Asian Development Bank

Greater Mekong Subregion

Capacity Building for Efficient Utilization of Biomass for Bioenergy & Food Security in the GMS [TA7833-REG]

Output 4: Knowledge Product Series

4b: Analysis of Biochar Samples from the Greater Mekong Subregion

August 2014

Landell Mills
DEVELOPMENT CONSULTANTS

nexus Carbon for Development

KEY DATA

Name of Project:	Capacity Building for Efficient Utilization of Biomass for Bioenergy & Food Security in the GMS TA-7833 REG
Contractor:	Landell Mills Limited (LML), Bryer-Ash Business Park, Trowbridge, Wiltshire, BA14 8HE, UK Tel: +44 1225 763777 (www.landell-mills.com) in consortium with: Nexus Carbon for Development (Nexus), #33 E3 Sothearos Blvd, Corner St. #178, Phnom Penh, CAMBODIA (www.nexus-c4d.org)
Contracting Authority:	Asian Development Bank (ADB)
Start/End Date:	15 Dec 2011 - 15 June 2015
Budget:	N/A
Beneficiary:	Ministries of Agriculture of Cambodia, Lao PDR and Viet Nam
Location:	Greater Mekong Subregion, incl. Cambodia, Lao PDR and Viet Nam

QUALITY ASSURANCE STATEMENT

Version	Status	Date
Output 4: Knowledge Product Series - KP#04b: Analysis of Biochar Samples from the GMS	Final	28/08/2014

	Name	**Position**	**Date**
Prepared by:	Dr. Simon Shackley	Biomass Specialist	
Checked by:	Mr. Simon Foxwell	Director, Asia/Pacific	

ACKNOWLEDGEMENTS

Report submitted by
LANDELL MILLS LTD

CONTENTS

FIGURES

ACRONYMS

ADB	Asian Development Bank
BCFs	Biochar Compound Fertilisers
BQM	Biochar Quality Mandate
BSC	Bamboo Stem Char
CAE	Carbon Abatement Efficiency
CAM	Cambodian Biochar Samples
CLV	Cambodia, Lao PDR and Viet Nam
CSF	Carbon Stability Factor
DAE	Department of Agricultural Engineering,
EBC	The European Biochar Certificate
ESG	Environmental Scientifics Group Ltd
GMS	Greater Mekong Sub-Region
H/C	Hydrogen / Carbon
HHT	High Heating Temperature
IARC	International Agency for Research on Cancer
IBI	International Biochar Initiative
LOD	Limit of Detection
LOI	Loss On Ignition
MAFF	Ministry of Agriculture, Fisheries and Food, UK
MARD	Ministry of Agriculture and Rural Development, Vietnam
MDA	Modified Dry Ashing
O/C	Oxygen / Carbon
OELs	Occupational Exposure Limits
OHS	Occupational Health And Safety
PAHs	Polycyclic Aromatic Hydrocarbons
PAS	Publicly Available Specification
RHC VN	Rice Husk Char from Viet Nam
RHB	Rice Husk Biochar
RSC	Rice Straw Char
SFRI	Soil & Fertilizer Research Institute (Viet Nam)
TLUD	Top-Lit Updraft
UEDIN	University Of Edinburgh
US EPA	US Environmental Protection Agency
VN	Viet Nam
XRD	X-Ray Diffraction

1. EXECUTIVE SUMMARY

1.   A number of intiatives are promoting the idea of *'biochar compound fertilisers' (BCFs)* in climate-friendly agricultural systems. BCFs are defined as: '*Combinations of biochar with organic and inorganic constitutents, either mixed or combined into granules or pellets*.' In order to evaluate BCFs it is necessary to understand the properties of their individual constituents.

2.   This paper presents data on a set of biochar samples typical of those which might be used in the Greater Mekong Subregion (GMS) as a constitutent of BCFs or as a pure biochar soil amendment. The biochar samples used are rice husks, rice straw, bamboo, acacia, maize straw and empty maize cobs.

3.   The analysis finds that all nine samples of biochar from the GMS are safe to use in agricultural soils. All samples meet the quality threshold requirements of voluntary biochar standards published by the International Biochar Initiative, European Biochar Certificate and Biochar Quality Mandate. These quality thresholds relate to potentially toxic elements such as heavy metals and persistent organic pollutants (e.g. polycyclic aromatic hydrocarbons).

4.   Four of the biochar samples were analysed to test whether they meet the technical definition of biochar according to the three voluntary standards. As the temperature of pyrolysis increases (from 350°C to 650°C), the extent of carbonization also increases and the stability of the carbon in the biochar is greater. All four samples tested showed evidence of carbonization such that they can be clearly classified as biochar. There was insufficient supply of the other five biochar samples to perform this additional analysis.

5.   The total beneficial nutrients in the biochar samples were measured, including: calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn) and phosphorus (P). K is the most commonly extractable (and therefore available) element from the biochar samples, followed by Ca. Biochar derived from maize feedstocks is relatively high in P and Mg.

6.   Conventional soil science extraction methods tend to underestimate the quantities of total beneficiail nutrients in biochar compared to biochar-specific methods. Leaching experiments in soil columns were undertaken in order to measure how much of the total nutrients would be available to plants. In most cases, the total nutrients are not all plant-available. For example, there is a low total availability of Ca and Mg. There is 10-50% availability of P in most circumstances and 30-90% availability of K. There are a few examples where more nutrient was leached-out than was measured in the total, e.g. for P and K; the reason for this phenomenon is not fully understood.

7.   A method to simulate the stability of the biochar carbon over 100 years was undertaken and used to calculate the climate-change relevant carbon storage potential of each biochar sample. The biochar carbon storage potential per ton of biochar ranged from 0.25 tons of carbon (C) per ton of rice husk biochar, to 0.8 tons C per ton of acacia, bamboo and maize cob biochar.

8.   When heated to temperatures $>800^{\circ}$C, high silica-containing feedstocks such as rice husk and rice straw have the potential to convert from an amorphous to a crystalline form. Crystalline silica – in particular *cristobalite* – can cause a serious lung disease called silicosis which is linked to cancer.

9.   Rice husk biochar produced by gasification at temperatures $>900^{\circ}$C was analyzed using X-Ray Diffraction (XRD) and shown to contain 8% cristobalite by weight with an average size of 10nm. Such rice husk biochar is dangerous to human operators who are exposed to it and appropriate health and safety measures must be taken, in particular use of personal respirators designed to filter out the tiny particles.

10.   Rice husk biochar produced by pyrolysis is produced at a much lower conversion temperature range of 450-550°C. Either Cristobalite does not form at all or else forms in very small amounts that are not dangerous, although it appears that localized heating within reactors can occasionally be appreciably higher so careful monitoring of internal temperatures is required.

11.   The results presented here characterize the biochar constituents which make up BCFs. The biochar materials sampled are all safe to use and contain beneficial, if modest, amounts of nutrients. Use of gasifier rice husk as a constituent of BCFs is not recommended without undertaking special safety precautions to protect again silicosis.

2. SAMPLE SOURCING

12. Four samples were obtained from the 'Chiveak Tyung' Cambodian (CAM) stove – which is a Top-Lit Updraft (TLUD) design, adapted from existing models, with a capacity of approxiately 35kg feedstock. Four feedstocks were tested: rice straw, rice husk, corn (maize) cobs and corn straw. The precise source of each feedstock is not known. The High Heating Temperature (HHT) in the kiln is estimated at approximately $450^{o}C$ to $550^{o}C$ but no actual measurements have been undertaken.

13. Five samples were obtained from Viet Nam (VN) produced in a TLUD drum kiln designed by Professor Stephen Joseph and Mr Khoi. The HTT of the kiln was reporting as $750^{o}C$, in the upper compartment declining to $450^{o}C$ in the part of the kiln where the biochar is produced. Two sources of rice straw feedstock were used, one from research site and one commercial, in addition to rice husk; bamboo stem and *acacia* stem feedstock.

14. The Viet Namese biomass was acquired from farmers who participated in the biochar research led by Dr Vinh and Soils and Fertilizer Research Institute (SFRI) colleagues in Thai Nguyen and Thanh Hoa provinces. The rice straw was kept in households for feeding buffalo, while the acacia wood and bamboo were used for cooking. Two different rice varieties were grown – one based on farmers' own seed (rice straw sample one) and the other a hybrid which required higher levels of synthetic fertilizer (urea and potassium) (rice straw sample two). The precise amounts of fertilizers added in each case to the rice crop is not known and the actual amounts of straw removed from the field also appears to differ (with some farmers removing most of the straw; others about ½ of the above-ground straw). Equivalent information on the source of the Cambodian feed stocks is not available.

3.   SAMPLE TESTING

15.   The samples were designated as listed in *Table 1*. Details of the sampling methods and replications are explained under each section heading.

16.   Since biochar is a relatively novel material with some unusual properties, existing accredited soil science laboratory methods are not always appropriate and adapted methods were applied. As yet, there are no accredited analytical methods for biochar specifically, though the scientific community is currently developing these. For some tests, we commissioned two different methods in order to allow for a comparison of the accredited soil science method with the modified method proposed by the biochar research community. The two laboratories used were: Environmental Scientifics Group Ltd. (ESG), and; University of Edinburgh (UEDIN), School of GeoSciences.

3.1   ASH CONTENT

17.   The ash content of the biochar samples is show in *Table 1* and *Figure 1*. Differences between the ESG and UEDIN methods are not large, but due to small quantities available to UEDIN, the ESG results are considered to be higher quality.

Table 1: Sample ID and ash content by laboratories: ESG Ltd. & UEDIN (Loss on Ignition method)

Sample	Rice straw char 1	Rice husk char	Bamboo stem char	Acacia stem char	Rice straw char2	Rice straw char	Maize cob char	Maize straw char	Rice husk char
Designation	RSC VN	RHC VN	BSC VN	ASC VN	RSC2 VN	RSC Cam	MCC Cam	MSC Cam	RHC Cam
Source	Soil and Fertilizer Research Institute, Viet Nam					DAE, MAFF, Cambodia			
Quantity (g)	22	24	19	20	19	35.5	70	51	83
Ash content (% DW) (ESG)	42	45	9	4	43	35	8	11	42
Ash content (% DW) (UEDIN) (less accurate than ESG)	48	57	8	4	46	36	3	11	43

Figure 1: Ash content of biochar samples (ESG Ltd. & UEDIN)

18.   As expected, ash content is much higher in arable crop residues than in woody residues, indicating higher nutrient content in both straw feedstocks and associated chars. The ash content of the rice husk char (RHC) appears to be lower (42-45%) than in previous studies of gasifier rice husk biochar (Shackley et al., 2012), where a range of 58-67% was measured. This is understandable since pyrolysis occurs at a lower

temperature than gasification and hence more organic material remains during pyrolysis compared
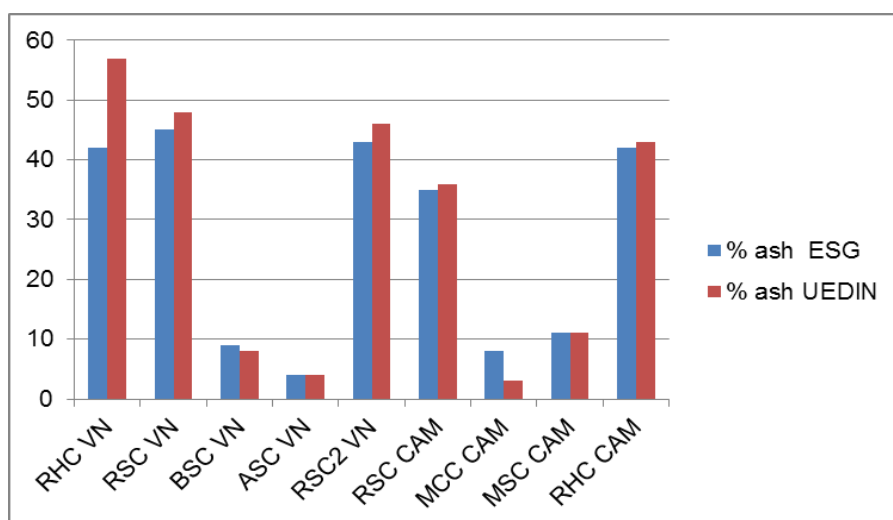
to gasification and ash concentrates in the gasifier char. It is not known why the Cambodian RSC are lower in ash than those from Viet Nam, but it might be due to lower pyrolysis temperatures, though lack of temperature measurements mean that we cannot be sure.

3.2   ELEMENTAL ANALYSIS

19.   Elemental analysis includes measures of the total quantities of four key elements: carbon (C); hydogen (H); nitrogen (N), and; sulfur (S).

20.   C, H, N, S and moisture content was determined only for the four CAM biochar samples. This is because there was not sufficient material for elemental analysis of the five VN samples to be undertaken. As is usually the convention, oxygen was calculated by difference and the results are plotted in *Figure 2* on a Van Krevelen diagram, which plots H/C ratio versus O/C ratio. Woody lignin materials have a H/C ratio of c. 0.8-1.4 and an O/C ratio of c. 0.4-0.6. The conventional definition of biochar is that the H/C ratio should be ≤ 0.7 and O/C ratio ≤ 0.4 (see the box at bottom left-hand corner of *Figure 2*). The four CAM samples have all undergone thorough carbonisation and fulfill the definition of biochar.

21.   The accelerated ageing method (Section 10) provides higher values of stable carbon in the chars (e.g. 83.31% for corn cob char compared to 80.44% from ESG; 74.35% for maize straw char cf. with 70.56% ESG), though the differences are minimal between rice husk and straw char samples.

