Project Reference Number: RUSD2011-01CMY-Sun

Assessment and Promotion of Strategies and Techniques for Biomass Use in Countryside of China -Concentrating on Agricultural Straw Residue

RUSD: Resource Utilisation and Pathways for Sustainable Development

for Global Change Researc

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Assessment and Promotion of Strategies and Techniques for Biomass Use in Countryside of China - Concentrating on Agricultural Straw Residue

Project Reference Number: RUSD2011-01CMY©- Sun Final Report submitted to APN

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OVERVIEW OF PROJECT WORK AND OUTCOMES

Minimum 2pages (maximum 4 pages)

Non-technical summary

To improve the recycling of agricultural biomass residue in China, the present project surveyed the recycling patterns of agricultural waste biomass in Japan by literature reading and field visiting. Meanwhile, the situation of agricultural straw recycling in Tianjin suburb, China was investigated as a case study. Moreover, as a new approach of straw recycling, biochar was studied systematically to elucidate its possible effects on plant growth, soil microflora, and fate of several pollutants. To disseminate the advanced strategies and technologies in biomass recycling, a monograph titled "Biochar and Environment" was written to be published; a workshop was held; and a website was constructed. It was found that in Japan, there is a long history of good practice to use agricultural and other biomass residues, such as wood chip to generate energy and soil fertilizers; In Tianjin, the recycling of agricultural biomass residue has achieved much progress, however, the reuse rate is still low and techniques were lagging. The study on biochar found that biochar could promote the growth of wheat and vegetables, immobilize heavy metals and PAHs. Moreover, biochar could influence the hydrolysis and microbiodegradation of pesticides, and the impact varied with the structure of the biochars. This could be manipulated during the pollution control of pesticides.

Objectives

The main objectives of the project were:

1. To find the best scheme on the recycling of agricultural straw for China

2. To disseminate the selected advanced Japanese strategies and techniques to Chinese decision makers, scientists, and farmers, raising their awareness

3. To help Chinese scientists to build capacity to conduct innovative study on biomass reuse

Amount received and number years supported

The Grant awarded to this project was: Year 1: US\$28,000 Year 2: US\$27,000

Activity undertaken

Innovative research on biochar was conducted. Different kinds of biochar that were produced from different agricultural wastes and under different pyrolyzing temperatures were examined. The impacts of applying biochars into soil on the growth of plants, soil enzyme, soil microorganism diversity, mobility of heavy metals and hydrophobic organic compounds, and dissipation pathways of pesticides were comprehensively studied.

The situation of waste recycling in Japan was studied by literature survey and field visiting. In September, 2012, the participants from Nankai University visited Hokkaido and Tokyo to investigate the utilization of biomass and biochar in Japan accompanied by Professor Morita and Professor Matsuda, the Japanese members of this project. We visited the experimental farm of Hokkaido University, Recycling Centre of Furano City in north Hokkaido, Shimokawa Town of north Hokkaido, and the experimental farm of the University of Tokyo, and got direct impression of the situation of waste recycling in Japan. Not only the agricultural waste, but also living waste, such as rubbish and electrical appliance were well recycled.

The situation of agricultural waste recycling in the suburb of Tianjin was also studied in comparison. The amounts and structures of agricultural waste in 2011 were estimated, and



meanwhile the reuse of these agricultural waste was analyzed. According to the agricultural structure and geographic condition, recommendation on how to better use the agricultural waste was proposed.

A workshop on "Biochar and Environment" was held on 13 of April, 2013. Over sixty participants (farmers, students, officers, and company people) took part in the workshop, and Prof Sun gave a presentation with the same title with the workshop. A brochure named "Biochars and Climate Change & Agricultural Production" was dispatched to the participants in the workshop.

To disseminate waste recycling to more people, a monograph of "Biochar and Environment" in Chinese has been finished and now is being edited by the publisher and will be published in Aug, 2013 by Chemical Engineering Publisher, China. Meanwhile, a website named "Forum of Biochar in China" in Chinese was constructed (www.shengwutan.org).

Results

(1) Innovative research on biochar

The study on biochar found that the structure of biochar varied a lot with the raw materials and pyrolyzing temperatures. Hence, the properties of different biochars should be systematically studied so that proper biochars could be selected according to different purpose. The impact of biochar, crushed straw and composted straw were compared, it was found that biochar could promote the growth of wheat and vegetables, while crushed straw inhibited the plant growth in some cases due to the anaerobic condition and N speciation (more NH_4^+), and composted straw usually contains less carbon per unit weight. Moreover, biochar could immobilize heavy metals and hydrophobic compounds, such as PAHs, which could reduce the bioavailability of these pollutants. As for pesticides, biochar could influence the hydrolysis and microbiodegradation of pesticides, and the impact varied with the structure of the biochars. This could be manipulated during the pollution control of pesticides.

(2) Comparison of situation of waste recycling between Japan and China

According to literature survey and field visit, we realized that good system has long been set up in Japan for the recycling of waste. There is huge forest resource in Japan, and the forestal waste has well been utilized as energy and soil fertilities, and biochar was sold in the market. Not only the natural resource, but also the living waste such as rubbish and electric device, are all well managed for recycling. In general, Japan is a recycling social. In China, the recycling of agricultural waste has progressed much in recent years, and direct incineration of agricultural straw has been abandoned gradually. The amount and structure of agricultural waste as well as the reuse situation was surveyed in Tianjin. About 70% of the waste was reused, however, the reuse ratio was low in some towns. The most usual way to recycle the agricultural straw is direct applying of crushed straw, and composted straw is seldom used and biochar has never been used in field. Hence, the reuse ways should be advanced and diversified.

(3) Dissemination activities

To disseminate to results of this project, a workshop on "Biochar and Environment" was held on 13 of April, 2013. Over sixty participants (farmers, students, officers, and company people) took part in the workshop, and Prof Sun gave a presentation with the same title with the workshop. A brochure named "Biochars and Climate Change & Agricultural Production" was dispatched in the workshop. The PowerPoint had over 100 slides, covering four topics of "Biochar and their properties", "Biochar and global change", "The effects of biochar on agricutural ecosystem and agricutural plants", and " the effects of biochars on the fate of pollutants". The brochure included 8 pages, which briefly introduced the concept and benefit of biochar, the hazard of buring agricultural waste, biochar and agricultural production, biochar and climate change.

Meanwhile, a website named "Forum of Biochar in China" in Chinese was constructed to enlarge the dissemination range (www.shengwutan.org). The theme of the website is "black (biochar) jacks up green". Six columns compose the website, the first is "homepage", where the objective of the website is illustrated and the support from APN was also acknowledged. The second column is "Recycling of agricultural waste and biochar", and the third column is "biochar and climate change", the fourth one is "biochar and agricultural production", and the fifth one is "biochar and remediation of contaminated environment". In these columns, the typical research progress in our project and from related literature were introduced. From the website, the visitor can access to websites of "Asia-pacific network for global change research", "Biochar-international action", "UK biochar research centre". The website will exert great effect on disseminating the results of this project, will promote the understanding of biochar research, will help more people to know APN.

Relevance to the APN Goals, Science Agenda and to Policy Processes

The content and organization of this project are in accordance with the goals of APN and activities under CAPaBLE: strengthening international cooperation on regional special problem causing global change; improving capacity for innovative research in developing countries; and to set up platform to connect scientific research to policy-making and practice.

Self-evaluation

The project has been finished with high quality. First, great achievements were obtained on innovative research on biochar, 5 papers were published on peer-reviewed journals (three on international journals), and much results will be summarized into more papers in near future. As for the dissemination activities, a monograph on biochar was finished, a brochure was designed and dispatched, and a website was set up. A drawback of the project is the lacking of effective contraction with decision makers, and we plan to send the CD of this project to more government officers.

Potential for further work

Biochar is a new idea, which could simultaneously resolve the climate change, waste reuse and soil deterioration. It has been practiced for long time in Japan that the agricultural and forestal wastes are produced into carbonaceous material and applied to farmland. With the deepening of biochar related study, some advantage and disadvantage of biochar have been revealed, and systematical research, including environment, energy and social aspects, should be conducted before this gigantic innovation could be implemented globally. Hence, the team of Nankai University hope to cooperate with Japanese scientists and scientists from other Asian countries to further the research on biochar and exert more impact from Asian countries on this fatal issue.

Publications (please write the complete citation)

(1) A monograph of "Biochar and Environment" in Chinese has been finished and now is being edited by the publisher and will be published in Aug, 2013 by Chemical Engineering Publisher, China.

