD value is not only applicable to well-defined goethite but also to ill-defined hydrous ferric oxide (HFO). Calculation of the CD value has the advantage that the number of adjustable model parameters is strongly reduced (50%). Calculated CD values have been made available for the relevant surface complexes of As(III), As(V), PO<sub>4</sub>, CO<sub>3</sub> and H<sub>4</sub>SiO<sub>4</sub> and are used in this project.

The adsorption experiments as well as the CD modeling identify phosphate as a major competitive ion in groundwater systems. This phosphorus can be released by reductive dissolution of iron hydroxides and is also produced by mineralization of organic matter. The effect of both, carbonate and alkali earth ions, has found to be more limited, in particular in multi-component systems with PO<sub>4</sub> and As. The model also predicts a limited effect of silicic acid.

Arsenic may also interact with other iron oxide minerals, like ill-defined HFO. In this project, a model has been formulated that links the adsorption behavior of HFO to crystalline goethite. This approach results in a common set of binding parameters for

interaction with particular surface groups of which the relative presence differs between both materials. The model has been tested for the binding of As(III) and As(V).

#### *Conclusions*

The arsenic binding to iron oxide is particularly sensitive to the presence of phosphorous in groundwater systems. The interaction of (H)CO<sub>3</sub>, Ca & Mg ions and silicic acid, is relatively small in As-PO<sub>4</sub> systems. The major effects can be predicted with the CD model for goethite and HFO systems.

06 **Popular summary to inform the general public (1/2 to 2 pages of text) in Dutch.**

The funding organisations of TRIAS (SKB, NWO-ALW and Delft Cluster) want to inform a more general audience about the results of the TRIAS Research projects. That is why we ask you to give an executive summary of the project in a popularising way and written in the Dutch language.

**Wereldwijd wordt Arseen (As) aangetroffen in grondwater aquifers. Het meest uitgesproken voorbeeld hiervan is te vinden in Bangladesh. Over de oorzaak wordt gespeculeerd. Bij de opgestelde hypothesen spelen ijzer (Fe) oxide en organische stof een belangrijke rol. IJzeroxide kan, -beter dan aluminium hydroxide -, arseen binden. De As binding kan worden beïnvloed door de aanwezigheid van andere stoffen die een competitieve binding met de deeltjes kan aangaan waardoor As vrijkomt. Een veel genoemde factor is de mate van aëratie of anaërobie van het sediment, die o.a. bepalend is voor de vorm waarin arseen aanwezig is, d.w.z. As(III) of As(V). Deze beide vormen verschillen in adsorptiegedrag. Reductieprocessen beïnvloeden ook aanwezige ijzeroxiden in een sediment. IJzeroxide kan deels oplossen waarbij Fe(II) bicarbonaat ontstaat. Daarbij komen ook de aan het ijzeroxide gebonden stoffen vrij. Bij natuurlijke ijzeroxiden is dit in het bijzonder fosfaat dat, vanwege de sterke binding, dominant aanwezig is aan het oppervlak, ook als de concentratie in oplossing nog relatief erg laag is. De drijvende kracht achter de reductie van een sediment is de microbiële afbraak van organische stof. Bij deze afbraak worden o.a. fosfaat en ammonium vrijgemaakt. Fosfaat komt ook vrij indien de microbiële afbraak van organische stof aerob verloopt.**

De stoffen zoals fosfaat en bicarbonaat, vrijgekomen in de genoemde processen, zullen een verhoogde competitie aangaan met het nog gebonden arseen, dat daardoor in versterkte mate vrij komt. Omgekeerd, kan arseen worden vastgelegd door de vorming van ijzeroxiden bij aëratie van grondwater, door injectie van zuurstofrijk water of als gevolg van wateronttrekking bij irrigatie. Het onderzoek in dit project is gericht op de bijbehorende chemische processen.