22.   Total carbon as determined by elemental analysis should, in principle, be higher than stable carbon via accelerated ageing, so the differences reported here are likely to be due to differences in: Loss on Ignition methods compared to accelerated aging method, and to difference in the precise laboratory procedures followed.

Figure 2: Elemental Analysis results expressed as H/C versus O/C ratio

Page 5
Analysis of GMS Biochar Samples / ADB TA7833-REG / July 2014
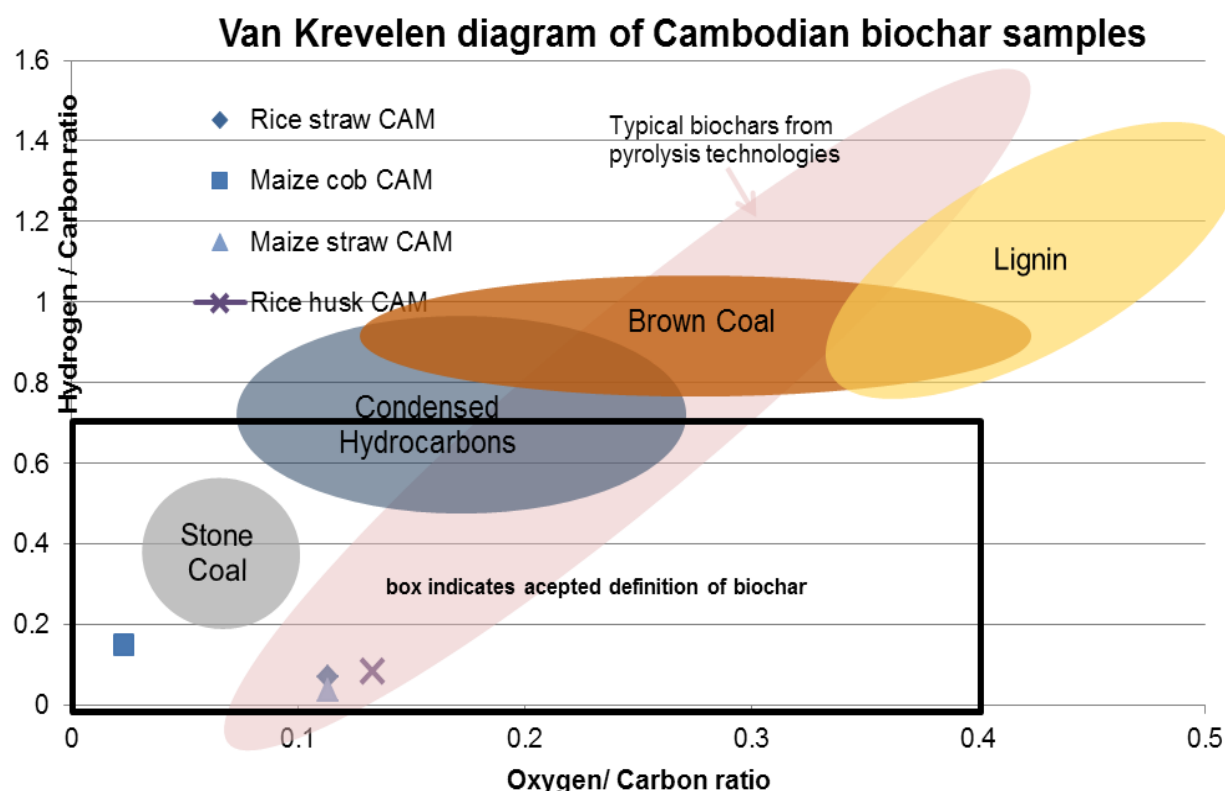
3.3   IMPACT OF PYROLYSIS PRODUCTION CONDITIONS UPON STABILITY OF THE RICE HUSK BIOCHAR

23.   An experimental bench-top pyrolysis unit was used at UEDIN to examine the stability of biochar-carbon in RHC as a function of the high heating temperature (HHT) of pyrolysis. The results are show in *Figure 3*.

24.   The RHC produced at 350°C does not qualify as biochar since the H/C ratio is somewhat too high (according to IBI, EBC and BQM guidelines and Schimmelpfenning and Glaser (2012)). There is an inverse relationship between H/C v. O/C ratio and the pyrolysis high heating temperature (HHT), as illustrated in *Figure 4.* This is consistent with our understanding of pyrolysis since at the HHT, more non-carbon atoms, including H, will be disproportionately removed (compared to carbon) as volatile molecules from the biomass in the process known as carbonization.

Figure 3: Biochar Carbon Stability in Rice Husk Biochar as a function of Pyrolysis Temperature
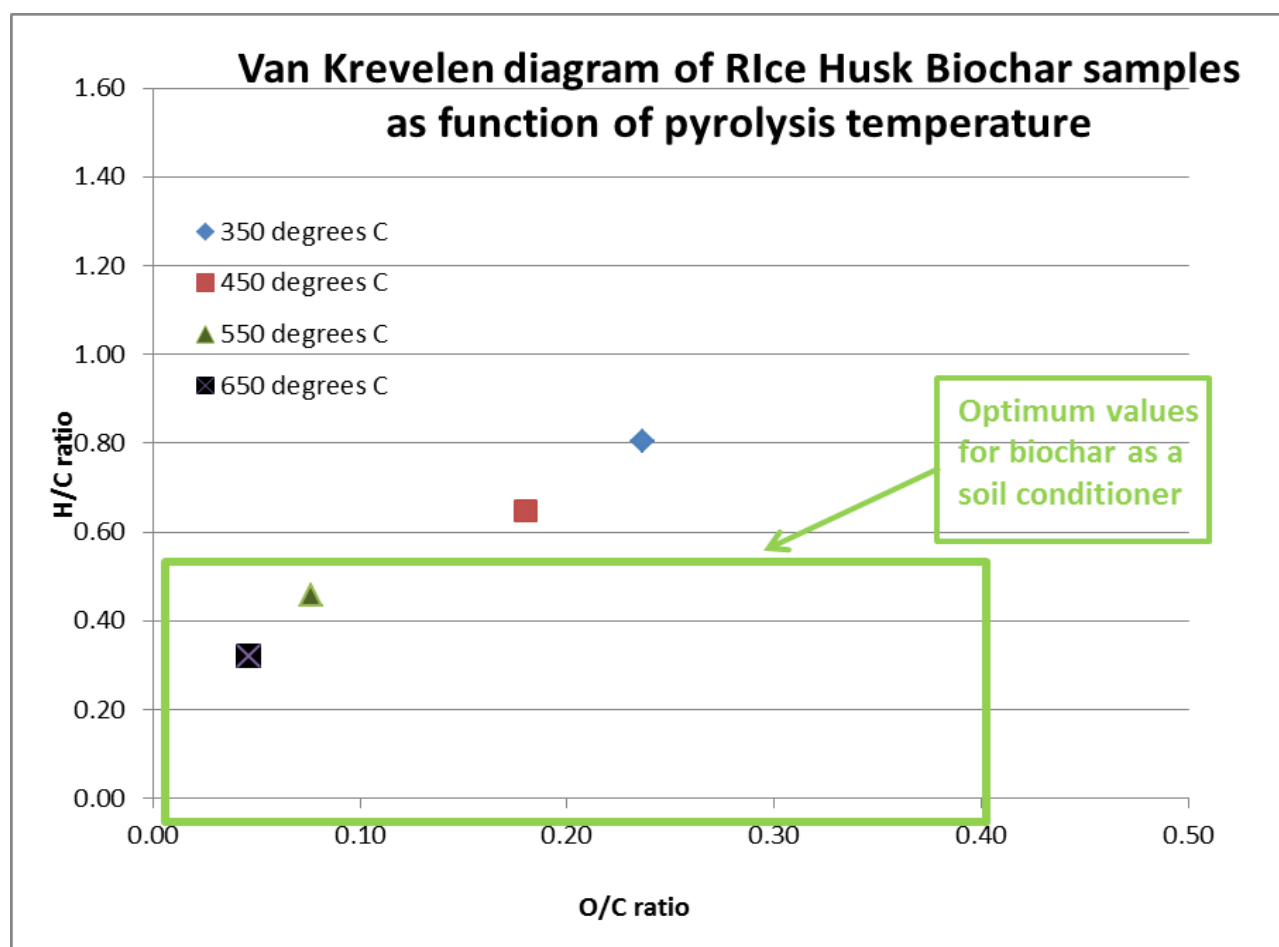
Source: derived from data in Crombie et al., 2013

25.   As the HTT of pyrolysis increases the yield of biochar decreases as shown in *Figure 5* (blue line). However, there is a marked increase in the stability of biochar (as measured by the accelerated ageing method described in Section 10) (red line) at 450°C, with a further inflection point at around 550°C. The traditional way of measuring fixed carbon, e.g. for the purposes of assuring the quality of charcoal as a fuel, uses so-called proximate analysis. The green line in *Figure 5* shows that proximate analysis underestimates the recalcitrance of carbon in biochar compared to accelerated ageing and hence may not be an appropriate analytical method to use for measuring biochar stability.

Figure 4: Inverse relationship between H/C ratio in rice husk char produced at different temperatures
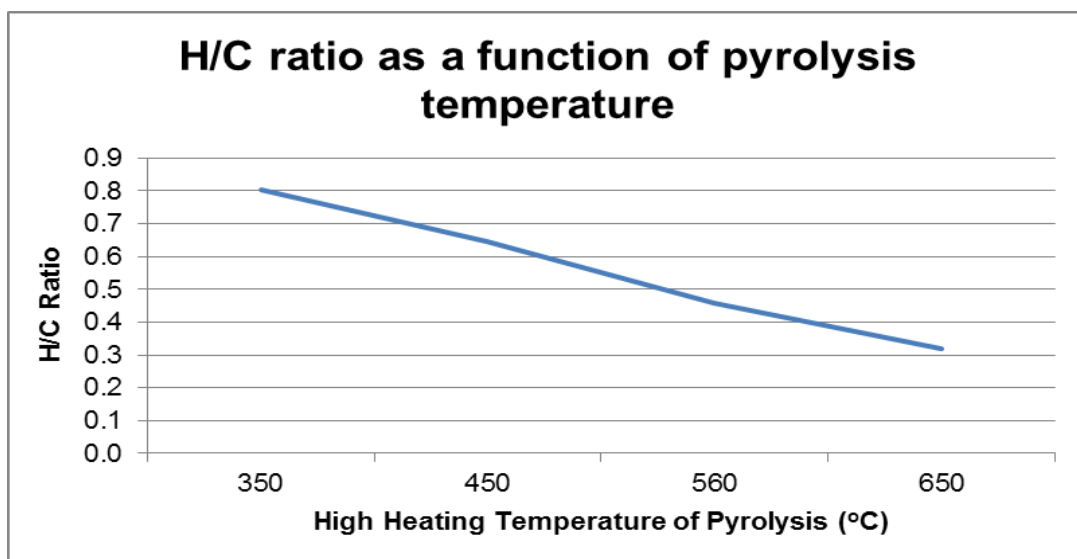
Source: derived from data in Crombie et al., 2013

Figure 5: Relationship between percentages of recalcitrant carbon using accelerated aging methods (red line) versus fixed carbon (proximate analysis – green line)
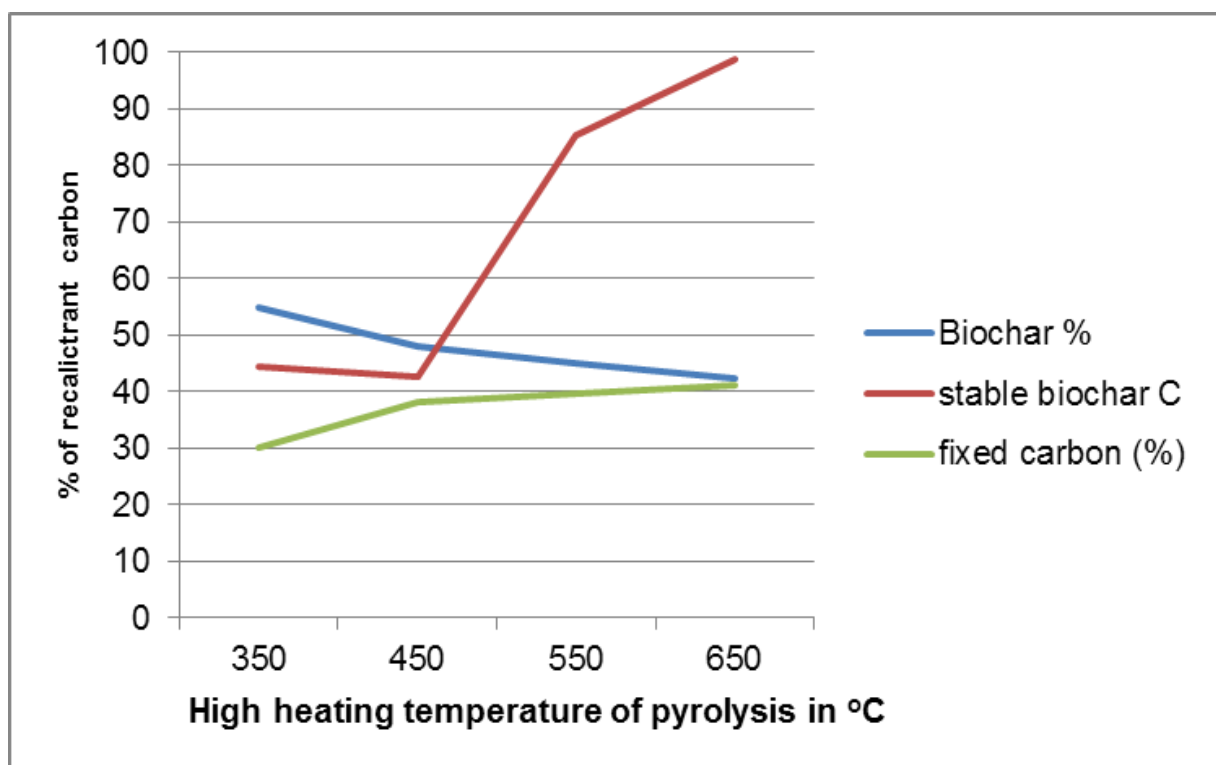
Source: derived from data in Crombie et al., 2013

3.4   POTENTIAL TOXICANT

26.   There are two main types of toxicants that can be associated with biochar. Heavy metals such as cadmium, zinc, arsenic, lead, copper and so on. In too high concentrations in soils, they are selectively absorbed by plants and end up in the food chain where they may be toxic to humans and animals which eat the food. Results for heavy metals from the nine samples tested are shown in *Figure 6.*

27.   The second type of toxicant is organic molecules called polycyclic aromatic hydrocarbons (PAHs).The convention is to measure the 16 PAHs ($\sum$16 PAHs) considered to the most toxic by the US Environmental Protection Agency (US EPA).