(2) Several peer-reviewed journal papers have been published

i. Peng Zhang, Hongwen Sun*, Li Yu, Tieheng Sun. Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: Impact of structural properties of biochars. Journal of Hazardous Materials, 2013, 244-245:217-224

ii. Wen Zhang, Hongwen Sun*, Lei Wang. Influence of the interactions between black carbon and soil constituents on the sorption of pyrene. Soil and Sediment Contamination, 2013, 22: 1-1

iii. Ting Wang, Hongwen Sun*. Biosorption of heavy metals from aqueous solution by UV-mutant Bacillus subtilis, Environ Sci Pollut Res, 2013 available on line

iv. 李力,陆宇超,刘娅,孙红文*,梁中耀.玉米秸秆生物炭对Cd(II)的吸附机理研究. 农业环境科学学报,2012,31,2277-2283

Li Li, Yuchao Lu, Ya Liu, Hongwen Sun, Zhongyao Lian. Study on the adsorption mechanisms of Cd(II) by corn straw biochar. Journal of Agro - Environment Science, 2012, 31, 2277-2283



v. 张鹏,武健羽,李力,刘娅,孙红文*,孙铁珩.猪粪制备的生物炭对西维因的吸附与 催化水解作用.农业环境科学学报,2012,31,2:416-421

Peng Zhang, Jianyu Wu, Li Li, Ya Liu, Hongwen Sun*, Tiehang Sun. Sorption and catalytic hydrolysis of carbaryl on pig-manure-derived biochar. Journal of Agro - Environment Science, 2012, 31,2:416-421

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Acknowledgments

The authors wish to pay their due gratitude to Asia-Pacific Network for Global Change Research.

TECHNICAL REPORT

Minimum 15-20 pages (excluding appendix)

Preface

Global Changes, including climate change, deterioration of farm soil, and exhaustion of fossil resource, are great challenge on the way of human sustainable development. Biomass is the product of plant photosynthesis, which absorb sun energy and inorganic nutrients from soil. To effectively use biomass resource is an key measurement which could simultaneously resolve the above big issues challenging human sustainable development, however only a part of biomass are well used and a lot are regarded as waste. The main objectives of the present project were to find and disseminate good measurement and practice of agricultural straw recycling and to set up innovative research capacity of Chinese scientists in related field. To do so, we surveyed and compared the recycling patterns of agricultural waste biomass in Japan and in Tianjin suburb, China. Moreover, as a new approach of biomass recycling, biochar was studied systematically to elucidate its possible effects on plant growth, soil microflora, and fate of several pollutants. Biochar is a new concept, which was proposed in 2005, however, it has drawn huge attention, including scientific research and practice promotion. To disseminate the advanced strategies and technologies in biomass recycling, a monograph titled "Biochar and Environment" was written to be published; a workshop was held; and a website was constructed. Hence, both technique and management aspect were involved in this project, which endow the project of capacity building of both technology and awareness of biomass recycling. This project was led by Prof Hongwen SUN in Nankai University, China, collaborated by Prof Shigenori Morita and Dr Hirotaka Matsuda from Nankai University. People from Agricultural Bureau of Tianjin gave support on local investigation and dissemination.

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1.0 Introduction

Modern human activities have caused green gases, mainly CO_2 , to accumulate in the atmosphere, which leads to earth warming and series of hazardous consequences. Meanwhile, with the increasing of population and the elevation of human living standard, heavy agricultural activities have led to deterioration of farm soil. Moreover, the speed up exploitation of fossil resource has raised the concern of the depletion of these non-renewable resource. Climate change, deterioration of farm soil, and exhaustion of fossil resource, and other big issues on the way of human sustainable development are named global change, which should be paid much attention so that we could find a way to avoid the disastrous situation in the future.

Only a part of agricultural plants occur as edible food, and majority of the biomass occur as waste straw, which is the most plentiful renewable resource. The estimated world amounts of agricultural straw is 2.9×10^9 ton. China is a big agriculture country, and the amounts of agricultural straw is the biggest in the world, being 10×10^8 ton. Hence, to better utilize this waste biomass bas become a big issue which will exert great impact on the way of human sustainable development. The recycling of waste agricultural straw has drawn much attention with the awareness of energy crisis, and good techniques and management patterns have been proposed and practiced. However, the technique level and practice extent varied a lot among different countries. In China, especially ten years ago, the agricultural waste are not well utilized, and some are incinerated randomly, releasing CO₂ and other pollutants into atmosphere. Japan is one of the countries that have good pattern of waste recycling throughout the whole society. As for the recycling of agricultural waste, Japan has been implementing Biomass Nippon strategy, and 'Biomass Town' mode is an up and coming mode in Japan, especially establishing the cascaded biomass utilizing system in some remote rural areas. In 'Biomass Town', waste biomass is converted to bio-energy and bio-product by methane fermentation, burning fuel for boiler, biofuel and animal feed, and so on. There are several ways to reuse the agricultural straw: as poultry feed; farmland fertilizer; fuel; and industry raw material, such as to produce paper. Some techniques (feed) are simple and used routinely, some (solid fuel and methane production) have been set up but need to be expanded practically, and others are on their way for innovative study, such as to turn straw into alcohol or biochar. Besides, how to utilize agricultural straw in a best scheme depends on many factors, including local agricultural structure, energy resource, government policy for global climate changing and sustainable development, scientist capacity to conduct innovative study, income and environmental awareness of the farmer, etc. The concept of making a different plan from region to region for cascaded biomass utilizing system bases on established evaluation method and standardized checking item. Hence, much work should be done to successfully transfer Japanese experience of "Biomass Town" to China.

Hence, the main objectives of this project were, 1) to find the best scheme on the recycling of agricultural straw for China; 2) To disseminate the selected advanced Japanese strategies and techniques to Chinese decision makers, scientists, and farmers, raising their awareness; 3)To help Chinese scientists to build capacity to conduct innovative study on biomass reuse.

2.0 Methodology

2.1 Innovative research on biochar

Different biomass wastes, including wood chip, corn straw, rice straw, wheat straw and pig manure were collected. These materials were dried first, and then pyrolyzed in Muffle oven in a closed container (lacking of oxygen) under different temperatures (350/400 °C and 700 °C) to acquire different biochars. The pristine biochars were further treated by HCl (deashing), oxidation, hydrolysis, and oximation to get modified biochars. In total, over 20 biochars were synthetized. The bulk/surface elemental composition, pore distribution/surface area, FT-IR, NMR, XRD and SEM features of the synthetized biochars were characterized.

Different biochars were used in different experiments:

(1) First, we compared the influence of three different straw recycling ways on the growth of wheat in pot experiment, e.g. the crushed raw straw (wheat straw), composted straw, and biochar derived from the straw. The chemical constituents in soil, soil microbial structure and enzyme, wheat yield and chlorophyll



content under different treatments were measured. Based on all these aspect, the advantage and disadvantage of biochar were discussed. In a parallel study, the effects of biochar (from corn straw and wheat straw) on amaranth (*Amaranthusmangostanus L.*) and lettuce (*Lactuca sativa var. ramosa*) were studied with rotten straw as a comparison. In this study, besides to the plant yield, the N speciation exchange was analyzed to support the mechanisms.

(2) Sorption ability of heavy metals by biochars were studied using Cd, Pb, Cr, and Hg as typical metals and biochars from pig manure and corn straw as typical biochars. Besides checking the heavy metal sorption capacity of biochar, the biochars were mixed with a mutagenic bacterial B38 (obtained under UV irradiation from *Bacillus subtillis*) to act as the carrier for bacterial, and adsorption capacity for heavy metals by these combined biosorbents were examined. Further, the fixation of heavy metals in soil of the above sorbents was checked in pot experiments for lettuce (*Lactuca sativa L.*), and the growth and heavy metal contents of the lettuce were measured. The remediation efficiency of different treatment was evaluated and mechanisms were elucidated by measuring soil properties and heavy metal speciation.

(3) Adsorption of pyrene, a four ring cyclic aromatic hydrocarbon on different biochars were studied. In this study, the biochars were acquired from wood chip under different temperatures, and the pristine biochars were further treated by oxidation, hydrolysis, and oximation to get modified biochars. The adsorption of pyrene on these different biochars was analyzed based on the structure of the biochar. Moreover, the adsorption of pyrene on the mixture of biochar and soil was also studied, and adsorption mechanism of the mixture was elucidated by checking the adsorption ability of biochar modified with dissolved organic matter and biochar mixed with clay.

(4) The influence of biochars on the fate of pesticides was studied. Two pesticides were studied, a carbamate insecticide, carbaryl, a triazine herbicide, atrazine. First, the adsorption of these two pesticides on 6 original biochars (derived from corn straw, wheat straw, and pig manure under two different temperatures of 350 and 700 °C, respectively) and corresponding deashed biochars were studied, and impact of ash on adsorption was discussed. Then, hydrolysis of the two pesticides were studied, catalytic hydrolysis mechanisms were elucidated by checking hydrolysis in biochar suspension with or without pH adjusted and in the leachate of biochars. Finally, the dissipation of pesticides in sterile and non-sterile soils spiked with biochars was studied, and the contributions of chemical hydrolysis and biodegradation were discussed.