De natuur is uiterst heterogeen. De variatie in de soort en de concentratie van stoffen is groot en belemmert generalisatie in geval van een empirische benadering. Daarentegen is in het systeem het chemische proces op microscopische schaal een constante factor. Dit microscopische proces moet echter geschaald of vertaald worden naar de schaal waarop de metingen en de interpretatie plaatsvinden. Met moderne in-situ spectroscopische technieken kan de microscopische structuur van een stof gebonden aan een oppervlak worden vastgesteld. Een stof kan verschillende complexen vormen. De relatieve bijdrage van deze verschillende complexen kan variëren met bijvoorbeeld de pH of de hoeveelheid van de gebonden stof. De hoeveelheid en de verdeling van de lading in het oppervlaktecomplex speelt hierbij een essentiële rol. In dit project hebben we laten zien dat de ladingsverdeling samenhangt met de structuur van het gevormde oppervlakte complex en met name met de relatieve bindingslengten in het complex. Deze eigenschap beïnvloedt de pH-afhankelijkheid en concentratie-afhankelijk van de adsorptie. De bindingslengten in een oppervlaktecomplex zijn bepaald met kwantumchemische berekeningen. Deze relatieve bindingsafstanden kunnen worden omgezet in een ladingsverdeling die vervolgens kan worden ingepast in het gebruikte oppervlakte-complexeringsmodel waarmee vervolgens de adsorptie kan worden uitgerekend. Toepassing liet echter zien dat er discrepantie was tussen de ladingsverdeling die werd berekend en die werd gevonden uit data-analyse. De afwijking is juist zeer prominent bij een oppervlaktecomplex dat essentieel is in deze studie, n.l. dat van arseniet  $\text{As(III)}$ . Het op deze wijze ontdekte verschijnsel bleek het gevolg van de verandering in de oriëntatie van watermoleculen in de nabijheid van het oppervlak door de vorming van het complex. Gelukkig kon binnen het project een theorie worden ontwikkeld die op zeer eenvoudige wijze hiervoor kan corrigeren. Het nieuwe gereedschap maakt het mogelijk de benodigde ladingsverdeling onafhankelijk vast te stellen waardoor deze niet meer uit data analyse moet worden gevonden. Data zijn slechts nodig ter bepaling van de intrinsieke bindingsconstante. Op dit moment zijn berekende ladingsverdelingen beschikbaar voor de oppervlakte complexen van arseniet, arsenaat, carbonaat, fosfaat, kiezelzuur en sulfaat.

In dit project is de As adsorptie aan goed gedefinieerde ijzeroxidendeeltjes (goethiet) experimenteel bestudeerd voor enkelvoudige systemen met  $\text{As(III)}$  en met  $\text{As(V)}$  afzonderlijk en in combinatie. Ook is het effect van bicarbonaat ( $\text{HCO}_3^-$ ), fosfaat ( $\text{PO}_4^{3-}$ ) magnesium (Mg) en calcium (Ca) op de binding van beide vormen van arseen onderzocht. De adsorptieconstanten zijn bepaald in simpele systemen door toepassing van het CD model. Vervolgens is de competitie van bicarbonaat en fosfaat voorspeld met het CD model en getoetst aan de verzamelde experimentele gegevens. Met

het CD model werd een goede overeenkomst gevonden tussen voorspelling en experiment. Dit is ook gevonden voor de interactie met Ca en Mg.

Het model en de data zijn gebruikt om de hoofdfactoren vast te stellen die de adsorptie van arseniet ( $\text{As(OH)}_3$ ) en arsenaat ( $\text{AsO}_4$ ) aan ijzeroxide deeltjes reguleren bij condities relevant voor grondwater. De analyse toont aan dat fosfaat een dominant ion is in het reguleren van het adsorptiegedrag van zowel arseniet als arsenaat. De effecten van bicarbonaat ionen zijn gering. Dit kan ook worden gezegd voor opgeloste calcium en magnesium ionen. Voorspelling van de invloed van silica in het natuurlijke concentratie bereik wijst op een geringe invloed in  $\text{As-PO}_4$  systemen.