28.   Based on these values, all samples pass the standard quality threshold set for biochar by three separate voluntary standards: International Biochar Initiative (IBI); Biochar Quality Mandate (BQM)), and; European Biochar Certificate (EBC). The IBI uses a single threshold, while both the EBC and BQM have a two-tier system. The EBC with *basic* and *premium* quality biochar and the BQM with *standard* and *high* quality biochar designations. In both cases, the two grades associated with different maximum permissible limits (MPLs), with lower toxicant levels in the high or premium classifications. The MPLs for the three voluntary standards are given in *Table 2.*

29.   Not all the samples qualify as the High Quality BQM biochar with respect to arsenic. Bamboo stem char (BSC VN) does not qualify as High Quality BQM biochar with respect to arsenic, chromium and molybdenum, while rice hush char (RHC VN) does not quality as High Quality BQM biochar with respect to molybdenum.

30.   The PAHs extraction method used a relatively less-aggressive method (dicholoromethane solvent with sonication extraction). A more aggressive method (such as toluene with Accelerated Solvent Extraction) would likely have extracted more PAHs (Hilber et al. 2012). However, the appropriate aggressiveness of the extraction is still a moot point for soil scientists. Super-aggressive extractions will inevitably remove a lot of PAHs that would be unlikely to exit from the biochar, at least in the shorter-term, by which time microbial degradation should be at work. Furthermore, the total PAHs extracted from biochar are different from the bio-available PAHs and most experts consider that bio-available amounts will be lower than the totals (Hale et al., 2012).

Table 2: Standards for Potential Toxicants in Biochar (sources: IBI (2012), EBC (2012) and BQM (2014) and Publicly Available Specification (PAS100) for composts

PTE	IBI MPL (mg/kg dry matter)	PAS 100 (for composts) MPL (mg/kg dry matter)	European Biochar Certificate basic biochar (mg/kg dry matter)	European Biochar Certificate premium biochar (mg/kg dry matter)	BQM, High Grade Quality (mg/kg)	BQM, Standard Grade Quality (mg/kg)
Arsenic	12-100	n/a	n/a	n/a	10	100
Cadmium	1.4-39	1.5	1.5	1	3	39
Chromium	64-100	100	90	80	15	100
Copper	63-1500	200	100	100	40	1500
Lead	70-500	200	150	120	60	500
Mercury	1 to 17	1	1	1	1	17
Manganese	n/a	n/a	n/a	n/a	3500	
Molybdenum	5 to 75	n/a	n/a	n/a	10	75
Nickel	47-600	50	50	30	10	600
Selenium	1-100	n/a	n/a	n/a	5	100
Zinc	200-2800	400	400	400	150	2800
$\sum$16 PAHs	6 to 20	n/a	12	4	20	20

In conclusion, all the nine biochars can be designated as clean biochars that can be safely used in soils.

Figure 6: Levels of potential toxicants (heavy metals and PAHs) in biochar samples (y axis units are in mgkg^{-1}
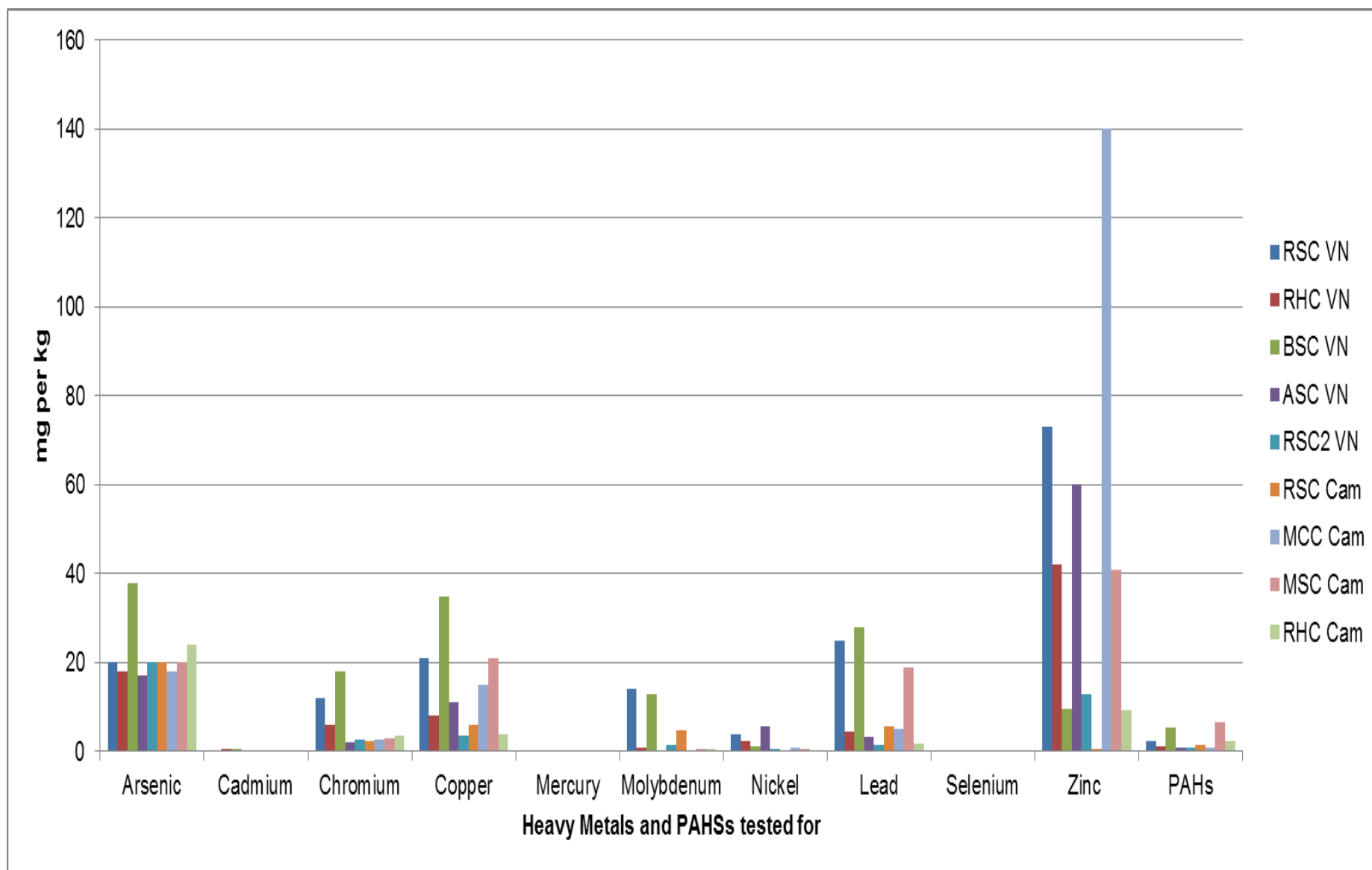
3.5 LEVELS OF TOTAL BENEFICIAL ELEMENTS

31.   Beneficial elements are shown in *Table 3* and *Figure 7* for calcium, potassium, magnesium, manganese and phosphorus for the ESG value followed by the UEDIN value in *Figure 8.* It can be seen that the total extracted values can vary by large amounts due to different extraction methods. The ESG method uses aqua regia extraction at 750°C for 4 hours which is a conventional method used by soil science laboratories. The UEDIN extraction follows Enders & Lehmann (2012) – modified dry ashing (MDA) - which is a more biochar-specific method and involves a single dry ashing at a lower temperature (500°C) for 8 hours, following by wet digestion in HNO_3.

32.   *Figure 9* compares the conventional with the MDA extraction methods. The conventional method produces lower extraction levels than the MDA method. This is especially the case for potassium (K) and, in one case, for Magnesium (Mg). Note, however, that there is no consistent pattern between biochars produced from different feedstocks. e.g., for maize (corn) cob char, the conventional extraction method gave a slight increase in K, while for acacia wood biochar, the MDA gave a 450% increased K extraction. In the case of Magnesium (Mg), there was a 20 – 60% decrease in extraction from two rice straw char samples from Viet Nam when the conventional method was used compared to the MDA method. Yet, the MDA method gave over a 500% larger Mg extraction from rice straw char sample from Cambodia compared to the conventional method.

Table 3: Levels of Nutrients in Biochar Samples (Totals using conventional soil analysis (ESG) and using modified dry-ashing (MDA)

Sample (all in mgkg^{-1})	Calcium (Ca)	Potassium (K)	Magnesium (Mg)	Manganese (Mn)	Phosphorus (P)
RSC VN ESG	13,000	7600	1600	550	1700
RSC VN UEDIN	10,785	12,100	2175		1615
RHC VN ESG	6,500	6300	1200	230	2100
RHC VN UEDIN	4,875	13,100	1455		2260
BSC VN ESG	4,300	5500	610	310	830
BSC VN UEDIN	2,460	12,700	1330		1605
ASC VN ESG	7,700	3000	1900	480	800
ASC VN UEDIN	2430	16,550	1055		870
RSC2 VN ESG	2400	15,000	3100	79	3000
RSC2 VN UEDIN	4600	44,300	4980		3300
RSC CAM ESG	1900	9400	390	49	2000
RSC CAM UEDIN	3015	30,700	2525		2825
MCC CAM ESG	870	17,000	1800	39	3400
MCC CAM UEDIN	380	13,900	1220		2370
MSC CAM ESG	4300	17,000	7400	48	7600
MSC CAM UEDIN	2620	23,650	4490		4610
RHC CAM ESG	690	2300	380	87	700
RHC CAM UEDIN	740	6500	655		625

Source: after Enders & Lehmann, 2012. (UEDIN)

33.   Even with the same extraction method, quite a lot of variation is shown across chars from the same feedstock produced from different locations and using different technologies.

For example, rice straw char sample one has a lot more (five times) calcium than the second sample, which in turn contains a lot more (two times) potassium than the first sample. This may be a result of larger synthetic chemical inputs being used in the case of the cultivation of the second rice crop. Maize-derived chars are relatively high in potassium and phosphorus. Maize straw char is also relatively high in magnesium.

Figure 7: Total Ca, K, Mg, Mn and P contents of biochar (y axis units are in mg kg^{-1}) (using ESG total extraction values, conventional soil analysis method)
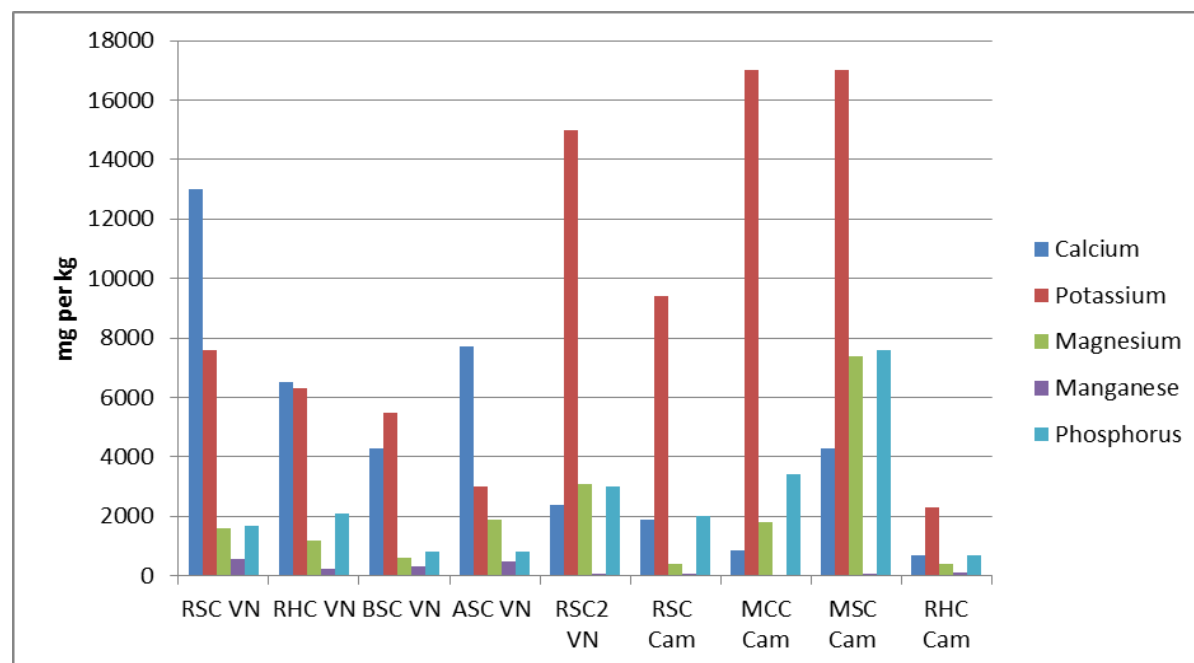