2.2 Comparison of current state of agricultural biomass waste recycling in Tianjin and Japan

The investigation was conducted by Bureau of Agriculture in Tianjin. Tianjin is the third largest city in China, however, its suburbs still have agricultural activity. In the central city of Tianjin, there are six administrative districts, and outside the central city, there are 9 suburbs engaged in agricultural activity, and each having its agricultural office. The data on agricultural biomass recycling were collected by this agricultural executive management system.

We have got an general impression of source recycling in Japan from the literature provided by Japanese collaborators. In September, 2012, the participants from Nankai University visited Hokkaido and Tokyo to make a field investigation on the re-utilization of biomass and biochar in Japan accompanied by Professor Morita and Professor Matsuda, the Japanese members of this project. First, we visited the experimental farm of Hokkaido University, where there were several devices for biomass waste recycling. Then, we visited the Recycling Centre of Furano City in north Hokkaido and Shimokawa Town of north Hokkaido. Finally, we also visited the experimental farm of Tokyo and learned the research on producing alcohol from energy plants

2.3 Dissemination activities

A workshop on "Biochar and Environment" was held on 13 of April, 2013 under the assistance of Agricultural Bureau in Tianjin. Over sixty participants, including 30 farmers, 20 students, 10 officers and company people took part in the workshop. Prof Sun gave a presentation with the same title with the workshop. A brochure named "Biochars and Climate Change & Agricultural Production" was designed by project group and dispatched in the workshop. A website named "Forum of Biochar in China" in Chinese was constructed to enlarge the dissemination range.



3.0 Results & Discussion

3.1 Innovative research on biochar

Biochars are materials produced by pyrolyzing biomass residues under limited oxygen. It was proposed in 2005, and has become a hotspot globally. Systematic innovative studies around biochar have been conducted in this project, and the main research results are as followed.

3.1.1 Synthesis and Characterization of biochars

Great difference existed in the composition and structure of various biochars derived from different feedstock and temperatures. Biochars derived from pig-manure contained high content of ash, up to over 50%. Biochars derived from agricultural straws had relatively low ash contents, and biochars derived from maize straw contained lower ash than that those derived from the rice straw. The biochar derived from wood chip had the lowest ash content, less than 2%. The ash contents of biochars increased with elevated pyrolyzing temperature. Specific surface area and porosity of biochars were influenced by feedstock and temperature. Porosity and specific surface area increased with increasing temperature. The specific surface area of biochar derived from straws was larger than that of biochars derived from pig-manure. The biochars consisted of organic moiety including aliphatic carbon and aromatic carbon and inorganic moiety containing phosphate, carbonate, and other minerals. In addition, chemical functional groups, such as hydroxyl, carboxyl and carbonyl, were also bound on the surface of biochars. Most of organic surface of the biochars was covered by inorganic ash and the pores on surface of biochars were also obstructed. Hence, the ash may change the surface properties of biochars. As the pyrolyzing temperature increased, amorphous organic carbons were transformed to crystalline carbons, proportion of aromatic carbon increased, and surface functional groups decreased. The ash of biochars could be removed efficiently by acid treatment, and organic carbon and porosity of biochars were consequently recovered. Figure 1 shows the SEM photography of different biochars. It can be seen that biochars from corn had a structure of sieve plate with pore on it; biochar from wheat straw had a structure of rod-shape structure; while biochas from pig manure had a granular structure with pores inside the particle. The morphology of biochars had a deep influence on the property of biochars.

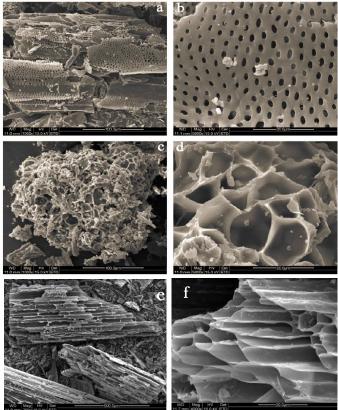


Fig.1 SEM photography of corn biochar (CBC), wheat biochar (WBC) and pig manure biochar (PBC) (a: CBC \times 1000; b: CBC \times 5000; c: PBC \times 1000; d: PBC \times 5000; e: WBC \times 1000; f: WBC \times 5000;)



Figure 2 shows the FTIR spectrum of different biochars. It can be seen that with the elevation of pyrolyzing temperature, the O-contained group and aliphatic carbon decreased; while aromatic carbon and inorganic moiety increased. Deashing led a reduction in inorganic mineral and an increase of O-containing groups and aromatic carbon. This is because more aromatic group were uncovered after the ash was removed.

Table 1 shows the elemental composition of different biochars. When the ash content is high, the elemental change with temperature did not show a unit trend with the pyrolyzing temperature. HCl treatment could effectively remove ash, and the ash content was reduced from over 50% to less than 6%. After the ash was removed, the C increased, and O and N decreased with the pyrolyzing temperature. Accordingly, aromaticity as indicated by H/C increased and polarity of the organic moiety as indicated by (O+N)/C decreased with the pyrolyzing temperature.

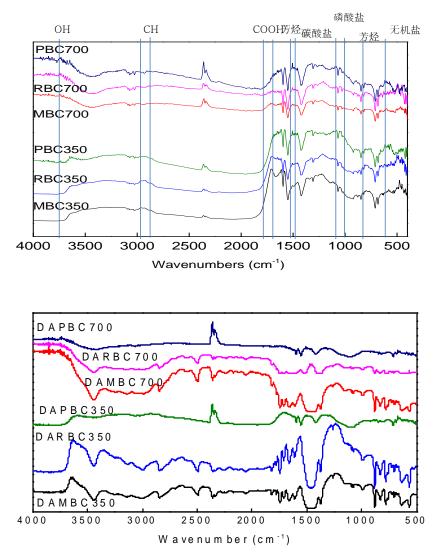


Fig. 2 FTIR spectra of biochar (BC) derived from pig manure(PBC), maize straw (MBC), and rice straw (RBC) under pyrolyzing temperature of 350 and 700, DA represents deashing



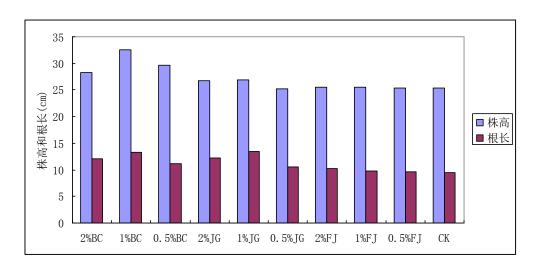
-	Biochars*	Eleme	ntal Con	positio	n (%)	Ash(%)	Ator	nic ratio ^ª
-	-	С	Н	Ν	0		H/C	(O+N) /C
	PBC350	31.58	2.36	3.80	16.93	45.33	0.90	0.51
	PBC700	25.16	1.12	2.05	4.83	66.84	0.53	0.21
	MBC350	58.92	3.36	1.00	21.29	15.43	0.68	0.29
	MBC700	43.77	1.47	1.27	31.62	21.87	0.40	0.57
	RBC350	44.52	2.69	1.64	22.04	29.11	0.73	0.40
	RBC700	56.76	2.39	0.10	2.55	38.20	0.51	0.04
	DAPBC350	66.68	4.44	7.58	20.03	1.27	0.80	0.32
	DAPBC700	74.22	2.79	4.97	11.48	6.54	0.45	0.17
	DAMBC350	67.11	3.89	1.06	26.73	1.21	0.70	0.31
	DAMBC700	83.73	2.66	0.89	8.38	4.34	0.38	0.08
	DARBC350	65.89	3.22	2.45	24.61	3.83	0.59	0.31
	DARBC700	88.26	2.42	2.06	0.89	6.28	0.33	0.03

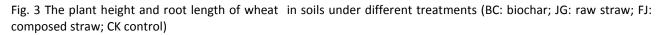
In the names of biochars, BC represents biochars; P represents pig manure; M represents maize; R represents rice; DA represents deashing; the numbers of 350 and 700 represent the pyrolyzing temperatures.

3.1.2 Influence of biochars on the growth of plants and soil fertility and enzyme

First, we compared the influence of three different straw recycling ways on the growth of wheat, e.g. the crushed raw straw, composted straw, and biochar. Generally, biochar and crushed straw treatments could increase plant height, root length and biomass to certain extents with biochar being better than the crushed straw (Fig. 3). Crushed straw could greatly promote the growth of root, and the underground biomass was significantly higher than those of the other two treatments. The enhancement on wheat growth by composted straw was not obvious. The chlorophyll content and nutrient elements in the wheat were determined (Fig. 4, 5 and 6). Similarly, biochar and crushed straw both showed positive effect to promote the chlorophyll content and nutrient elements in the wheat, while the rotten straw had no significant promotion. This is due to that the composted straw used in this project contained low organic matter. All the three treatments enhanced the soil enzyme activities. The activity of saccharase in soil was enhanced in the order of biochar > crushed straw > composted straw (Fig. 7).