Arseen kan reageren met verschillende typen van ijzeroxiden. In dit project is o.a. aandacht besteed aan de binding van arseen aan amorf ijzeroxide (HFO), dat door velen wordt beschouwd als de reactieve ijzerfractie in sedimenten. HFO bestaat uit extreem kleine deeltjes met een zeer groot reactief oppervlak per massa-eenheid. De basisstructuur van HFO vertoont belangrijke overeenkomsten met het nauwkeurig bestudeerde goethiet en de typen van oppervlaktegroepen zijn mogelijk zeer vergelijkbaar. Een belangrijk verschil is de verhouding waarin deze groepen voorkomen op beide materialen. Een gevoeligheidsanalyse heeft bovendien aannemelijk gemaakt dat de berekende ladingverdelingen ook toepasbaar moeten zijn op dit amorf ijzer oxide. In dit project is daarom een model ontwikkeld dat de beschrijving van de reactiviteit van beide materialen verbindt. Het leidt tot een gemeenschappelijke set van parameters. Slechts de verhouding in type van oppervlaktegroepen is verschillend. Het model is succesvol toegepast op de adsorptie van  $\text{As(III)}$  en  $\text{As(V)}$ . Niet onbelangrijk is te vermelden dat recent op grond van Mössbauer spectroscopie gesteld wordt dat in een omvangrijke serie onderzochte sedimenten de ijzeroxide-fractie bestaat uit nano goethiet en niet HFO.

#### Conclusies

Experimentele karakterisering en modelering van het adsorptie gedrag van  $\text{As(III)}$  en  $\text{As(V)}$  in ijzeroxide systemen met een variabele samenstelling van de oplossing, toont aan dat voor condities die relevant zijn voor grondwatersystemen, fosfaat, meer dan bicarbonaat en kiezelzuur, het adsorptiegedrag van beide vormen van arseen bepalen. Deze hoofdfactoren zijn modelmatig gekwantificeerd in een modern oppervlaktecomplexeringsmodel waarin de ladingverdeling en bindingslengte een centrale rol spelen.

De modellering maakt het mogelijk om in een eerste orde benadering berekeningen te doen over de verwachte variatie in de binding en het in oplossing gaan van arseen bij wisseling van de biogeochemische grondwatercondities. Het model kan o.a. worden

toegepast als gereedschap in de beschrijving van de mobiliteit van arseen in natuurlijke systemen en worden gekoppeld aan transportmodellen die de effecten van aëratie van grondwater systemen simuleert.

- 07 What impact and relevance has this project's outcome for practicing soil protection and/or soil remediation? Again, please motivate.

**The main factors that determined the binding of Arsenic to oxide particles have been identified and quantified. This enables a first order semi-quantitative calculation of the expected variation in the binding and release of As(III) and Av(V) for changing conditions in aquifers. The model can be applied in design of soil and groundwater remediation. The quantification in a chemical model enables its use as a tool in the description of the mobility in natural systems by coupling to transport models or by calculation of the expected  $K_d$  values. Calibration on natural samples can improve the quality of such an approach. Such calculations may also contribute to soil protection policies.**

- 08 Please list the presentations held in connection to this project  
**2-3 June 2004 'Soil & Water' Netherlands Scientific Symposium 'Arsenic and Bicarbonate Adsorption on Goethite' poster TRIAS and SSEO, Zeist, Netherlands**

**23-26 January 2005 1st International Conference on Environmental Science and Technology, 'Arsenic and Bicarbonate Adsorption on Goethite' presentation, American Academy of Sciences, New Orleans, Louisiana, USA.**

**4-5 June 2005 'Soil & Water' Netherlands Scientific Symposium 'Arsenic adsorption on goethite' presentation, TRIAS and SSEO, Zeist, Netherlands**

**26-30 March 2006 'Adsorption of Metals to Geomedia', 231st ACS National Meeting, 'Arsenic adsorption. From molecular level to field scale' presentation, Atlanta, Georgia, USA**

- 09 Please list publications (published and submitted) in connection to this project. Please indicate publication took place in either a refereed journal, a non-refereed journal (incl. conference proceedings); whether it was published as a chapter of a book, as a monography or as a dissertation.

**Refereed Journals:**

**T. Hiemstra, W.H. van Riemsdijk**

**On the relationship between charge distribution, surface hydration, and the structure of the interface of metal hydroxides. Journal of Colloid and Interface Science 301 (1-18) 2006.**

**M. Stachowicz, T. Hiemstra, W.H. van Riemsdijk**  
**Surface speciation of As(III) and As(V) in relation to charge distribution. Journal of Colloid and Interface Science 302 (62-75) 2006.**

**To be submitted:**

**M. Stachowicz, T. Hiemstra, W.H. van Riemsdijk,**  
**The arsenic-bicarbonate interaction on goethite particles. To be submitted to Environmental Science and Technology**

**M. Stachowicz, T. Hiemstra, W.H. van Riemsdijk**  
**Linking the arsenic adsorption on goethite and amorphous iron (hydr)oxide. To be submitted to Geochimica Cosmochimica Acta**

**Planned:**

**M. Stachowicz, T. Hiemstra, W.H. van Riemsdijk. D.G. Kinniburgh.**  
**Multi-component interaction with Arsenate and Arsenite on iron oxides: towards field conditions.**

**Thesis**

**M. Stachowicz. Preliminary title: Solubility of Arsenic in multi-components systems: From the microscopic to the macroscopic scale.**

- 10 Please list Patent applications or other professional products (including contracts, articles in the popular media, contributions to documentaries or scientific television or radio programs, CD-ROMS, DVD or other (electronic) media).