Figure 8: Total Ca, K, Mg and P contents of biochar (y axis units are in mg kg^{-1}) (using UEDIN total extraction values, modified dry ashing method)
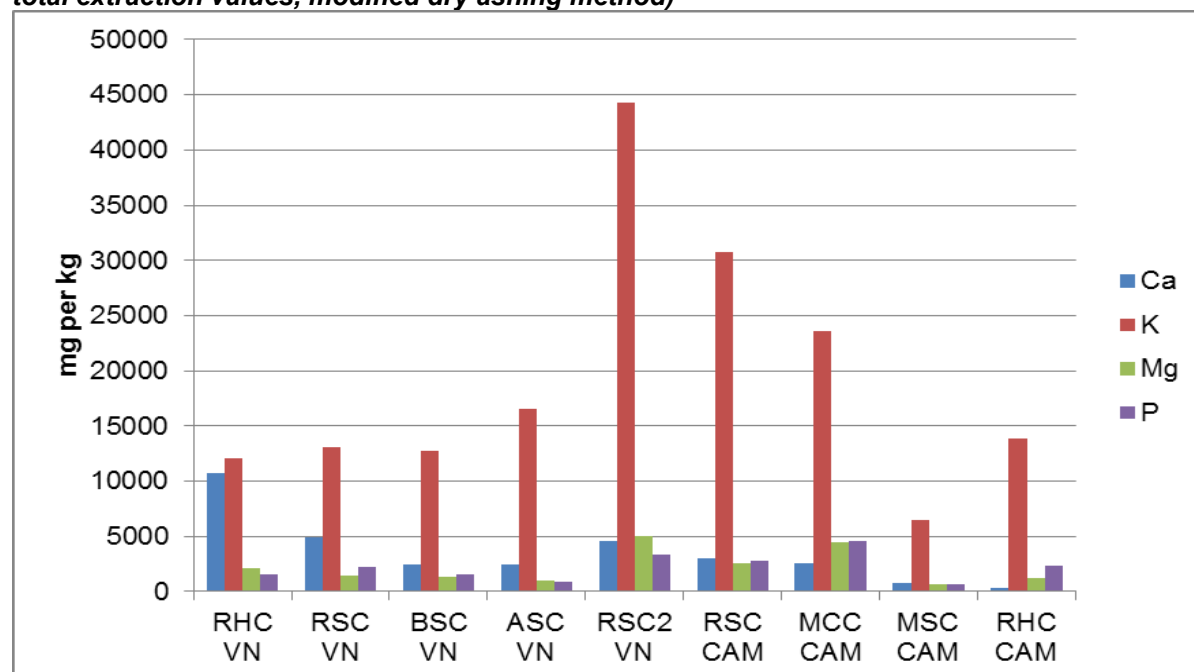
Figure 9: Conventional extraction method minus MDA method (y axis is in % relative to extraction using conventional soil science extraction method) for total Ca, K, Mg and P
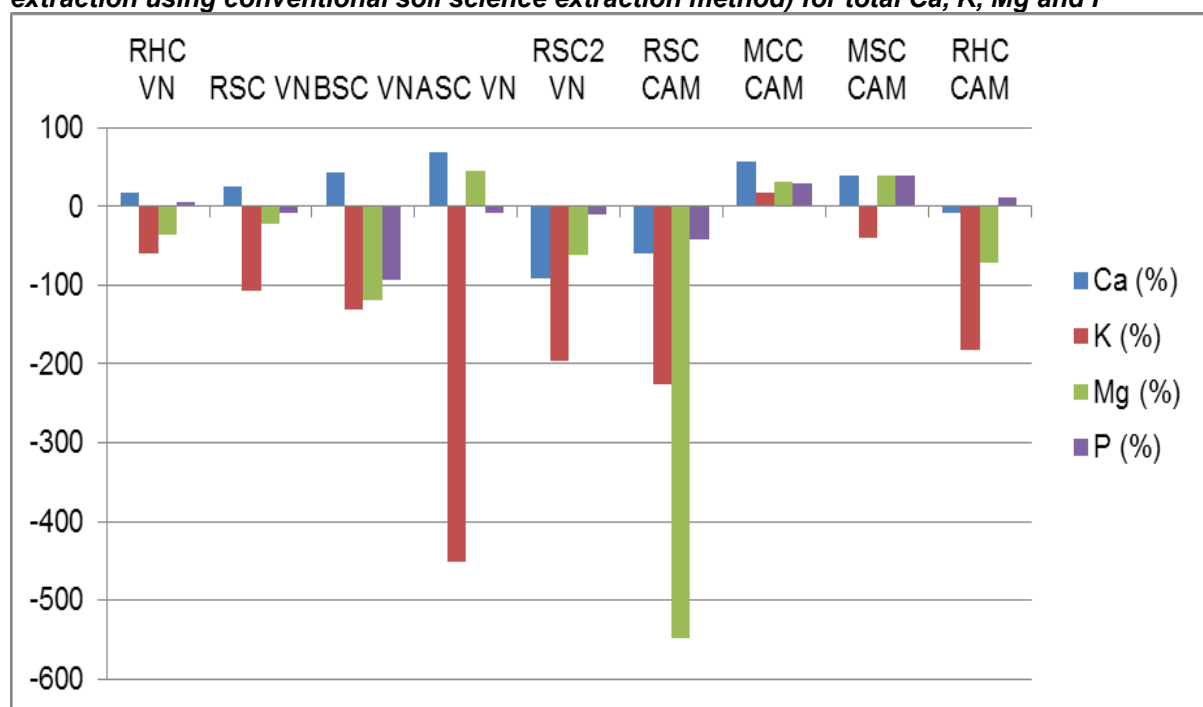
34.   While the samples looked clean, the presence of soil attached to the feedstock that was pyrolyzed cannot be ruled-out. If this was the case, then it would introduce other elements that would explain why the elemental properties of biochar from similar feedstocks are not consistent. Furthermore, if clay was used as an additive during pyrolysis, as was reported for Viet Nam, then there would have been addition of elements which will appear in the analysis of totals.

35.   Different quantities of elements within the growing media (soil) will also influence plant uptake. Where large particle size feedstock samples are being pyrolyzed – such as corn cobs – there may be different elemental properties in different parts of the plant; hence, the particular part of the sample used in the analysis could help explain variation.

3.6   EXTRACTABLE NUTRIENTS

36.   Biochar was leached in order to calculate the extractable nutrients from the biochar, i.e. the levels of phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg) that are extractable from the biochar by plants, using a similar method to Angst & Sohi (2012). This gives the total amount of plant available nutrients that will be available over approximately 2 years.

37.   *Figure 10* shows the available nutrients in milligrams per gram of biochar. *Figure 11* shows the plant available nutrients as a percentage of the total as determined by the MDA extraction method.

38.   It can be seen that there is a very low availability of total Ca (<5%) and Mg (in most cases, with just one sample having >20% availability). With regards to phosphorus (P), there is between 10% and 50% availability in most circumstances. However, in one case (maize corn cob char from Cambodia) more P is released than is in the total (120%).

39.   In the case of potassium, the % nutrient release varies from 28% to 94%. However, there is one outlier where there is 250% release. Apparent extraction during leaching experiments of more than the total is not a new result. In other research, repeated extractions appear to remove more than the totals, by 100-150% in the case of P (pers.com. Dr Teri Angst). One explanation for this discrepancy is that the method used for total analyses is not adequate and hence is not measuring real totals.

Figure 10: Plant available nutrients from biochar determined using soil leaching column experiments (mg g^{-1})
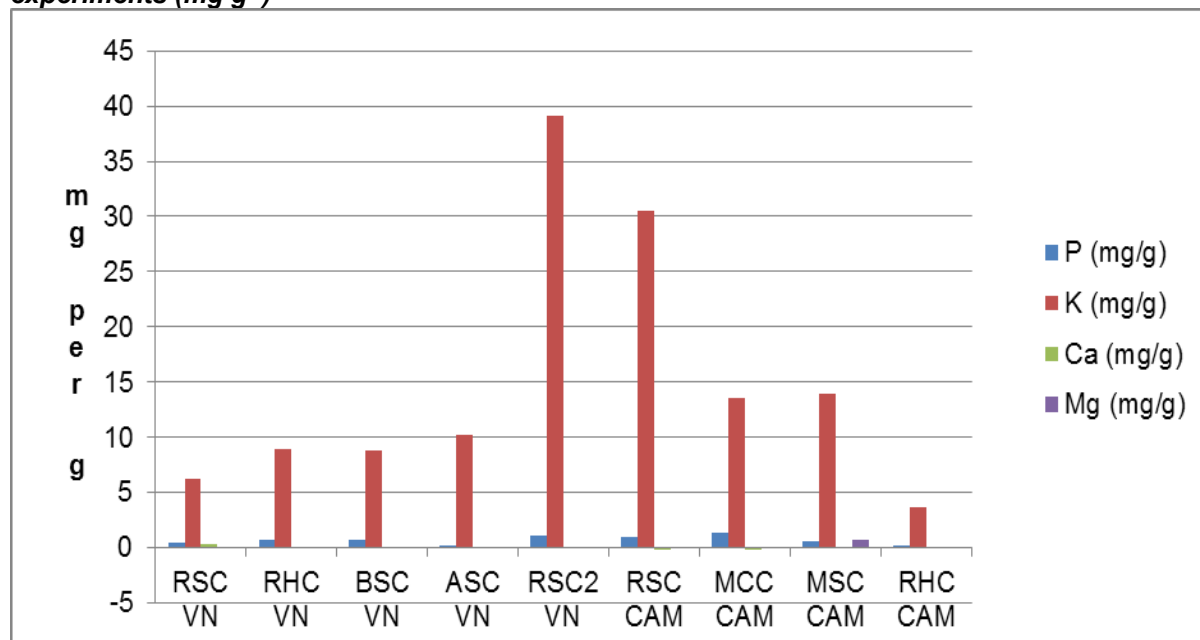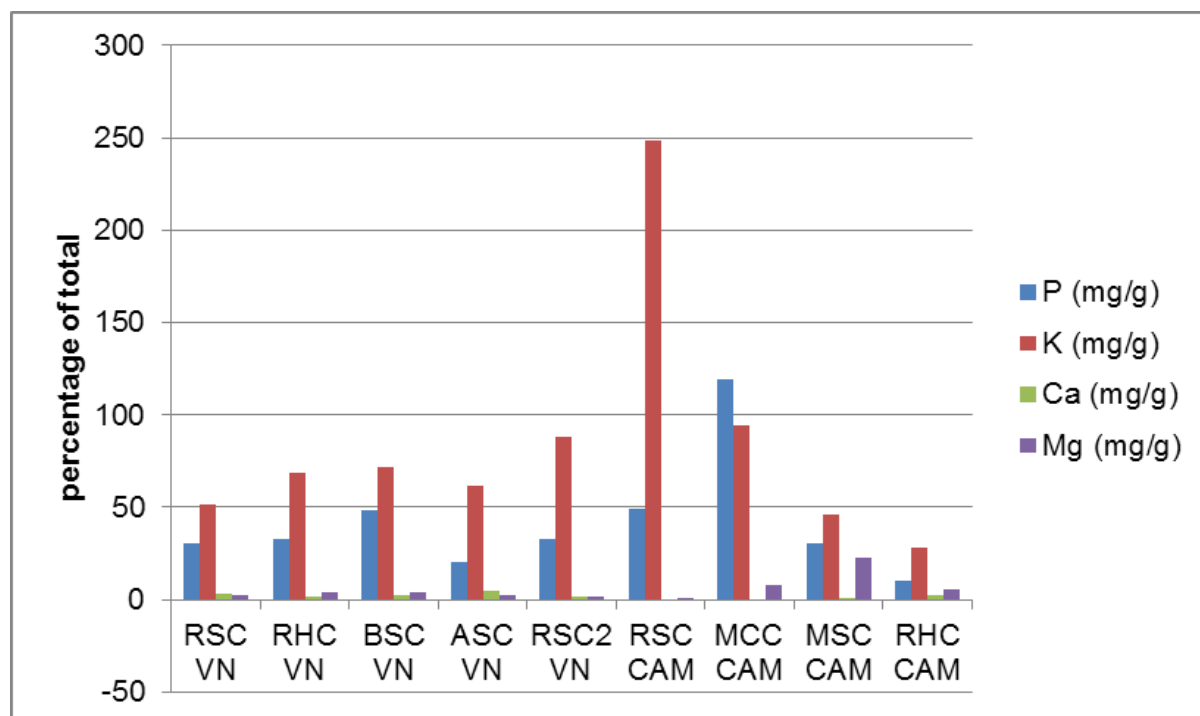

Figure 11: Plant available nutrients expressed as a percentage of totals using the MDA extraction method (y axis is quantity released from column experiments as a % of the total)

40.   *Figure 12* illustrates the plant available nutrient addition to one hectare assuming a 10 ton biochar per hectare application rate. Rates of P addition vary from a few kg ha^{-1} to 14 kg ha^{-1} (equivalent to c. 7 to 32 kg P_2O_5 ha^{-1}). For the higher rates, e.g. from maize corn cob biochar, the available P is sufficient to supply the P requirements of rice growing on Cambodian soils and about 30% of the P requirement for most vegetables. The amounts of available K are much higher than required by rice however, varying from 50% higher than required (rice husk biochar), 250% higher (rice straw and acacia biochar) to as much as 1300% higher (Vietnamese rice straw biochar where high levels of synthetic chemical inputs have been used as well as clay additives which will retain cations such as K$^+$). While the leaching experiment is intended to simulate release over a two year period, it appears that most of the nutrients are released in the 1st and 2nd leachings.