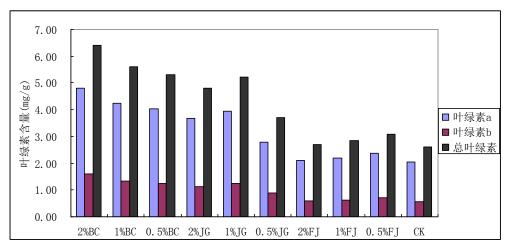


Fig. 4 The chlorophyll content in wheat in soils under different treatments (BC: biochar; JG: raw straw; FJ: composed straw; CK control)

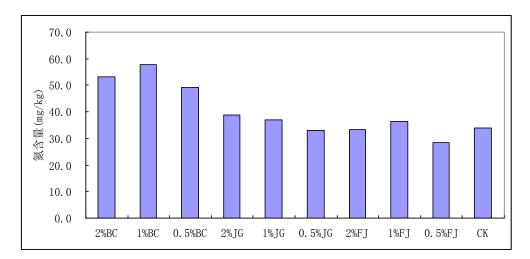


Fig. 5 The nitrogen content in the wheat under different treatments (BC: biochar; JG: raw straw; FJ: composed straw; CK control)



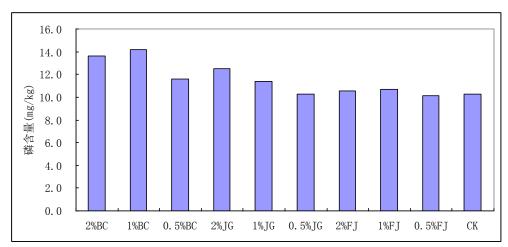


Fig. 6 The phosphorus content in the wheat under different treatments (BC: biochar; JG: raw straw; FJ: composed straw; CK control)

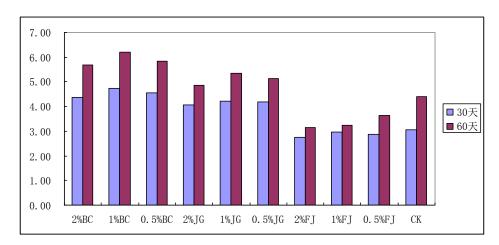


Fig. 7 The saccharase activity in soils planted with wheat under different treatments (BC: biochar; JG: raw straw; FJ: composed straw; CK control)



CK; Corn straw; Corn biochar; Corn biochar+N; Wheat straw; Wheat biochar; Wheat biochar+N



CK; Corn straw; Corn biochar; Corn biochar+N; Wheat straw; Wheat biochar; Wheat biochar+N

Fig. 8 Plant growth in soils amended with straws and biochars



Then, we compared fertilizing effects between straw-derived biochar and original straw on the growth of vegetable and flower. Corn-derived and wheat-derived biochars, as well as corn straw and wheat straw, were applied in pot experiment to the soil before two types of plants, amaranth (*Amaranthus mangostanus L.*) and lettuce (*Lactuca sativa var. ramosa*), were grown. Increase of biomass production was observed in all biochar-added treatments and decrease was observed in all straw-added treatments relevant to untreated soil (Fig. 8). N-fertilizer addition strengthened the enhancement. A close link among biomass production, tissue mineral N-content (internal N level, mainly ammonium and nitrate in this study) and soil content (external N level) was revealed. Biochar application increased the external and internal nitrate content, thus enhanced plant productivity, while straw application increased external and internal ammonium content, and reduced productivity (Fig. 9, 10).

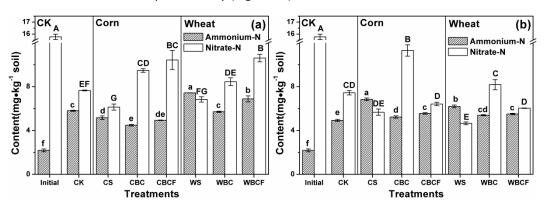


Fig. 9 Effects of treatments on mineral N levels of the soil for growing amaranth (*Amaranthus mangostanus L*.)(a) and lettuce(*Lactuca sativa var. ramosa*) (b) . Initial level before seeding is also performed for comparison. Data show means \pm SE of independent triplications. Different small letters indicate significant differences(p=0.05) for ammonium in each treatment, and capital letters indicate significant differences(p=0.05) for nitrate in each treatment.

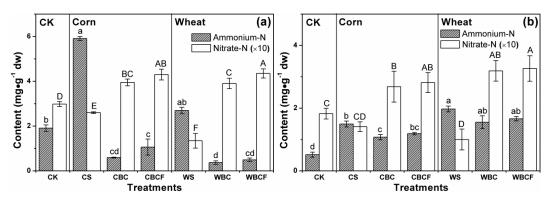


Fig. 10 Effects of treatments on mineral N levels of amaranth (*Amaranthusmangostanus L*.)(a) and lettuce(Lactuca sativa var. ramosa)(b) in plant tissues. Data show means \pm SE of independent triplications. Different small letters indicate significant differences(p=0.05) for ammonium in each treatment, and capital letters indicate significant differences(p=0.05) for nitrate in each treatment. Note: Nitrate is shown as 10 folds of real concentration in figure.

Two probable mechanisms of alteration of nitrogen supply by biochar and straw were suggested through sustainable releasing experiment and bottle incubation experiment: (a) both biochar and straw can retain mineral-N ions as well as release them sustainably for plant uptake, with biochar performing better than straw in nitrate retention; and (b) biochar promoted nitrification and had little impact on nitrogen mineralization, hence raised nitrate level, while straw had positive effects on nitrogen immobilization, and promoted denitrification hence raised ammonium level. Dicyandiamide (DCD) was applied to biochar-added soil. DCD is used as an agricultural nitrification inhibitor by blocking the process of oxidizing ammonium compounds into nitrites, which is the first step of nitrification. DCD significantly raised the ammonium-N content and diminished nitrate-N relative to individual biochar-added soil(p<0.05), indicating



that the nitrification promotion was alleviated by DCD (Fig. 11). The results confirmed that the straw-tobiochar process has meaningful agricultural and environmental implication.

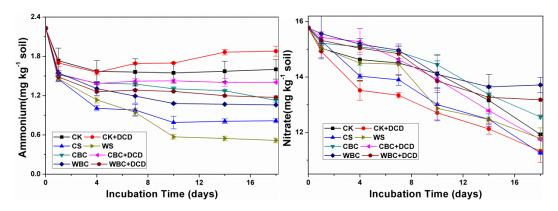


Fig. 11 Measurements of ammonium-N(left) and nitrate-N(right) in soil with different treatments in aerobic incubation. Data show mean s±SE of independent triplications (p=0.05). Dicyandiamide (DCD) was applied to biocharadded soil as an agricultural nitrification inhibitor by blocking the process of oxidizing ammonium compounds into nitrites.

3.1.3 Influence of biochars on the mobility of heavy metals

Biochars showed high sorption capacity to heavy metals. Biochars from corn straw (CBC) had a high affinity to Hg ions, while biochars from pig manure (PBC) had a high adsorption capacity for Pb ions (Fig. 12). The adsorption increased with the dose of biochar, and under high dose of biochar, almost 100% of the two heavy metals were adsorbed from aqueous phase. Hg ions competed for the same adsorption sites with Pb ions on the biochar surface. The SEM photographs showed significant differences in the structure between CBC and PBC (Fig. 1). The CBC materials looked like sieve plates with polyporous structure, while the PBC materials were polyporous structure with lacunose surface. Thus, PBC could provide more adsorption activity sites for heavy metal binding. The oxygen-containing functional groups, such as the hydroxyl, carbonyl, carboxyl groups, and the aliphatic ethers groups (C-O-C) in cellulose of CBC can enhance ion exchange with heavy metal ions.

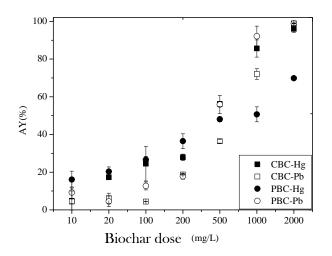


Fig. 12 Dose-dependent adsorption of Pb and Hg on biochars, CBC (biochars from corn straw) and PBC (biochars from pig manure).

CBC and PBC were tested as the B38 mutant carrier (a mutant species with higher immobilizing capacity for heavy metals) in the adsorption of heavy metals (Fig. 13). It can be seen for Pb, the mixture bioadsorbent of B38 and biochars showed greater adsorption capacity; while for Hg, a reduced adsorption capacity was observed. This is because B38 shows quite greater adsorption capacity for Pb as compared to Hg. When mixed, B38 covered the surface of biochar and the adsorption of the mixture bioadsorbent is mainly dependent on B38. Hence, we may select different adsorbent for different heavy metals.