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Part II

Detailed information, primarily intended for administrative and statistical use by NWO-ALW

- 11a Under item 5 you have filled in the main research objectives. Please list all the original research objectives as indicated in the project's application and both indicate as well as motivate, to what extent these goals were realised, and/or whether the original research objectives had to be adapted.

**The main original objectives of the project as formulated under 5) are:**

**1) Characterization of the adsorption behavior of As(III) and As(V) in well-defined (goethite) as well as in ill-defined (HFO) iron oxide systems with a variable solution chemistry focusing on the influence of ions relevant for groundwater systems, e.g. carbonate, phosphate, calcium, magnesium and silicate.**

*The goal is fully achieved for the well-defined systems. For the first time in literature, the internal As(III) en As(V) competition on goethite has been measured as well as the competition of both As species with carbonate and the competition of As(III) with phosphate.*

*Originally, an experimental study of the interaction of As with freshly formed iron oxides was also planned. This has not been realized. Three important reasons can be given. 1) Experimental problems and technical failures of analytical equipment during the first year have considerably delayed the progress of the project. 2) The experimental setup of the counterpart has changed, making this approach less relevant. 3) During the course of the project, new literature data have pointed to the relevance of nanogoethite rather than HFO in sediments.*

**2) Description and prediction of the experimental results with surface complexation models (SCM) based on a mechanistic approach, including information from the microscopic scale.**

*The goal is achieved better than expected. A major breakthrough has been realized with new fundamental insight in the adsorption behavior of ions in general, in particular the role of the structure of surface complexes and the role of interfacial water. These*

*developments are well beyond the scope of this geochemically oriented project and are considered as highly relevant for surface sciences in general and for many applications in colloid chemistry and environmental sciences.*

3) To contribute to the understanding of the main factors ruling the binding and release of arsenic under field conditions, and to develop simplified chemistry that can be used in models for aeration of groundwater.

*Both, the experimental results and the test of the SCM modeling, enable the prediction of variation in the release of arsenic through desorption from iron oxides upon changes in the groundwater conditions and chemical composition. Phosphate is identified as a major ruling factor rather than other oxyanions that have been suggested in literature. Phosphate is suggested to be released due to biogeochemical changes in the sediments in which iron and organic matter may play a role. In principle, the model may be implemented in solute transport models of various scales. No simplified version of the model is formulated since application in the transport modeling approaches of the counterpart is at present not (yet) relevant.*

11b Did the project also include objectives which were not scientific? For instance, did the project also intend to apply research results, or strengthen the economic position of certain businesses?

**The project intended to increase the insight in the main factors that regulate the binding of As and to quantify this chemistry in a SCM model. This knowledge is relevant for the development of subsurface aeration and cleaning technology for drinking water production. This perspective was a driving force to provide tools that may be used in order to develop technological solutions.**

11c Did the project's aims include the expanding the (international) network of contacts (at what level), providing education, improve communication, serve as input for policy drafting or policy decisions, etc.? Please motivate.

**This was not an explicit goal since we have already a strong international network in this area. We had during the period two visiting professors from the USA in the group. Both came to work with us because of our expertise in the area of ion adsorption in environmental systems. One of them did work that was very closely related to the work of the TRIAS project.**

12 Do the results obtained match the original objectives? Please provide a short motivation why they do or don't.

**Yes, as motivated in 11a**

- 13 Will the results of this project serve as input for an initiative integrating/and or generalizing input from several projects, for instance into a (numerical) model, or into more understanding at the higher/system level? If so, was this intended and optimised from the beginning or did it occur by chance/spontaneous? Please elaborate.