41.   In the case of a number of biochar samples (including the two rice straw and maize samples) there may be too much K addition. If there was a high background concentration of K in the soil, formation of excess salts in the soil could become a problem from further K additions via biochar. The balance between the N, P and K additions for particular crops in a given soil need to be considered through creation of biochar compound fertilizers (BCFs), which combine biochar with other organic and inorganic constituents.

Figure 12: Available plant nutrients assuming a 10 ton per hectare biochar application rate in units of kilograms per hectare
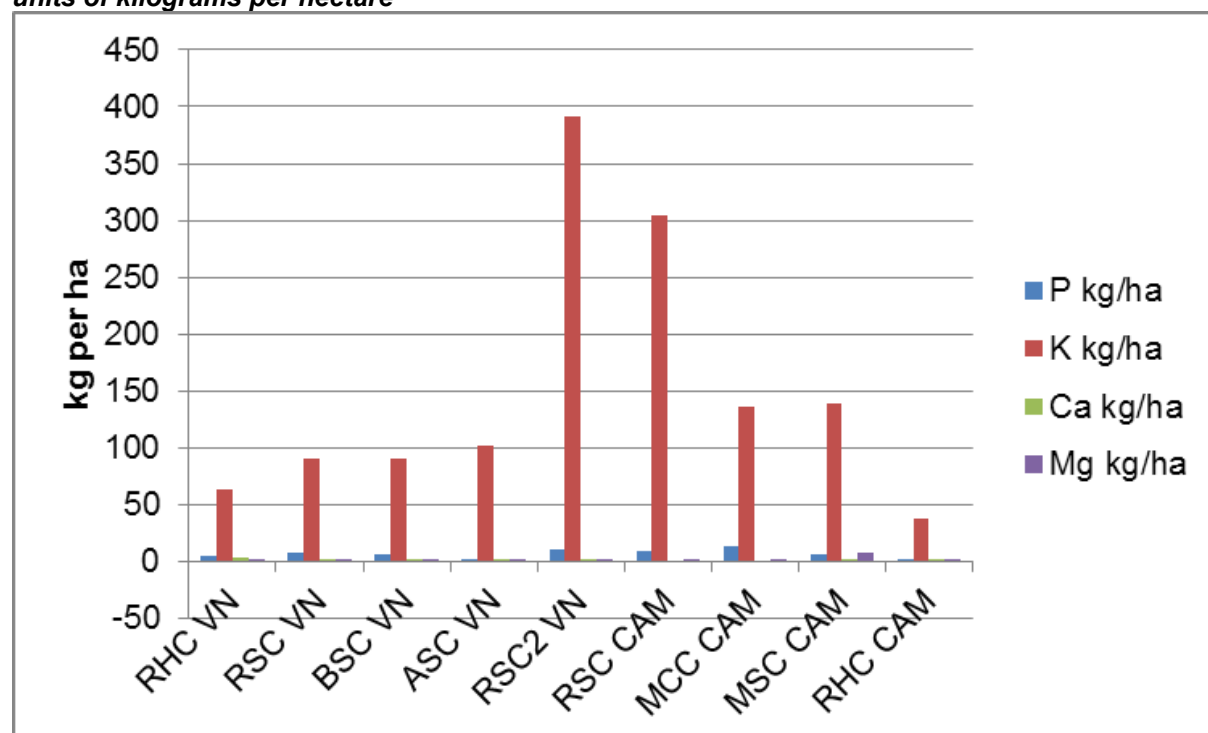
42.   The pH change induced by biochar in acidic soils will likely increase the availability of P that is already in the soil. i.e., the iron oxides will be reduced which will limit their capacity for binding P, hence increasing its availability to plants. The amount of nutrient in the biochar itself will generally be less important than the impact of biochar upon soil chemistry (especially increasing soil pH) and subsequent change in availability to plants of nutrients already within the soil. (Though *retention* of nutrients could be a critical factor in explaining the benefits of biochar addition). An overall increase in soil pH could be detrimental, however, with pH values of > 6.5 potentially reducing the availability of plant macro- and micro-nutrients (Novak et al., 2013).

3.7   STABILITY OF BIOCHAR

43.   The long-term stability of biochar, as represented as the fraction of biochar carbon that will remain as recalcitrant carbon in the soil for at least 100 years (and hence be relevant to carbon sequestration and reducing atmospheric emissions of CO_2) was calculated using the accelerated ageing method of Cross & Sohi (2012). The recalcitrant carbon fraction is also known as the carbon stability factor (CSF) of fresh biochar. The results are presented in *Figure 13.*

44.   The carbon content of biochar from the same feedstock can vary quite considerably. For example, the rice husk biochar samples analyzed had a carbon content of 30-46% (compared to a range in the literature of 29 – 36% (Shackley et al., 2012)). Use of pyrolysis rather than gasification will increase the carbon content of chars. Carbon content of rice straw meanwhile varies from 40-50%. Bamboo, acacia and maize (corn) cob and straw biochar samples contain between 75 – 80% carbon.

45.   In terms of stability, the biochars tested are all relatively stable with a minimum CSF of 73% for rice husk biochar from Cambodia and maximum CSF value of 98% for bamboo and acacia wood biochars from Viet Nam. The differences in carbon content and in stability are likely to be a consequence of differences in feedstock (e.g. rice husk contains c. 20% silica) and in the pyrolytic conditions within the equipment used to produce the biochar. Incomplete carbonization may have occurred in the case of some feedstocks, e.g. parts of the biomass (may not have been exposed to temperatures of 400 – 500°C that are required to achiever 80 – 90% stability. Lack of even heating of biomass feedstocks occurs if there is inconsistent particle size or if there is aggregation which shields part of the biomass. In order to fulfil the requirements of long-term (climate change relevant) carbon storage, consistent reproducible methods will be required to measure the long-term stable carbon content of biochar from equipment with a consistent design.

Figure 13: The % 'fresh' carbon of each biochar sample (blue) on a weight basis and the % of carbon in fresh biochar that is stable (Carbon Stability Factor) over at least 100 years (red).
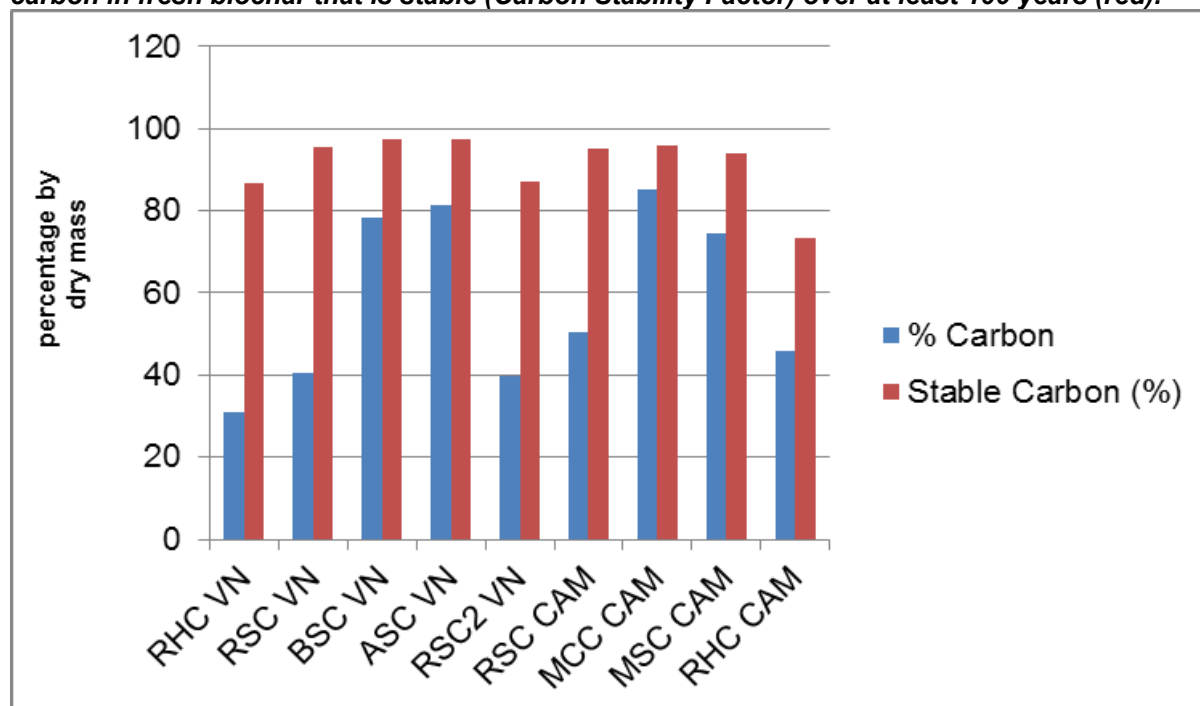
46.   Due to the high silica content of rice husk and straw, the fresh carbon content of such biochars is lower per ton. The bamboo, acacia wood, corn cob and corn straw all contain more fresh carbon and can store a larger amount of stable carbon in biochar per ton. The ability of woody and corn chars to store more carbon per ton of biochar over 100 years is not due to higher stability of the biochar carbon, but due to the higher starting level of carbon in the feedstock itself, resulting in a higher carbon content of the biochar.

47.   In order to calculate the long-term stable carbon per ton of biochar the fresh carbon content is multiplied by the CSF. This is shown in *Figure 14.* To convert to CO_2 (equivalent) multiply the values in Figure 14 by 3.667. e.g., rice husk biochar stores about 1 ton CO_2e (equivalent) per ton biochar, while corn cob char stores about 3 tons CO_2e per ton biochar. To calculate the total carbon abatement per ton of feedstock it is necessary to know the efficiency of the conversion of biomass to solid char. For example if one third of the rice husk feedstock is converted to solid char, then carbon abatement would be 0.33 ton CO_2(e) per ton feedstock since three tons of rice husk as used to produce one ton of rice husk biochar.

48.   Taking account of the conversion efficiencies of the different technologies used to produce the nine biochar samples, *Figure 15* expresses tons of CO_2 (equivalent) storage in biochar on a time scale of > 100 years per ton feedstock. i.e. the data indicates the carbon abatement efficiency (CAE) of pyrolysis utilizing different feedstocks (excluding any indirect impacts of biochar in the soil that might influence greenhouse gas emissions and excluding any energy use of pyrolytic gases or liquids or energy start-up requirements). The lower-ash content feedstocks have a higher CAE, up to around 1 ton CO_2 per ton feedstock which is consistent with the literature.

49.   All feedstocks indicate positive carbon abatement, however, so in all cases CO_2 is being removed from the atmosphere and stored in soils for > 100 years, hence contributing to climate change mitigation. However, this assumes no indirect impacts upon soil process which might increase or decrease net carbon abatement. Recent evidence on reduction of nitrous oxide (N_2O) emissions from biochar addition to soils suggests that there is a propensity for a reduction (a meta-analysis of experimental data suggests that, on average, there is a 50% reduction in fluxes of N_2O from soils from biochar application – which would make an indirect contribution to net carbon abatement from biochar application) (Cayuela et al., 2014).