Finally, the above sorbents were applied into a contaminated soil to check their capacity for remediation of heavy metal contamination. All the four amendments (two biochars and two combined materials of B38 and the two biochars) could inhibit the bioaccumulation of heavy metal pollutants by lettuce (*Lactuca sativa L*.). The lettuce grew better than the control in the treatments of two combined materials, i.e. biochar from corn straw and B38 (SCB), and biochar from pig manure and B38 (SPB) (Fig. 13). Application of single biochar or B38 could not promote the growth of lettuce.

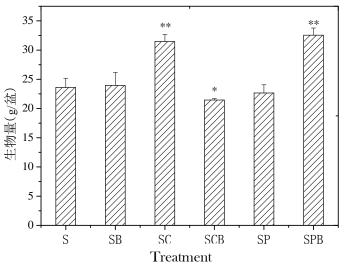


Fig. 13 Growth of lettuce (*Lactuca sativa L*.) under different treatments (S: control; SB: B38; SC: biochar from corn straw; SCB: biochar from corn straw and B38; SP: biochar from pig manure; SPB: biochar from pig manure and B38)

treatment		Cd		Cr			
	Concentration (mg/kg)	Reduction (%)	standard	Concentration (mg/kg)	reduction (%)	standard	
S	0.52	-	0.20	4.42	-	0.50	
SB	0.40	23.08		3.75	15.16		
SC	0.32	37.96		3.18	27.82		
SCB	0.16	68.64		2.62	40.69		
SP	0.17	67.39		2.25	49.04		
SPB	0.06	87.65		1.33	69.95		
treatment		Hg			Pb		
	concentration (mg/kg)	reduction (%)	standard	concentration (mg/kg)	reduction (%)	standard	
S	0.79	-	0.01	5.33	-	0.30	
SB	0.40	49.37		4.14	22.33		
SC	0.59	25.96		0.89	83.26		
SCB	0.41	48.94		0.33	93.73		
SP	0.34	57.68		0.27	94.90		
SPB	0.15	80.66		0.21	96.06		

Table 2 Heavy metal concentrations in the edible parts of lettuces

(S: control; SB: soil amended with B38; SC: soil amended with CBC; SCB: soil amended with CBC and B38; SP: soil amended with PBC; SPB: soil amended with PBC and B38).

Both of single B38 and biochars could inhibit the adsorption of heavy metals (Cd, Hg, Pb, and Cr) by lettuce. The combined materials of SCB and SPB showed greater efficiencies, with SPB (PBC and B38) exhibiting the maximum remediation efficiency among the four treatments, and the Cd and Pb concentrations in the edible part of plants were below the maximum levels of contaminants in foods (Table 2).

To explain the mechanism of immobilization of heavy metals, soil properties (Table 3) and heavy



metal speciation (Table 4) were measured. It can be seen that B38 reduced soil pH and biochar increased soil pH, and generally, the soil pH did not change a lot, only within \pm 0.4 unit. Soil organic matter increased under all treatments, while dissolved organic matter (DOM) increased under the treatments containing biochar derived from corn, and decreased under the treatments containing biochar derived from pig manure. DOC exist in solution, can enhance the release of heavy metals from soil to solution. This can explain why biochar from corn straw showed less heavy metal immobilization capacity as compared to biochar from pig manure.

 Treatment	pН	CEC (cmol/kg)	OM (%)	DOC (mg C/L)
S	7.4	17.5	1.6	99.5
SB	7.0	18.1	2.6	88.3
SC	7.4	15.3	3.3	287.4
SCB	7.2	16.0	3.5	200.9
SP	7.8	10.2	2.1	83.0
SPB	7.5	12.6	3.0	70.4

Table 3 Soil properties under different treatments

(S: control; SB: soil amended with B38; SC: soil amended with CBC; SCB: soil amended with CBC and B38; SP: soil amended with PBC; SPB: soil amended with PBC and B38).

Heavy metals were extracted by different methods, i.e. DTPA, M3, and BCR1. It can be seen from Table 4 that all the treatments led to a reduction in extractable amounts of heavy metals. However, not all extractable amounts had significant correlation with those in lettuce. For the three cationic metals, Cd, Hg, and Pb, DTPA showed good predicting; while for the anion Cr, BCR1 showed better predicting.

Table 4 Results of extractable heavy metals of rhizosphere soils, and the linear correlation coefficients (r^2) between metal concentrations in the edible parts of vegetables and extracted metals from soils by different extraction methods

Treatments		Extractable heavy metal contents (mg/kg)						Correlation	
		S	SB	SC	SCB	SP	SPB	coefficients (\vec{r})	
DTPA	Cd	0.88	0.55	0.48	0.32	0.45	0.31	0.84*	
	Cr	0.62	0.38	0.37	0.33	0.34	0.38	0.45	
	Hg	0.07	0.04	0.05	0.04	0.04	0.03	0.94**	
	Pb	3.00	2.61	2.46	2.17	2.24	2.00	0.85^{*}	
M 3	Cd	1.65	1.38	0.50	0.48	0.57	0.40	0.80	
	Cr	6.10	5.54	5.70	3.19	5.32	4.84	0.25	
	Hg	0.08	0.08	0.07	0.05	0.07	0.04	0.49	
	Pb	2.41	1.64	1.01	0.93	1.03	0.89	0.93**	
BCR1	Cd	1.53	1.30	1.38	1.17	1.37	1.19	0.63	
	Cr	6.48	6.18	5.89	5.14	5.51	4.71	0.91**	
	Hg	0.07	0.07	0.06	0.06	0.06	0.05	0.51	
	Pb	4.15	2.75	2.76	1.19	1.18	0.99	0.78	

(S: control; SB: soil amended with B38; SC: soil amended with CBC; SCB: soil amended with CBC and B38; SP: soil amended with PBC; SPB: soil amended with PBC and B38).

3.1.4 Sorption on biochars of a typical hydrophobic compounds-pyrene

Biochars have extensively been studied on their high adsorption capacity for hydrophobic compounds in the literature. In this project, two biochars derived from wood chip under two pyrolyzing temperatures (400 and 700 °C) were modified by hydrolysis, oxidation, and oximation so that the adsorption of biochars could be connected with their structure. Pyrene, a four ring polycyclic aromatic hydrocarbon was selected as a typical hydrophobic compound. It can be seen that for 700BC, hydrolysis could not affect pyrene adsorption significantly, while oxidation and oximation inhibited the sorption with oxidation showing greater inhibition. This is because that 700BC was acquired under high pyrolyzing temperature, and contained high level of aromatic carbon, which endowed it high adsorption capacity.



Hydrolysis is too week to change its aromatic structure, and did not show any significant effect on pyrene adsorption. Oxidation introduced more O-containing groups, while oximation introduced more N-containing groups. The polarity and hydrogen bond formation tendency of O is greater than N, which is unfavorable for the hydrophobic pyrene to access to the interior sorption sites of aromatic carbon in biochar. This could explain why oxidation brought a greater inhibition. Compared to 700BC, 400BC contained more flexible carbon and polar groups due to the lower pyrolyzing temperature. For 400BC, oxidation and hydrolysis led to a reduction in pyrene sorption, while oximation enhanced the sorption. We ascribed this phenomena to that after oximation, more N atoms were introduced to substitute O atoms, and this made the surface of 400BC less polar and is favorable for pyrene to access to the interior sorption sites (Fig. 14).

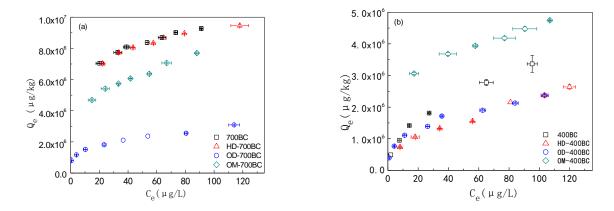


Fig. 14 Sorption isotherms of pyrene on 400BC and 700 BC and their modified products.HD: hydrolysis; OD: oxidation; OM: oximation

The sorption capacity of pyrene on biochars mixed in soil was also tested. Biochar and soil did not adsorb pyrene independently, and the sorption capacity of biochar for pyrene decreased after biochar was applied in soil (Fig. 15). Moreover, the condition and time under which biochar and soil contacted also exert effects on pyrene adsorption. Under wet condition, extending contact time of biochar and soil led to a further reduced sorption capacity. This could be ascribed to the interactions of biochar and soil constituents, and water molecules favored the interaction between soil and biochar. To check for the possible mechanism, the sorption of biochar modified with different constituents of soil particle were checked. First, DOM extracted from the two soils (paddy soil, PS; black soil, BS) attenuated pyrene sorption by biochars (Fig. 16), and this could be ascribed to the blockage of micropores and reduced accessibility to interior sorption sites. DOM residues in aqueous phase could bind pyrene and also lead to a reduction in pyrene sorption onto biochar. Different DOM exerted different effects on biochar sorption, with PSDOM causing greater reduction in pyrene sorption onto biochar as compared to BSDOM. This may be due to the higher initial concentration, greater adsorbed amount, and higher polarity of PSDOM. After correction of the sorption reduction due to DOM, there was still some difference between the predicted value and experimental value. The effects of another soil constituent, clay was also checked (Fig. 17). Clay could also reduce the sorption capacity of biochar probably due to the adhesion of clay to the surface of biochar that increased the surface polarity and reduced the accessibility of the interior sorption sites.