**The project has a counterpart in Delft University who intends to develop a model that may calculate the transport of oxygen, iron, and arsenate in a groundwater aquifer in case of subsurface aeration of an aquifer. Experimental difficulties and a change of researchers involved gave that project an new direction which has been focusing mainly on the in-situ (trans)formation of iron oxides due to injection of oxygen-rich water. It has not been possible to study the corresponding interaction with As. Implementation of our surface chemical approach is therefore premature at this moment. It is noticed that the CD model is or will be soon implemented in codes for coupled-reactive transport of respectively ECOSAT and PhreeqC. The latter code is widely used by geo-hydrologists.**

- 14 To what extent has this research project pointed the way in which further research has to be undertaken? Please motivate the guiding role perceived.

**Unpublished recent experimental data in which the above CD model has been applied to soils have indicated that the apparent reactive surface area of these soils and the capacity to bind ions like phosphate are positively correlated with the amount of soil organic matter. The reasons for this finding are not yet clear, but unknown particle-organic matter interactions may play a role. This gap in knowledge can be a large obstacle in the application of the model to field systems and therefore needs to be resolved.**

**A "leitmotif" of our scientific approach is that nature is highly heterogeneous in chemical composition but that corresponding interactions are ruled by molecular-based interactions. These interactions need scaling from the molecular level to the macroscopic scale. In our opinion, this has yet been only partly achieved. The scaling requires at least two different steps. The developments of a) tools that link the microscopic scale to the macroscopic scale in well-defined systems that serve as proxy of the natural environment and b) tools that link this knowledge to natural materials. With respect to the first, we have made major steps forward as mentioned above in point 5, 6, and 11a-2. A major missing link is the lack of tools to model the interaction of organic matter with the inorganic elements at the surface of oxide particles and in addition a sensitive determination**

**of the type of reactive surfaces and the surface area. Based on the above mentioned unpublished results, it is hypothesized that organic matter may play a conclusive role in formation of reactive metal oxide (nano)particles and corresponding reactive surface area of natural oxide materials. The extent and conditions for the nano-particle formation are unclear but highly relevant, since they determine the reactive surface area of the soil oxide fraction.**

- 15 In what way, and to what extent, are the results reached of importance to research done by others? Please motivate or elaborate.

**As mentioned in 11a-2, this project has generated fundamental knowledge on the binding of ions to surface in general and therefore it is of great interest for surface sciences, catalysis, physical and colloid chemistry, but also environmental sciences including geo-, soil, water and marine chemistry.**

**Our charge distribution model has a 25 year history of development in which we have reached regularly (1981-1989-1996-2006) new major steps forward that we consider as breakthroughs. Our work as one of the leading scientists in this research area has reached the attention of a large range of other scientists working in various fields. The new step in the development of the theory, realized in this project, will stimulate these researchers in contributing to and testing of this theory or in application of it in their settings.**

- 16 Are you aware of any essential gaps or obstacles standing in the way of applying the results from your research project? Please elaborate.

**See 14**

- 17 Which new research questions were generated through this project?  
Were these new questions addressed within this research project itself?  
Or will these new questions, or the results from your research project lead to new research projects (to be) funded by either 1<sup>st</sup>, 2<sup>nd</sup>, or 3<sup>rd</sup> category funding or funding through international funding agencies? Please elaborate.

**See 11a-2 and 14**

- 18 In what way did you link this project to other projects within the TRIAS-program or link it to projects outside TRIAS? Did you cooperate within the TRIAS-program and did this cooperation lead to integrated results?

**No explicit linkages with projects other than that of our counterparts have been made.**

- 19 Can you elaborate on the impact on society as a whole of your results (e.g. societal organisations, NGO's, businesses, schools, municipal authorities, etc.)

**The project has a rather fundamental approach that has achieved its scientific goals and is of direct relevance for other researches (see 15). The theoretical developments will contribute to valuable practical applications, but cannot be pointed out explicitly.**

- 20 What actions were taken to disseminate the results in the direction of the general public, besides the usual scientific channels?

**The models developed within the scientific group have reached qualities that enable application in soil protection as has been communicated recently in Dutch in "Bodem": "Basis voor normstelling voor bodem en water: een fundamenteel Bodemchemisch perspectief" .**

- 21 Have the researchers involved obtained a new position or employment after the project came to an end? Please specify and elaborate!

**Not yet**

Wageningen, October 2006.