Figure 14: Tons of recalcitrant (long-term) stable carbon per ton of biochar
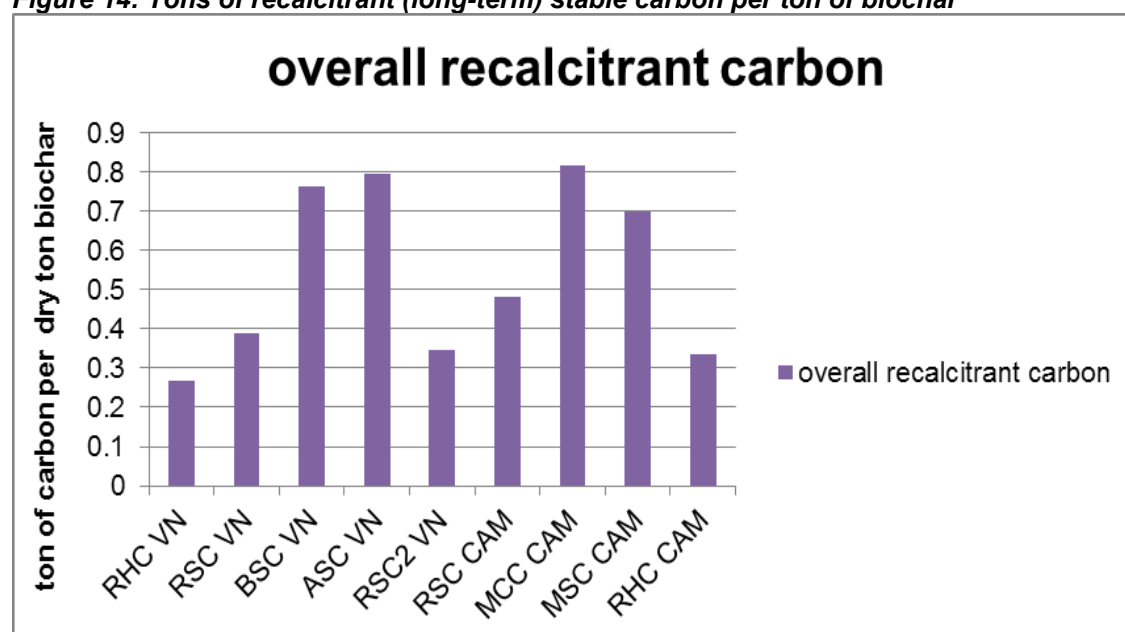
Figure 15: Carbon Abatement Efficiency due to stable carbon in biochar expressed as tons of CO$_2$ (equivalent) stored per ton feedstock pyrolysed
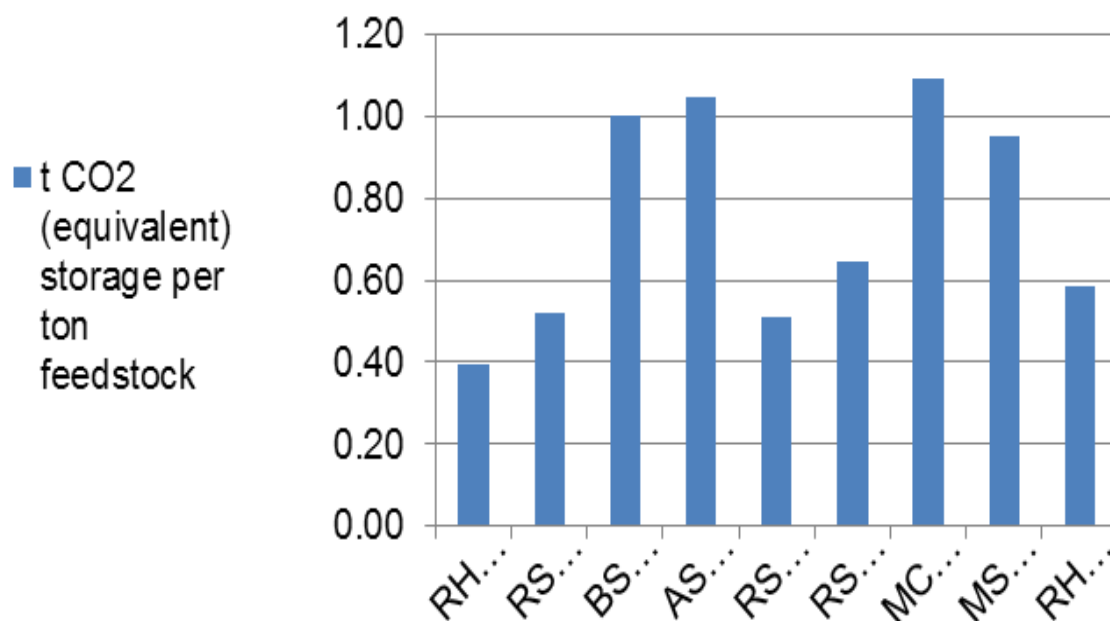
50.   Feedstocks with high ash content such as rice husk straw and husk have lower carbon conservation in the biochar relative to feedstock than woody feedstocks. Corn cob and straw appear to have the highest carbon conservation levels; however the data on starting carbon content of these feedstocks is less reliable than for the rice straw and husk.

Analysis of GMS Biochar Samples / ADB TA7833-REG / July 2014

4. HEALTH AND SAFETY ISSUES

51.   Rice husks contain approximately 20% silica in an amorphous form which is naturally occurring and a safe material (e.g. it is a key constituent of sand). It is generally believed that the silica in rice husks heated at lower temperatures (e.g. 400-500°C) remains in an amorphous form. It is also believed that the silica in rice husks heated at high temperatures (> 900°C) becomes crystalline, forming quartz and / or cristobalite (and tridymite at higher temperatures) (Shinohara & Kohyama 2004; Thy et al. 2006).

52.   Health issues associated with inhaling crystalline silica in the form of quartz or cristobalite have been raised. Respirable silica is a Group 1 human carcinogen (IARC 1997, Rice 2000). Silicosis is a fibriotic lung disease caused by crystalline silica. Research has identified the risk of pneumoconiosis in Chinese workers where rice husk ash is produced and early silicosis in rice mill owners in Malaysia which might be linked to crystalline silica (Shinhara & Kohyama, 2004).

53.   The Belgian advanced industrial minerals company SIBELCO N.V. outlines the hazards of as follows:

> *"Prolonged and / or massive inhalation of respirable crystalline silica dust or cristobalite may cause lung fibrosis, commonly referred to as silicosis (a nodular pulmonary fibrosis caused by the deposition in the lungs of the fine respirable particles). Principal symptoms of silicosis are cough and breathlessness. People with silicosis are reported to have an increased cancer risk. Exposure to dust should be monitored and managed".*

54.   The exact mechanism by which crystalline silica becomes toxic in the lung is not known (Le Bond et al., 2008) and there is a lack of knowledge regarding the dose-response relationship. Most of what we do know about crystalline silica is based upon studies of quartz rather than cristobalite. The response to quartz has been found to be highly variable perhaps due to the heterogeneity of quartz (particle shape, size, surface properties, etc.) (ibid.).

55.   However, what is known is that the particle size is crucial in understanding potential risks. The respirable particles are defined as the mass fraction of inhaled particles which enter the alveolar region of the lung, which is that part which does not have ciliate hairs on the airways to remove particles from the lungs. Evidence suggests that crystalline silica particles with an aerodynamic diameter of less than 4µm constitute the respirable fraction (Horwell 2007).

4.1   X-RAY DIFFRACTION OF RICE HUSK CHAR FROM GASIFICATION AND RICE HUSK ASH

56.   Previous research has identified the presence of cristobalite and tridymite (another crystalline form of silica, which typically forms at higher temperature than cristobalite) in rice husk ash. Shinhara & Kohyama (2004) heated rice husk char samples to a range of temperatures and found that heating between 900°C to 1200°C for six hours resulted in 52-62% cristobalite content by weight along with 10-17% tridymite. Thy et al. (2006) found cristobalite forming in rice straw ash by a lower temperature of 767°C. Shackley et al. (2012) examined the form of silica in rice husk biochar produced in Cambodia as a by-product of gasification at temperatures of 900 – 1100°C.

57.   (XRD showed that there was a peak at 26.5^O but this angle is characteristic of both graphite and crystalline silica (quartz) so the result of that analysis was not conclusive. There

is, however, a peak at 21.8^0 2-theta which is characteristic of cristobalite and occurs in both the rice husk char and ash samples. Furthermore, peaks can be identified at 20.5^o, 21.6^o and 23.3^o 2-theta and these are characteristic of tridymite.

58.　　In subsequent (unpublished) work, in order to differentiate more clearly between graphite and crystalline silica, a powerful oxidative method developed by Cross & Sohi (2013) was used to remove the large majority of the carbon from the RHB (to 0.37% C by mass). This means that the graphite signal was removed from the XRD. The sample was then examined once again using XRD, as show in *Figure 16*.

59.　　There are several distinctive peaks corresponding to the signal of cristobalite. This is not surprising as crystalline silica begins to be formed from amorphous silica at temperatures >900^oC and the gasifier is operating at c. 900 – 1100^oC. A sample of rice husk char at c. 450^oC was then produced in a bespoke glass-ware laboratory-scale pyrolysis unit at the University of Edinburgh. The RHB was again subject to decarbonization using a powerful oxidation method and XRD performed on the sample. In this case, no cristobalite peak was found, the silica remaining in amorphous form, confirming the importance of the peak temperature in formation of crystalline forms of silica, though the time over which the material is exposed to heat is also a contributory factor.

Figure 16: XRD of rice husk char
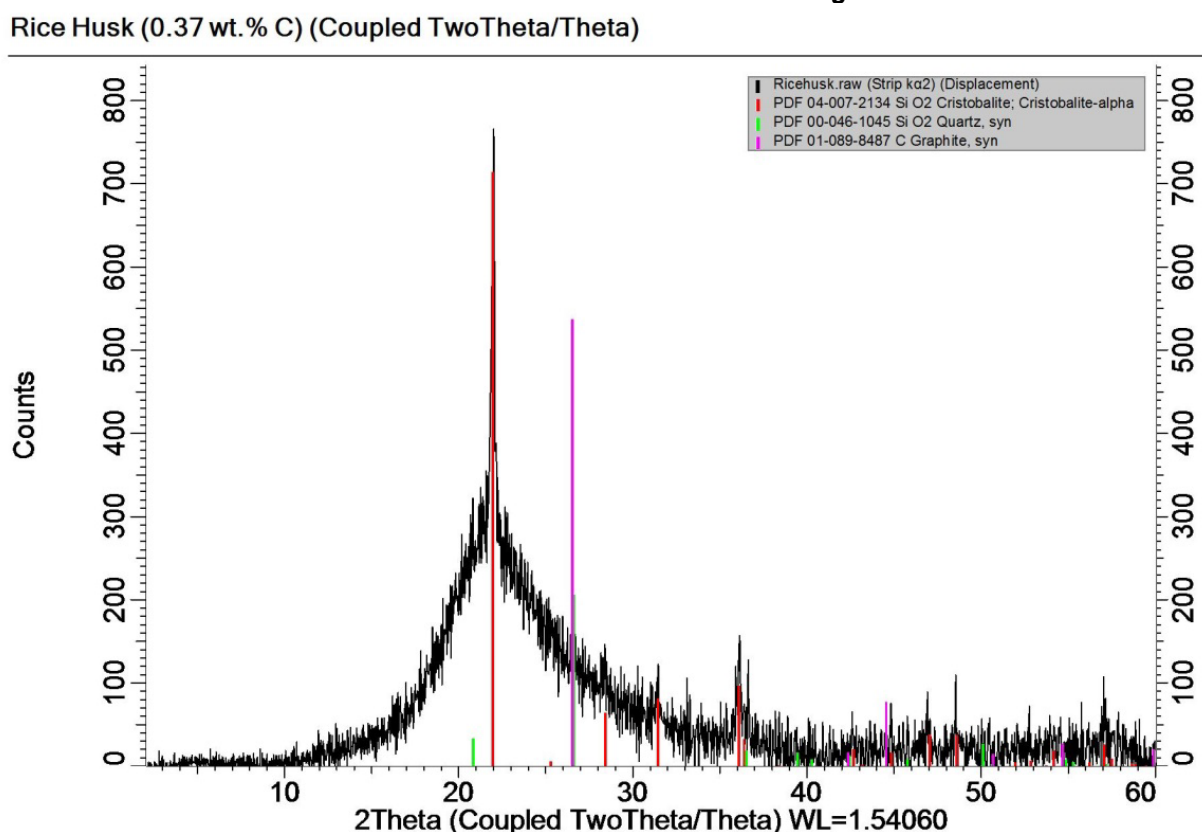
4.2　X-RAY DIFFRACTION OF RICE HUSK, RICE STRAW AND BAMBOO CHARS FROM PYROLYSIS

60.　　It is commonly assumed that pyrolytic chars from high silica-containing feedstocks will not contain crystalline silica because the conversion temperatures are not high enough (i.e. <900^oC), an assumption confirmed by the rice husk char produced at 450^oC in a well

instrumented and controlled piece of lab equipment. However many chars are produced in far less controlled and less instrumented equipment, such as kilns and scaled-up TLUD kilns.

61.   With the utilization of TLUD kilns in Cambodia, Laos PDR and Viet Nam for conversion of rice husk and rice straw into biochar, it is important to analyze the biochars produced to ascertain whether they contain cristobalite / quartz or whether the silicia remains amorphous.

62.   Samples were collected from the respective ministries of agriculture in Viet Nam and Cambodia and the majority of the carbon was removed using the same powerful oxidative method developed by Cross & Sohi (2013). The decarbonized biochar sample was then analyzed using XRD. The following samples were examined together with an indication of what was discovered:
  ▪   Rice husk char Cambodia (RHC CAM) – Quartz
  ▪   Rice husk char Viet Nam (RHC VN) - abundant Quartz plus trace Cristobalite
  ▪   Rice straw char Cambodia (RSC CAM) - Quartz plus Cristobalite
  ▪   Rice straw char Viet Nam (RSC VN) - Quartz plus Cristobalite
  ▪   Rice straw char Viet Nam sample 2 (RSC2 VN) - trace Quartz
  ▪   Bamboo stem char Viet Nam (BSC VN) - Quartz

63.   Some pyrolytic chars also seem to contain cristobalite. The finding is confusing since amorphous silica converts to cristobalite at a temperature of 900-1000°C and pyrolysis is expected to happen at a much lower temperatures – typically 400-600°C. Quartz forms at lower temperatures (>450°C) so its presence in pyrolytic chars is understandable. Thy et al. (2006) report the presence of cristobalite in rice straw ash when the straw was exposed to a temperature of 767°C so there is a precedent for the formation of cristobalite at lower-than expected temperatures.

64.   How cristobalite forms is unknown but a partial explanation includes: a) the actual temperatures in parts of the biochar-producing kilns, might be higher than expected – hot patches may develop which heat up locally to the right temperature for cristobalite formation (perhaps only 767°C in the case of rice straw); b) the presence of impurities such as Na, Mg, Al, Fe and Ca might allow formation of cristobalite at lower temperatures than normal by acting as stabilizing factors (Le Bond et al., 2010); c) some combination of (a) and (b).

65.   Note that there is considerable uncertainty in whether cristobalite is formed or not during pyrolysis. It was present in one out of two rice husk char samples and in two out of three rice straw char samples. Why it was not present in all rice husk and straw char samples is not known but its presence in rice straw char is consistent with the findings of Thy et al. (2006) if the kilns have localized areas of heating to c. 770°C.