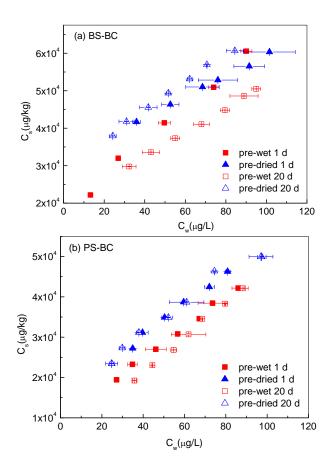
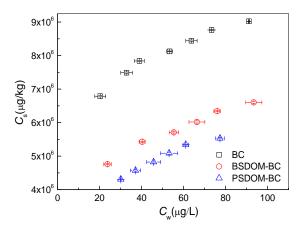
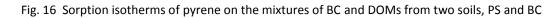


Fig. 15 Sorption isotherms of pyrene on the mixtures of (a) BS and BC, (b) PS and BC







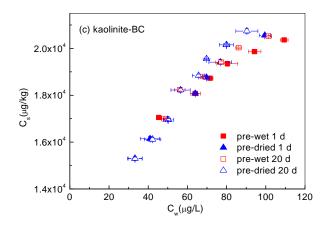
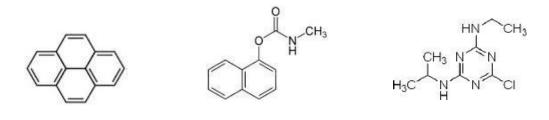


Fig. 17 Sorption isotherms of pyrene on the mixtures of BC and kaolinite



Structure of pyrene

Structure of carbaryl

Structure of atrazine

3.1.5 Influence of biochars on the fate of polar pesticides

Carbaryl is a carbamate insecticide, and atrazine is a triazine herbicide. First, the sorption of these two pesticides on different biochars were studied (Table 5 and Table 6).

E	Biochar	Freundli	ch parameter		$\lg K_{oc}$	
		Ν	lgK _f	R^2	0.5	20
F	PBC350	0.718±0.033	2.06±0.029	0.991	2.65	2.19
F	PBC700	0.302±0.015	2.85±0.018	0.990	3.66	2.54
[DAPBC350	0.615±0.058	3.35±0.045	0.965	3.64	3.03
[DAPBC700	0.448±0.075	3.70±0.071	0.874	4.00	3.11
1	MBC350	0.370±0.002	3.40±0.003	0.993	3.82	2.81
ſ	MBC700	0.220±0.042	4.09±0.040	0.935	4.68	3.43
[DAMBC350	0.459±0.027	3.81±0.023	0.987	4.15	3.28
[DAMBC700	0.279±0.045	4.32±0.029	0.904	4.61	3.46
F	RBC350	0.453±0.017	3.17±0.018	0.977	4.33	3.45
F	RBC700	0.311±0.050	4.18±0.069	0.924	4.63	3.53
[DARBC350	0.402±0.014	3.65±0.014	0.995	4.01	3.05
[DARBC700	0.210±0.027	4.45±0.024	0.920	4.74	3.48

Table 5 Freundlich sorption isotherms of carbaryl on different biochars

BC represents biochar; P, M, and R represent pig manure, maize, and rice; DA represents deashing; and the numbers represent pyrolyzing temperature.



Sorption of the two pesticides varied a lot among different biochars. The sorption was low on PBC (biochar from pig manure) as compared to those on biochars derived from agricultural straw, MBC and RBC. This is because the PBC contained greater content of ash. When pyrolyzing temperature increased, the sorption increased. When the ash was removed, the sorption capacity increased further. Theoretically, both organic carbon and inorganic mineral could combine pesticides. In order to evaluate the contributions of organic moiety and inorganic moiety to sorption, sorption capacity of pristine biochars was compared with sorption capacity predicted based on the sorption capacity of deahsed biochars, which the sorption was mainly ascribed to organic moiety. In most of the cases, the contribution of ash to sorption was negative though it can bind pesticide through polar interaction, hydrogen bond, and charge transferring. This is because the cover of ash simultaneously inhibited the sorption of organic moiety by occupying sorption sites, blocking nanopores, and lowering the accessibility of the interior sites. Significant correlation of sorption, with surface area, aromatic carbon, pore volume, and polarity did not exist.

Biochar	r Freundlich Parameter			I	gK _{oc}
-	п	lg <i>K</i> _f	R^2	0.5	20
PBC350	0.999±0.080	1.40±0.082	0.969	1.90	1.90
PBC700	0.330±0.023	2.77±0.030	0.976	3.57	2.50
DAPBC350	0.615±0.037	3.15±0.022	0.983	3.44	2.83
DAPBC700	0.427±0.041	3.55±0.032	0.957	3.85	2.93
MBC350	0.434±0.022	2.98±0.028	0.986	3.38	2.47
MBC700	0.132±0.003	3.88±0.003	0.995	4.50	3.10
DAMBC350	0.389±0.017	3.58±0.016	0.994	3.94	2.96
DAMBC700	0.231±0.002	4.03±0.002	0.999	4.34	3.10
RBC350	0.565±0.085	1.73±0.075	0.960	2.21	1.52
RBC700	0.212±0.011	2.78±0.008	0.996	3.26	2.00
DARBC350	0.261±0.004	3.41±0.002	0.914	3.81	2.63
DARBC700	0.184±0.015	3.72±0.009	0.904	4.02	2.71

Table 6 Freundlich sorption isotherms of atrazine on diffe	erent biochars
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BC represents biochar; P, M, and R represent pig manure, maize, and rice; DA represents deashing; and the numbers represent pyrolyzing temperature.

It was found that the two pesticides hydrolyzed in the presence of biochar (Table 7). Hydrolysis of carbaryl and atrazine in biochar suspensions varied a lot, with 7 d hydrolysis ratio being 19.9% to 90.6% for carbaryl and 6.4% to 63.4% for atrazine. Generally the hydrolysis atrazine was low than that of carbaryl. The hydrolysis occurred faster in the presence of PBC as compared to those of biochars from agricultural straws. Besides, hydrolysis was faster in the presence of biochars derived under higher pyrolyzing temperature and at higher biochar dose. The enhanced hydrolysis was first ascribed to the elevated pH in biochar suspension, since OH⁻ is a better nucleophilic reagent than H₂O. This could be confirmed by the hydrolysis of pesticides in pure background solution at different pH. To elucidate the possible mechanisms for hydrolysis, the pH of biochar suspension was adjusted to neutral. Under neutral condition, the hydrolysis of the two pesticides was still substantial, indicating that there were other mechanisms for catalytic hydrolysis. Both the mineral surface and dissolved metals could catalyze hydrolysis, and the latter was confirmed in biochar leachate. The leachate was measured to contain plentiful dissolved metals, and those transition metals are reported to be able to catalyze hydrolysis. The catalytic ability of pH and dissolved to the hydrolysis of atrazine was small as compared to the mineral surface.