4.3   QUANTIFICATION OF CRISTOBALITE IN RICE HUSK CHAR FROM GASIFICATION AND PYROLYSIS

66.   By using a spike of a reference material of a known concentration and response it is possible to quantify the amount of cristobalite in samples. New samples of rice husk char from both gasifier and TLUD style kilns (Cambodian Chiveak Tyung design) were prepared and decarbonized. The XRD result for the gasification sample is shown in *Figure 17* whilst that for the pyrolytic sample is illustrated in *Figure 18.*

67.   Both gasification and pyrolysis samples show a trace consisting of a very broad maximum around 22° 2-theta. In the figure and superimposed onto the sample trace are the sharp peaks of the CaCO3 spike added to quantify the amounts of any crystalline phases

present. Only in the gasification sample does a well crystallized phase occur. The peak for this phase is a small but reasonably well defined peak also centered on 22° 2-theta and is consistent with the presence of crystallites of cristoballite. Reitveld analysis implies that this peak represents 8% by weight of the sample and consists of crystals approximately 10 nm in size. No such peak occurs in the pyrolysis sample so no crystals of cristobalite are present. Tridymite also appears to be present in the gasified rice husk char.

Figure 17: XRD of rice husk char from gasification (CAM) with spiked reference material showing Cristobalite present at 22° 2-theta
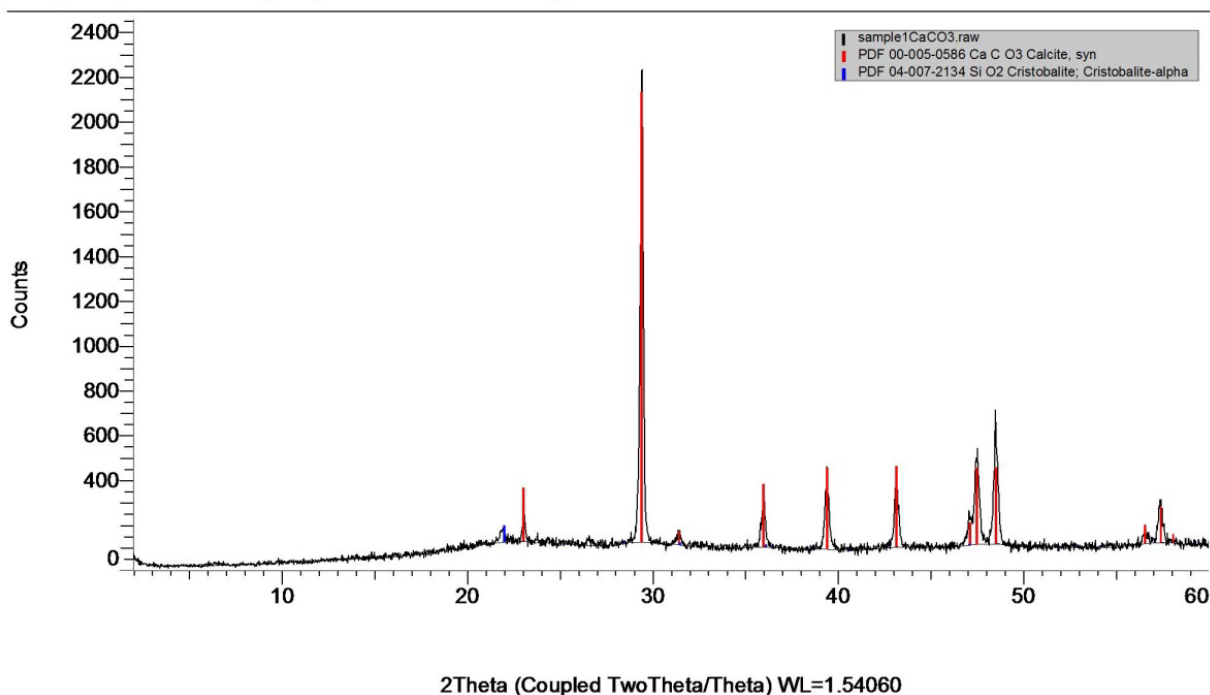
Figure 18: XRD of rice husk char from pyrolysis (CAM) with spiked reference material with no evidence of Cristobalite

Analysis of GMS Biochar Samples / ADB TA7833-REG / July 2014
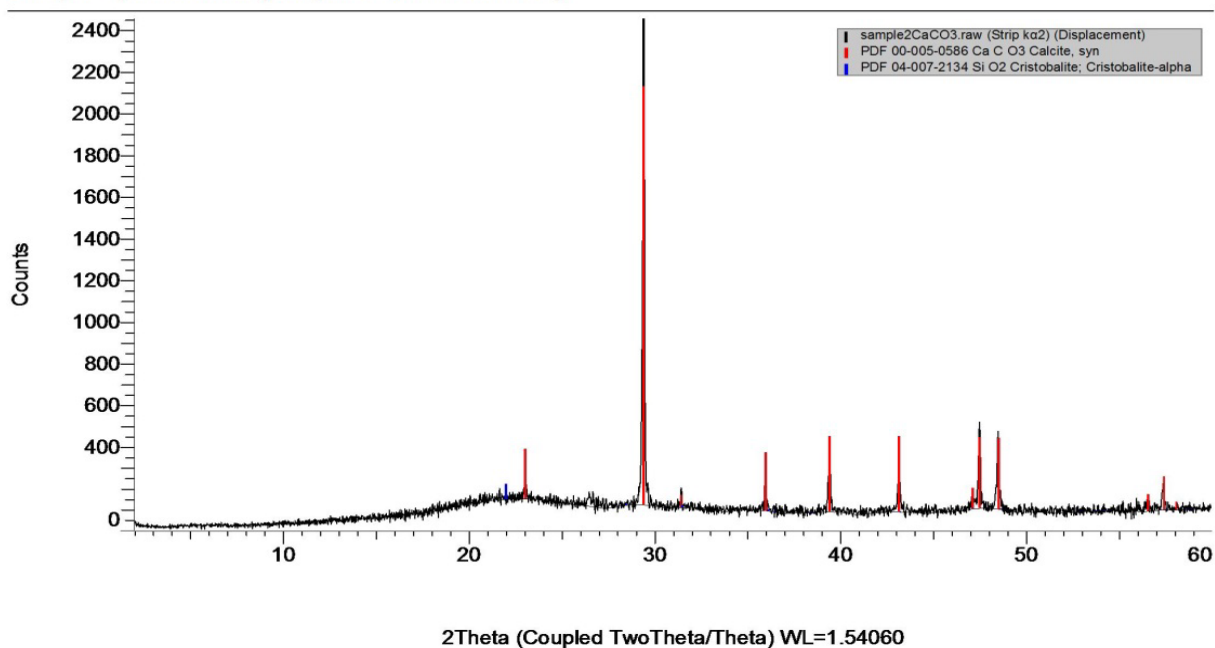
68.   The presence of a very broad bulge in the background centered on the 22° 2-theta position may be due to a large amount of cristobalite-structured material but of very small crystallite size. By manipulating the Reitvelt parameters it is possible to calculate a crystallite size for this peak of less than 1 nm. At this size the concept of crystallinity blurs into that of glassy states and diffraction patterns of silicate glasses look very similar to the background curves of both samples.

4.4   SUMMARY OF X-RAY DIFFRACTION STUDIES.

69.   Cristobalite has been identified in all three separate samples of rice husk gasification char examined. Quantification has now established that cristobalite constitutes 8% by mass of the rice husk gasification char. At these levels it is a major presence, higher than reported cristobalite in the ash from other silicaceous feedstocks such as sugarcane bagasse ash (where it is 3% by weight) (Le Bond et al., 2010) though lower than the amounts found in rice husk ash heated to 900°C then up to 1200°C. The cristobalite is also present at a very small particle size (10 nm) which means it can enter the vulnerable part of the lung.

70.   The pyrolytically-derived rice husk char sometimes shows evidence of cristobalite (one sample out of four tested). Cristobalite appears in pyrolytically-derived rice straw char in two out of three samples tested. It is not known why cristobalite forms at the lower temperature of pyrolysis but it is possible that localized heating is much higher than the average pyrolytic conversion temperature. It is also likely that impurities such as metals in the material allow formation of cristobalite at lower than normal temperatures. While cristobalite formation during pyrolysis appears to be less frequent and unpredictable compared to its formation during gasification, it cannot be ruled out.

5.   OCCUPATIONAL HEALTH AND SAFETY IMPLICATIONS

71.   Given the presence of cristobalite, it is necessary to consider adoption of appropriate operational occupational health and safety (OHS) measures when producing, storing, mixing and applying rice husk and straw biochar to soils (*Figure 19*).

72.   To assess the OHS risk it is necessary to understand the exposure pathways. If the char is kept in sealed containers and not allowed to escape into the atmosphere, the risk of exposure is greatly reduced. If, on the other hand, char is allowed to escape into atmosphere and to be suspended in air where people are breathing then there is a high risk of exposure.

73.   An OHS survey of exposure conditions in different settings is required to determine the risk of exposure. Such a survey would measure the occupational exposure level as mg per m^3 of air in the working environment. Occupational Exposure Limits (OELs) have been established for cristobalite by many different national authorities. The OEL for cristobalite in most countries ranges from 0.05 to 0.3 mg/m^3. Any quantity above that threshold requires the adoption of special measures to limit OHS risks.

74.   Care should be taken at all times to avoid exposure of workers to rice husk and straw char dust at the gasifier (or pyrolysis) unit, during removal, storage and application to soil. Personal respirators should be worn when there is any risk of exposure above the OEL. The filter on the respirators needs to be selected to prevent intrusion of 10nm cristobalite particles.

1. **Occupational exposure controls: Provide appropriate exhaust ventilation and filtering at the places where dust can be generated. Wash hands before breaks and at the end of the workday. Remove and wash soiled clothing.**

2. **Respiratory protection: In case of exposure to dust over occupational exposure limits wear a personal respirator in compliance with national legislation.**

3. **Eye protection: In case of exposure to dust over regulatory limits wear safety glasses with side-shields.**

4. **Environmental exposure controls: No special requirements. There is no reported ecotoxicity for silica, a naturally occurring substance widelyspread on earth.**

5. **Handling. Avoid dust formation. Provide appropriate exhaust ventilation at places where dust is formed. In case of insufficient ventilation, wear suitable respiratory equipment**

6. **Storage. Ensure trapping of dust produced during the loading of silos. Keep containers closed and store the bagged products in a way preventing accidental bursting.**

7. **Waste from residues / unused product can be landfilled in compliance with local regulations. The material should be buried to prevent airborne respirable dust being emitted. Where possible, recycling should be preferred to disposal.**

8. **Packaging. In all cases dust formation from residues in the packaging should be avoided and suitable worker protection be assured. Use sealed receptacles / store rooms.**

Source: SIBELCO N.V.

Figure 19: Exposure controls for Cristobalite

75.   The Ankur gasifier now comes with an enclosed auger for conveying the rice husk char into sacks which are sealed around the outlet. This is an important advance in reducing char dust entering the atmosphere but only provided the change-over of bags does not involve expulsion of dust into the surroundings. An appropriate seal mechanism or use of low pressure to suck back dust during change-over should be sufficient to keep dust from entering the ar.

76.   The char then has to be handled carefully at the site where it is prepared for soil application. This would involve wetting the material immediately to prevent dust formation and keeping the material moist throughout processing. Once it is fully integrated into the top soil, it is unlikely to constitute a hazard. However, if the char is applied to the surface of the soil and then dries, it will be easily re-mobilized by wind erosion and enter the atmosphere increasing the exposure risk to humans working in the fields.

77.   An appropriate protocol for thorough integration into top-soil (e.g. by ploughing) is therefore required. Another option is to pelletize the rice husk gasification biochar with clay, biomass, NPK, ash, etc., in which case the cristobalite would not be accessible, provided the pellet itself is sufficiently robust and not too brittle.

78.   Due to the potential for char to be blown about during windy days, it is recommended that char application to field is avoided when it is windy. Furthermore, it is recommended that a face mask / personal respirator is worn by operatives during field application. Where cristobalite occurs, the Belgian chemical company SIBELCO outlines exposure controls as described in *Figure 19.*

TECHNICAL APPENDIX: DATA IN TABULATED FORMAT

The samples were collected in June 2013 and tested in August-September 2013.