Experimental system	7 d hydrolys	is extent	рН
	Carbaryl	atrazine	
Neutral background solution	14.1±5.6	8.0±0.1	6.5±0.1
Alkaline background solution	100±0.1	16.1±3.0	9.1±0.3
PBC350 L suspension	23.5±3.5	12.6±1.5	7.1±0.1
PBC350H suspension	59.1±4.3	21.2±4.2	7.9±0.3
PBC700L suspension	67.9±3.3	14.9±3.1	7.6±0.2
PBC700H suspension	90.6±7.5	63.4±6.5	9.1±0.2
MBC350L suspension	19.9±1.5	6.4±1.5	6.5±0.5
MBC350H suspension	29.1±4.2	12.2±4.2	7.0±0.3
MBC700L suspension	35.4±3.1	12.6±3.1	7.6±0.2
MBC700H suspension	78.6±6.5	29.1±6.5	9.0±0.6
RBC350L suspension	21.9±1.8	11.7±1.5	6.5±0.5
RBC350H suspension	44.6±2.5	19.5±4.2	0.1±0.3
RBC700L suspension	55.0±4.2	14.8±3.1	8.5±0.2
RBC700H suspension	81.1±5.4	41.9±6.5	9.1±0.6
PBC350 suspension with pH adjusted to neutral	29.1±0.2	21.8±2.3	6.8±0.1
PBC700 suspension with pH adjusted to neutral	59.3±2.0	33.5±0.1	6.8±0.2
MBC350 suspension with pH adjusted to neutral	24.0±2.3	10.3±0.3	6.7±0.1
MBC700 suspension with pH adjusted to neutral	30.2±0.1	21.2±0.4	6.9±0.2
RBC350 suspension with pH adjusted to neutral	30.9±2.3	12.2±1.3	7.0±0.2
RBC700 suspension with pH adjusted to neutral	46.9±0.1	22.0±0.5	6.8±0.2
PBC350 leachate	65.2±0.6	16.1±0.2	7.9±0.1
PBC700 leachate	100±0.1	19.4±0.3	6.8±0.3
PBC350 leachate with pH adjusted to neutral	37.6±0.2	8.5±0.1	9.1±0.1
PBC700 leachate with pH adjusted to neutral	40.0±0.4	11.8±0.4	6.8±0.3
MBC350 leachate	18.3±0.6	3.3±0.2	6.7±0.1
MBC700 leachate	87.5±0.1	8.3±0.3	9.1±0.3
MBC350 leachate with pH adjusted to neutral	14.8±0.9	2.6±0.9	6.9±0.1
MBC700 leachate with pH adjusted to neutral	7.6±0.4	6.5±0.4	6.3±0.2
RBC350 leachate	16.9±0.6	10.5±0.3	7.3±0.1
RBC700 leachate	89.4±0.1	11.3±0.5	9.1±0.4
RBC350 leachate with pH adjusted to neutral	7.9±0.7	7.1±0.2	6.4±0.1
RBC700 leachate with pH adjusted to neutral	15.4±0.3	7.7±0.4	6.8±0.2

Table 7 Hydrolysis of carbaryl and atrazine under different conditions

Finally, the effect of biochars on the fate of the two pesticide in soil was checked by spiking biochars into soil (Fig. 18 and 19). When the soil was sterilized, the dissipation of pesticides was mainly ascribed to hydrolysis, and biochars derived under high temperature and applied at high dose showed greater enhancement. This is because these biochars could enhance soil pH and contained more mineral



surface. On the other side, some biochars could inhibit pesticide hydrolysis due to that adsorption reduced the accessibility of the pesticide. In non-sterilized soil, pesticide was removed both through hydrolysis and biodegradation. Generally, biodegradation was inhibited in the presence of biochar due to the lowered bioavailability of sorbed pesticide. Exception occurred for biochar derived from maize straw under lower temperature. In this case biochar favoured the activity of microflora. These findings indicated that we can change the effects of biochar on the fate of pesticide by choosing proper biochar, which can be utilized when we try to manipulate the fate of pesticides.

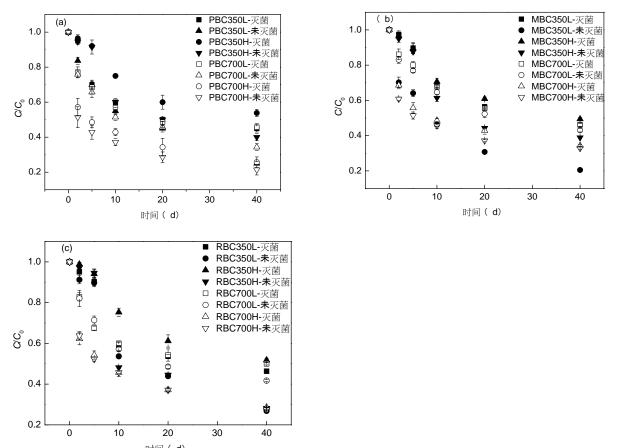


Fig. 18 Degradation of carbaryl in soil amended by biochars (a) PBC (b) MBC (c) RBC H: 5% biochar, L: 0.5% biochar

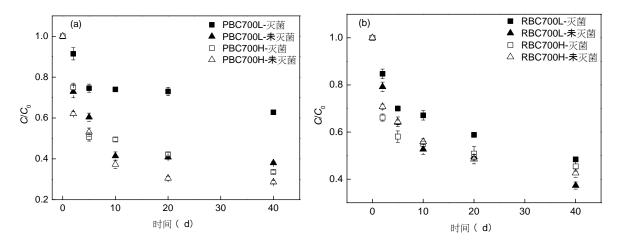


Fig. 19 Degradation of atrazine in soil amended by biochars (a) PBC (b) RBC H: 5% biochar, L: 0.5% biochar



3.2 Comparison of current state of agricultural biomass waste recycling in Tianjin and Japan

3.2.1 Investigation on current state of agricultural waste biomass recycling in Tianjin

The situation of recycling of agricultural waste biomass in the suburbs of Tianjin was investigated. In the recent five years, the theoretical straw amount and collectable amount keep in constant, being 2.31×10^5 and 2.01×10^5 ton in 2007, 2.26×10^5 and 1.97×10^5 ton in 2008, 2.31×10^5 and 2.01×10^5 ton in 2007, 2.26×10^5 and 1.97×10^5 ton in 2008, 2.31×10^5 and 2.01×10^5 ton in 2009, 2.32×10^5 and 2.02×10^5 ton in 2010, and 2.38×10^5 and 2.02×10^5 ton in 2011 (Fig. 20). Based on the statistical data in 2011, the agricultural straw included rice straw 9.14×10^4 ton, wheat straw 5.0×10^5 ton, corn straw 1.18×10^6 ton, bean straw 2.07×10^4 ton, cotton straw 2.6×10^5 ton (Table 8).

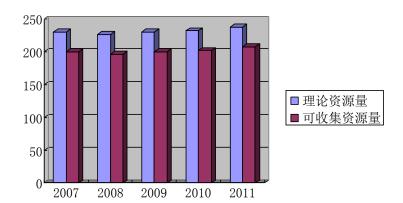


Fig. 20 The theoretical and collectable amounts of agricultural straw in Tianjin in recent five years (unit $\times 10^4$ ton)

Crop Type	Rice	Wheat	Corn	Bean	Oil materials	Cotton
Total production	10.71	54.2	94.38	1.69	0.64	7.23
Ratio of straw and fruit	1.04	1.2	1.36	1.59	2.77	4.00
Theoretical straw amount	11.15	65.04	128.36	2.69	1.77	28.92
Collection ratio	0.82	0.77	0.92	0.77	0.92	0.91
Collectable amounts	9.14	50.08	118.09	2.07	1.63	26.32

Table 8 Estimation of straw resource in Tianjin suburbs in Tianjin (unit $\times 10^4$ ton)

Currently, about 70% of the waste straw is re-utilized, mainly as fertilizer (20.3%), feed (15.7%), fuel (29.6%), base for producing edible fungi (a good practice, but very less), and raw material for producing paper (4.9%) (Fig. 21).

Some problems still exist in promoting the practice of recycling agricultural straw. (1) In some towns, the agricultural straws are not recognized as a resource but a waste, farmers are still keeping the bad custom of incineration of agricultural straw, and hence dissemination of recycling these resource should be strengthened. (2) The effective management and supporting policy from government is lack, and no financial support is given to extend the recycling of agricultural straw. (3) The utilization pattern of the waste straw still should be diversified and advanced. For example, the pattern of applying straw back to farmland is mainly by direct applying of crusaded straw, and this covers 1/4 of the agricultural land in the suburbs of Tianjin. However, to treat the straw by composting or to make it into biochar before it is applied to farmland have not been used in large scale.



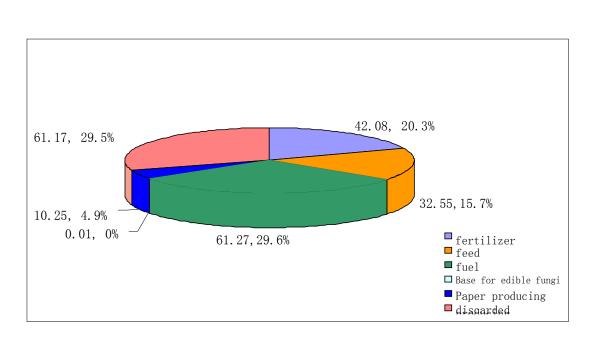


Fig. 21 The composition of recycling of agricultural straw in Tianjin (unit $\times 10^4$ ton)

3.2.2 Mutual visits Field visiting of biomass waste recycling in Japan

In September, 2012, the participants from Nankai University visited Hokkaido and Tokyo to investigate the utilization of biomass and biochar in Japan accompanied by Professor Morita and Professor Matsuda, the Japanese members of this project. First, we visited the experimental farm of Hokkaido University, where we met Prof. Hajime Araki, the Manager of the experimental farm of Hokkaido University, and Associate Prof. Nobuyuki Tsuji, Center for Sustainability Science of Hokkaido University. The farmer manager introduced the cycling system in the farm. The farm is opened to scientists who want to do related research not only confined to professors in Hokkaido University but also to researchers from all over the Japan, so it provides a very good platform for related scientific research. There were several devices for biomass waste recycling in the farm. The most impressive one is a pellet fuel, which was produced from the stem of tomato, and was burnt in the green house in the farm to generate heat in winter. 2) We visited the Recycling Centre of Furano City in north Hokkaido. There, the useful materials, such as bottles, metals, and worn clothing, were separated from the solid waste for reuse. There is a shop for selling the used goods. In China, with the elevation of people living level, a lots of goods especially clothes furniture, and small electric devices that can be used are discarded in big cities. Meanwhile, the economic development was unbalanced in China, in some remote poor rural area, there is only one quilt for the whole family. However, the system to transfer the discarded goods from big cities to remote rural area has not well set up. The residents in city do not know how to treat their old goods. In Furano city, the remnant that cannot be recycled was pressed into solid fuel. In China, the division of rubbish has not been carried out. 3) In Shimokawa Town of north Hokkaido, there are large area of forests and plenty of biomass resources. We visited some facilities burning woods for power and heating, and a factory which produced charcoal and biochar from woody biomass. The biochar was being sold in the market to neighbor farmers for several years. To enough use the land resource, poplar trees were planted along the road. The poplar trees grow very fast, and they can be cut for used in three to five years. 4) We also visited the experimental farm of The University of Tokyo, where we met Dr. Sekiya Nobuhito, Institute for Sustainable Agroecosystems Services, Graduate School for Agricultural and Life Sciences, the University of Tokyo. He is a member of a biofuel projected led by Prof Shigenori Morita. In this project, they are responsible to survey the proper energy plant that can be used to produce alcohol (Fig. 22).





Fig. 22 Project members visited the farm of the farm of Hokkaido University, biochar producer in Furano, crushing device of chip wood in Shitagawa City, and methanol production plants in the farm of University of Tokyo

3.3 Dissemination activities

To disseminate to results of this project, a workshop on "Biochar and Environment" was held on 13 of April, 2013 under the assistance of Agricultural Bureau of Tianjin. Over sixty participants, including 30 farmers, 20 students, 10 officers and company people took part in the workshop took part in the workshop. Prof Hongwen Sun gave a presentation with the same title with the workshop (Fig. 23). The presentation PowerPoint contained over 100 slides. In the presentation, Prof SUN started the talk from carbon cycle, depletion of farmland and hazard of randomly discarding of agricultural waste. Then, the concept of biochar was proposed. The main content of the presentation was biochar, and four aspects were introduced, including 1) Biochar and their feature; 2) Biochar and global change; 3) Effects of biochar on farmland ecosystem and agricultural production; 4) Effects of biochar on the fate of different kinds of pollutants. From this presentation, the local officers on agricultural affairs and farmer got awareness of the relationship of agricultural straw recycling and global change and the sustainable development of human kind. They showed great interest in the application of biochar.

To further extend the dissemination range, a brochure named "Biochars and Climate Change & Agricultural Production" was designed and made up. The brochure included 8 pages, which briefly introduced the concept and benefit of biochar, the hazard of buring agricultural waste, biochar and agricultural production, biochar and climate change. The brochure was dispatched to the participants of the workshop (Fig. 24).

A website named "Forum of Biochar in China" in Chinese was constructed to enlarge the dissemination range (www.shengwutan.org). The theme of the website is "black (biochar) jacks up green". Six columns compose the website, the first is "homepage", where the objective of the website is illustrated and the support from APN was also acknowledged. The second column is "Recycling of agricultural waste and biochar", and the third column is "biochar and climate change", the fourth one is "biochar and agricultural production", and the fifth one is "biochar and remediation of contaminated environment". In



these columns, the typical research progress in our project and from related literature were introduced. From the website, the visitor can access to websites of "Asia-pacific network for global change research", "Biochar-international action", "UK biochar research centre". The website will exert great effect on disseminating the results of this project, will promote the understanding of biochar research, will help more people to know APN (Fig. 25).





Fig. 23 Workshop on "biochar and environment"

Fig. 24 Brochure on biochar



Fig. 25 Website of Forum of Biochar in China

4.0 Conclusions

To improve the recycling of agricultural biomass residue in China and contribute local force to avoid global change, the present project surveyed the recycling patterns of agricultural waste biomass in Japan by literature reading and field visiting. Meanwhile, the situation of agricultural straw recycling in Tianjin suburb, China was investigated as a case study. Moreover, as a new approach of straw recycling, biochar was studied systematically to elucidate its possible effects on plant growth, soil microflora, and fate of several pollutants. To disseminate the advanced strategies and technologies in biomass recycling, a monograph titled "Biochar and Environment" was written to be published; a workshop was held; and a website was constructed.

It was found that in Japan, there is a long history of good practice to use agricultural and other biomass residues, such as wood chip to generate energy and soil fertilizers. In Tianjin, the recycling of agricultural biomass residue has achieved much progress, however, the reuse ratio is still low and techniques were lagging. Besides to agricultural waste, the system to recycle urban rubbish and discarded good is lacking. Dissemination activities should be strengthened especially to decision maker, and meanwhile research capacity for advanced technology, such as producing alcohol and biochar should be improved.



The study on biochar found that the structure and properties of biochars vary greatly with the feedstock and pyrolyzing temperature, and should be studied systematically. Biochar could promote the growth of wheat and vegetables, which occur through improving the nutrient condition of the soil. Biochar can immobilize heavy metals, and it can also act as the carrier for microbes and strengthen the immobilization by mutant species. The research on the mechanisms of PAH adsorption by biochar revealed that the interactions of biochar and soil constituents was complex, influencing by the soil properties, water content and contacting time. Moreover, biochar could influence the hydrolysis and microbiodegradation of pesticides, and the impact varied with the structure of the biochars. This could be manipulated during the pollution control of pesticides.

5.0 Future Directions

Biochar is a new idea, which could simultaneously resolve the climate change, waste reuse and soil deterioration. It has been practiced for long time in Japan that the agricultural and forestall wastes are produced into carbonaceous material and applied to farmland. With the deepening of biochar related study, the advantage and disadvantage of biochar have been revealed, and systematical research, including environment, energy and social aspects, should be conducted before this gigantic innovation could be implemented globally. Hence, the team of Nankai University hope to cooperate with Japanese scientists and scientists from other Asian countries to further the research on biochar and exert more impact from Asian countries on this fatal issue. Biochar is a big issue related to global change.

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Appendix

<u>Workshops</u>

A workshop on "Biochar and Environment" was held on 13, April, 2013 at College of Environmental Science and Engineering, Nankai University.

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6.	孙红文	教授 南开大学环境学院	13512001619	39	程文芳	农民 东丽区南何庄村	15522149754
7.	张彦峰	副教授 南开大学环境学院	13752187405	40	孙亚芬	农民 东丽区南何庄村	15122764210
8.	马小东	副教授 南开大学环境学院	15202245920	41	孙宗芳	农民 东丽区南何庄村	15222620305
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11.	翟洪艳	讲师 天津大学环境学院	13752141665	44	何安太	农民 东丽区南何庄村	13820111519
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13.	赵莉	技师天津市环保监测站	18622039907	46	刘淑贤	农民 东丽区南何庄村	13612103340
14.	赵立杰	技师农业部环保站	15022434400	47	于成秀	农民 东丽区南何庄村	18602609068
15.	张稚妍	技师天津塘沽环保站	13820288018	48	苏玉涛	农民 东丽区南何庄村	13821768588
16.	辛颖	技师天津和平环保站	13920054197	49	王德文	农民 东丽区南何庄村	13752546510
17.	卢源	技师 南开大学环境学院	13752318183	50	何红卫	农民 东丽区南何庄村	13752576698
18.	张鹏	博士生 南开大学环境学院	15522486411	51	何安杰	农民 东丽区南何庄村	13821306139
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32.	任心豪	硕士生 南开大学环境学院	15822739203	65			
33.	姚义鸣	硕士生 南开大学环境学院	18722148386	66			



Funding sources outside the APN

The innovative research on biochar was co-supported by Natural Science Foundation of China (200,000 RMB) and the Fundamental Research Funds for the Central Universities (100,000 RMB)

The monograph of "Biochar and Environment" was co-supported by Asian Research Center (Nankai University) (2,5000 RMB).

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Glossary of Terms

BC: biochar; PBC: biochar from pig manure; MBC: biochar from maize straw; RBC: biochar from rice straw.

In the Appendix section, the report may also include:

For more detailed results and more references, the reader is recommended to read degree theses of Ph D and master candidates in Nankai University, who finished the thesis research under the support of this project.

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