TABLE A1: HEAVY METALS CONTENTS AS CALCULATED WITH ICP-AES AND ICP-MS9

Customer Reference	Laboratory Reference	As	Ca	Cd	Cr	Cu	Hg	K	Mg
	LOD	0.08	0.3*/3	0.01	0.03	0.2	0.006	20	0.03*/0.3
Rice straw char, SFRI, VN	ASC/11671.001	20	13000	0.28	12	21	0.03	7600	1600
Rice husk char, SFRI, VN	ASC/11671.002	18	6500	0.46	6.0	8.1	0.03	6300	1200
Bamboo stem char, SFRI, VN	ASC/11671.003	38	4300	0.57	18	35	0.061	5500	610*
Acacia wood char, SFRI, VN	ASC/11671.004	17	7700	0.01	2.0	11	0.02	3000	1900
Rice straw char 2, SFRI, VN	ASC/11671.005	20	2400	0.02	2.7	3.6	0.02	15000	3100
Rice straw char, DAE kiln, CAM	ASC/11671.006	20	1900	0.02	2.4	6.0	0.02	9400	390*
Corn (maize) cob char, DAE kiln, CAM	ASC/11671.007	18	870*	0.067	2.7	15	0.02	17000	1800
Corn (maize) straw char, DAE kiln, CAM	ASC/11671.008	20	4300	0.16	2.9	21	0.02	17000	7400
Rice husk char, DAE kiln, CAM	ASC/11671.009	26	690*	0.01	3.7	4.0	0.02	2300	380*
	ASC/11671.009D	22	690*	0.006	3.0	0.9	0.02	2300	380*
MQC Standard 2.5 mgL^{-1}		n/a	3.0	n/a	n/a	n/a	n/a	2.9	2.7
MQC Standard 25 µgL^{-1}		29	n/a	26	26	27	26	n/a	n/a
QC Standard 5.0 mgL^{-1}		n/a	5.0	n/a	n/a	n/a	n/a	4.9	5.3
QC Standard 10 µgL^{-1}		10	n/a	10	10	10	10	n/a	n/a
QC Standard 20 µgL^{-1}		20	n/a	20	20	20	20	n/a	n/a
QC Standard 40 µgL^{-1}		40	n/a	40	40	40	40	n/a	n/a

1. Results are expressed as mgkg^{-1} in the samples as received.
2. Results over an order of magnitude above the LOD are estimated to have an uncertainty of $\pm$ 20%.
3. Results within an order of magnitude of the LOD have a higher uncertainty and are reported to one significant figure.
4. The MQC Standard is expected to be 2.5 mgL^{-1} $\pm$ 20% for Ca, K, Mg, Mn, P and Zn and 25 µgL^{-1} $\pm$ 20% for As, Cd, Cr, Cu, Hg, Mo, Ni, Pb and Se.
5. The QC Standards for are expected to be 5.0 mgL^{-1} $\pm$ 20% for Ca, K, Mg, Mn, P and Zn and 10, 20 and 40 µgL^{-1} $\pm$ 20% for As, Cd, Cr, Cu, Hg, Mo, Ni, Pb and Se.
6. Suffix 'D' following the laboratory reference denotes duplicate sample analysis.
7. Results marked with a * have a corresponding LOD marked with a *.
8. n/a means not applicable.
9. Table Legend: CAM = Cambodia; DAE = Department of Agricultural Engineering, General Directorate of Agriculture, MAFF, Royal Government of Cambodia; SFRI = Soil & Fertiliser Research Institute, MARD, Government of Viet Nam; VN = Viet Nam.

TABLE A2: HEAVY METALS CONTENTS AS CALCULATED WITH ICP-AES AND ICP-MS 9 (CONTINUED)

Customer Reference	Laboratory Reference	Mo	Mn	Ni	P	Pb	Se	Zn
	LOD	0.008	0.06	0.1	6*/60	0.07	0.2/ 0.4*	0.5
Rice straw char, SFRI, VN	ASC/11671.001	14	550	4.0	1700	25	<0.2	73
Rice husk char, SFRI, VN	ASC/11671.002	0.80	230	2.4	2100	4.4	<0.2	42
Bamboo stem char, SFRI, VN	ASC/11671.003	13	310	1.1	830*	28	<0.4*	9.6
Acacia wood char, SFRI, VN	ASC/11671.004	0.35	480	5.7	800*	3.2	<0.2	60
Rice straw char 2, SFRI, VN	ASC/11671.005	1.5	79	0.6	3000	1.5	<0.2	13
Rice straw char, DAE kiln, CAM	ASC/11671.006	4.7	49	0.2	2000	5.8	<0.2	0.6
Corn (maize) cob char, DAE kiln, CAM	ASC/11671.007	0.25	39	0.86	3400	5.1	<0.2	140
Corn (maize) straw char, DAE kiln, CAM	ASC/11671.008	0.58	48	0.52	7600	19	<0.2	41
Rice husk char, DAE, CAM	ASC/11671.009	0.65	80	0.2	720*	1.8	<0.2	9.3
	ASC/11671.009D	0.11	94	0.2	680*	0.56	<0.2	7.5
MQC Standard 2.5 mgL^{-1}		n/a	2.7	n/a	2.8	n/a	n/a	2.7
MQC Standard 25 µgL^{-1}		25	n/a	27	n/a	25	25	n/a
QC Standard 5.0 mgL^{-1}		n/a	5.4	n/a	4.6	n/a	n/a	5.4
QC Standard 10 µgL^{-1}		10	n/a	10	n/a	10	10	n/a
QC Standard 20 µgL^{-1}		20	n/a	20	n/a	20	20	n/a
QC Standard 40 µgL^{-1}		40	n/a	40	n/a	40	40	n/a

1. Results are expressed as mgkg^{-1} in the samples as received.
2. Results over an order of magnitude above the LOD are estimated to have an uncertainty of $\pm$ 20%.
3. Results within an order of magnitude of the LOD have a higher uncertainty and are reported to one significant figure.
4. The MQC Standard is expected to be 2.5 mgL^{-1} $\pm$ 20% for Ca, K, Mg, Mn, P and Zn and 25 µgL^{-1} $\pm$ 20% for As, Cd, Cr, Cu, Hg, Mo, Ni, Pb and Se.
5. The QC Standards for are expected to be 5.0 mgL^{-1} $\pm$ 20% for Ca, K, Mg, Mn, P and Zn and 10, 20 and 40 µgL^{-1} $\pm$ 20% for As, Cd, Cr, Cu, Hg, Mo, Ni, Pb and Se.
6. Suffix 'D' following the laboratory reference denotes duplicate sample analysis.
7. Results marked with a * have a corresponding LOD marked with a *.
8. n/a means not applicable.
9. Table Legend: CAM = Cambodia; DAE = Department of Agricultural Engineering, General Directorate of Agriculture, MAFF, Royal Government of Cambodia; SFRI = Soil & Fertiliser Research Institute, MARD, Government of Viet Nam; VN = Viet Nam.

TABLE A3: ANALYSIS OF BOCHAR SAMPLES FOR C, H, N, S AND MOISTURE

Customer Reference	Laboratory Reference	Carbon	Hydrogen	Nitrogen	Total Sulfur	Analysis Moisture
Rice straw char, SFRI, VN	ASC/11671.001	IS	IS	IS	IS	IS
Rice husk char, SFRI, VN	ASC/11671.002	IS	IS	IS	IS	IS
Bamboo stem char, SFRI, VN	ASC/11671.003	IS	IS	IS	IS	IS
Acacia wood char, SFRI, VN	ASC/11671.004	IS	IS	IS	IS	IS
Rice straw char 2, SFRI, VN	ASC/11671.005	IS	IS	IS	IS	IS
Rice straw char, DAE kiln, CAM	ASC/11671.006	50.08	0.48	0.69	0.06	6.9
Corn (maize) cob char, DAE kiln, CAM	ASC/11671.007	80.44	0.05	0.49	0.03	9.6
Corn (maize) straw char, DAE kiln, CAM	ASC/11671.008	70.58	0.60	0.49	0.17	7.3
Rice husk char, DAE, CAM	ASC/11671.009	44.84	0.83	0.28	0.02	4.6

1. Results are expressed as % in the samples as received.
2. IS means insufficient sample was supplied to carry out analysis.
3. Table Legend: CAM = Cambodia; DAE = Department of Agricultural Engineering, General Directorate of Agriculture, MAFF, Royal Government of Cambodia; SFRI = Soil & Fertilizer Research Institute, MARD, Government of Viet Nam; VN = Viet Nam.

TABLE A4: ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (UESPA ∑16 PAHs) IN BIOCHAR SAMPLES TESTED

	Rice straw char, SFRI, VN (ng/g)	Rice husk char, SFRI, VN (ng/g)	Bamboo stem char, SFRI, VN (ng/g)	Acacia wood char, SFRI, VN (ng/g)	Rice straw char 2, SFRI, VN (ng/g)	Rice straw char, DAE kiln, CAM (ng/g)	Corn (maize) cob char, DAE kiln, CAM (ng/g)	Corn (maize) straw char, DAE kiln, CAM (ng/g)	Rice husk char, DAE, CAM (ng/g)
Naphthalene	190	370	1600	270	290	600	230	4200	770
Acenaphthylene	<50	<50	<250	<50	<50	<50	<50	860	<50
Acenaphthene	54	<50	<250	<50	<50	<50	<50	170	<50
Fluorene	93	<50	<250	<50	<50	62	<50	360	91
Phenanthrene	280	59	<250	<50	91	170	<50	480	360
Anthracene	57	<50	<250	<50	<50	<50	<50	<50	52
Fluoranthene	160	<50	<250	<50	<50	<50	<50	77	120
Pyrene	180	<50	<250	<50	<50	<50	<50	70	120
Benzo (A) Anthracene	210	<50	<250	<50	<50	<50	<50	<50	100
Chrysene	210	<50	<250	<50	<50	<50	<50	<50	130
Benzo (B) Fluoranthene	450	<50	<250	<50	<50	<50	<50	<50	140
Benzo (K) Fluoranthene	81	<50	<250	<50	<50	<50	<50	<50	<50
Benzo (A) Pyrene	190	<50	<250	<50	<50	<50	<50	<50	73
Indeno (1,2,3-CD) Pyrene	80	<50	<250	<50	<50	<50	<50	<50	<50
Dibenzo (A,H) Anthracene	<50	<50	<250	<50	<50	<50	<50	<50	<50
Benzo (GHI) Perylene	89	<50	<250	<50	<50	<50	<50	<50	<50

Table Legend: CAM = Cambodia; DAE = Department of Agricultural Engineering, General Directorate of Agriculture, MAFF, Royal Government of Cambodia; SFRI = Soil & Fertilizer Research Institute, MARD, Government of Viet Nam; VN = Viet Nam.

REFERENCES

Angst, T. and Sohi, S. (2012), Establishing release dynamics for plant nutrients from biochar, *CGB Bioenergy*, doi: 10.1111/gcbb.12023

Biochar Quality Mandate (BQM) (2014), www.britishbiocharfoundation.org

Cayuela et al. (2013), Biochar's role in mitigating soil nitrous oxide emissions: A review and meta-analysis, *Agriculture, Ecosystems and Environment*,

Crombie, K., Masek, O., Sohi, S., Brownsort, P. and Cross, A. (2013), The effect of pyrolysis conditions on biochar stability as determined by three methods, *GCB Bioenergy* 5: 122-131.

Cross, A. and Sohi, S. (2013), A method for screening the relative long-term stability of biochar, *GCB Bioenergy*, 5, 215–220

Enders, A. and Lehmann, J. (2012), Comparison of Wet-Digestion and Dry-Ashing Methods for Total Elemental Analysis of Biochar, *Communications in Soil Science and Plant Analysis*, 43: 1042-1052.

European Biochar Certificate (Ithaka Institute, Switzerland), http://www.european-biochar.org/en

Hale, S., Lehmann, J., Rutherford, D. et al. (2012), Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochar, *Environmental Science & Technology*, 46: 2830-2838.

Hilber, I., Blum, F., Leifeld, J., Schmidt, H-P. and Bucheli, T. (2012), Quantitative Determination of PAHs in Biochar: A Prerequisite To Ensure Its Quality and Safe Application, *Journal of Agricultural and Food Chemistry*, dx.doi.org/10.1021/jf205278v1

International Biochar Initiative's (IBI) Guidelines for biochar that is used in soils http://www.biochar-international.org/characterizationstandard

Horwell, C. (2007), 'Grain-size analysis of volcanic ash for the rapid assessment of respiratory health hazard', *Journal of Environmental Monitoring*, 9: 1107-1115.

IARC (1997), *Silica, some Silicates, Coal Dust and Para-aramid Fibrils*, International Agency for Research on Cancer, Lyon.

Le Bond, J., Williamson, B., Horwell, C., Munro, A., Kirk, C. and Oppenheimer, C. (2008), 'Production of potentially hazardous respirable silica airborne particulate from the burning of sugarcane', *Atmospheric Environment*, 43: 5558-5568.

Le Bond, J., Horwell, C., Williamson, B. and Oppenheimer, C. (2010), 'Generation of crystalline silica from sugarcane burning', *Journal of Environmental Monitoring*, 12: 1459-1470.

Novak, J. Cantrell, K., Watts, D., Busscher, W. and Johnson, M. (2013), 'Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks', *Journal of Soils and Sediments*, DOI: 10.1007/s11368-013-0680-8

PAS100 (2010), Publicly Available Specification for Compost; http://www.wrap.org.uk/content/bsi-pas-100-compost-specification

Rice, F. (2000), *Crystalline Silica*, *Quartz*, Concise International Chemical Assessment Document 24, Published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organization, and the World Health Organization, framework of the Inter-Organization Programme for the Sound Management of Chemicals, National Institute of Occupational Safety and Health, Cincinnati, OH, USA

Schimmelpfenig, S. and Glaser, B. (2012), 'One step forward toward characterization: some important material properties to distinguish biochars'*, Journal of Environmental Quality*, 41; doi:10.2134/jeq2011.0146: 1001-1013.

Shackley, S., Carter, S., Knowles, T., Middelink, E., Haefele, S., Sohi, S., Cross, A., Haszeldine, S. (2012). Sustainable Gasification-Biochar Systems? A Case Study of Rice-Husk Gasification in Cambodia Part I: Context, Chemical Properties, Environmental and Health and Safety Issues, *Energy Policy*, 42: 49-58.

Shinohara, Y and Kohyama, N. (2004), Quantitative analysis of tridymite and cristobalite crystallised in rice husk ash by heating, *Industrial Health* 42: 277-285.

Thy, P., Jenkins, B. Grundvig, S.,Shiraki, R. and Lesher, C. (2006), High temperature elemental losses and mineralogical changes in common biomass ashes, *Fuel* 85: 783–795.