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Study on Industrial Metabolism of Carbon in a Chinese Fine Chemical Industrial Park

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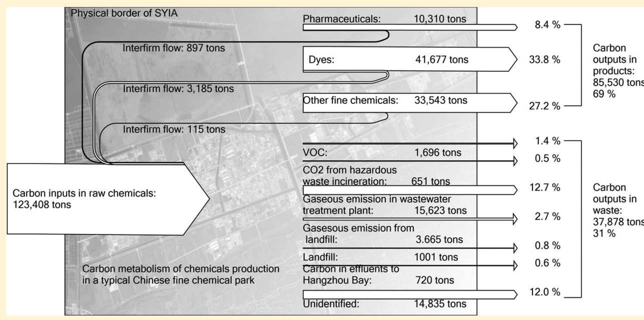
S Supporting Information

ABSTRACT: Carbon metabolism of a chemical industrial park remains scarce in literature, due to overwhelming data collection workload and intricate interfirm flow examination. Based on five-year intensive data collection and verification, this research presents the findings of one-year static carbon metabolism in a typical Chinese fine chemical industrial park. As to the total direct carbon input (0.38 million tons), 32% concern chemicals production, while the remaining 68% are related to energy conversion. Three common metrics, carbon efficiency, C factor, and E factor are applied to assess the performance of carbon flows. Based on an analysis of 380 raw chemicals and 130 chemical products, performance of the three kinds of chemicals, pharmaceuticals, dyes, and other fine chemicals, and the chemical industrial park as a whole are considered and compared with similar industrial area, respectively. The carbon efficiency of chemicals production is 69%, while the other 31% ends up in waste. The interfirm carbon flow accounts for 3.4% of the carbon inputs in raw chemicals. Pursuing local environmental goals (i.e., abatement of odor, chemical oxygen demand, and solid waste) results in greater CO_2 emissions, which runs against protection of the global environment. Options to improve carbon efficiency were also discussed from three aspects. This study lays groundwork for quantifying greenhouse gas emissions, benchmarking carbon efficiency, and conducting life cycle assessment on the park level.



1. INTRODUCTION

The chemical industry plays a vital role in the Chinese economy.[1] Chinese chemical industry has witnessed rapid expansion and now produces more than 40 000 categories of chemicals annually.[2] Fine chemicals account for 80% of China's domestic sales of chemicals.[3]

China has developed more than sixty national and provincial chemical industrial parks (CIPs) by the end of 2006, half of which primarily produced fine chemicals and were thus called fine chemical industrial parks (FCIPs).[4,5] CIPs bring about such advantages as space saving, water saving, energy saving, and pollution reduction thanks to infrastructure sharing.[6,7] However, most of Chinese CIPs are located near a river or a lake, which serves the main source of their water supply. The inherent high risks of CIPs to fragile ecosystems together with a series of high-profile chemical accidents over the past decade have resulted in an increasingly negative public perception of chemical industry and CIPs in China.[8] Therefore, environmental management and sustainable development of CIPs have turned into an important topic for research. Understanding and assessing material flows and resultant environmental emissions present a proper area to start with.

Substance flow analysis (SFA) is an important tool to study the metabolism of typical elements for a region or particular target.[9−12] This research is part of our series studies on the methods of regulating material metabolisms in a typical Chinese FCIP, Shangyu Industrial Area (SYIA) in Zhejiang province.[13,14] Detailed information on SYIA can be found in the ref.[13] Carbon forms the backbone of organic chemicals, and is also the key element in climate change. Carbon metabolism analysis lays the groundwork for quantifying greenhouse gas emissions (GHG), benchmarking carbon efficiency, and conducting life cycle assessment on the park level. Studies on carbon efficiency are also one of the key topics of sustainable development of chemical industry.[15] In this research, we focused on the carbon metabolism and the measures to improve carbon efficiency, by combing the major environmental issues of SYIA with climate change. Three commonly adopted metrics in chemical industry, carbon efficiency, C factor, and E factor, are

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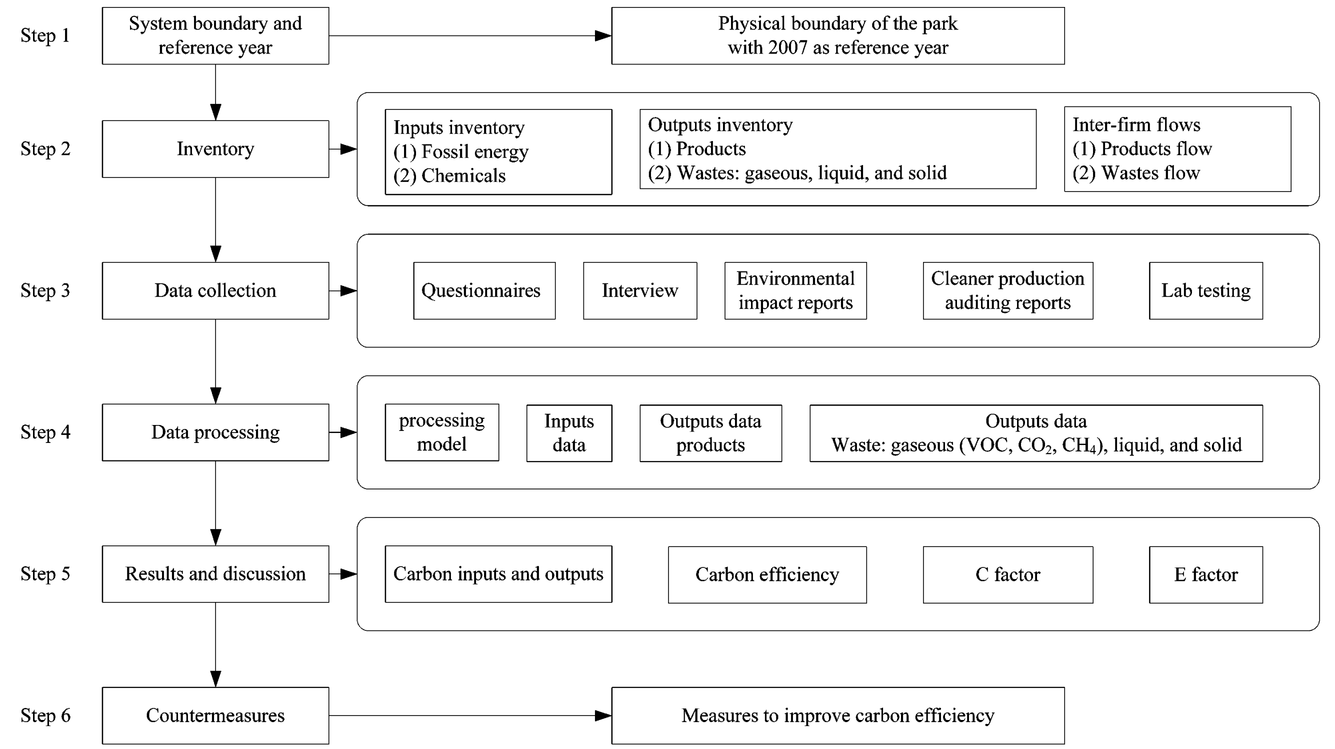

Figure 1. Schematic diagram of research procedure.

applied to assess the performance of carbon metabolism of SYIA. Carbon efficiency is no doubt one of the most important aspects of chemicals production.[15,16] C factor is a metric of the CO_2-burden for producing a product. E factor is a waste-minimization targeted metric. Carbon metabolism on a CIP, especially the FCIP, has the difficulty of heavy data collection and processing, which are caused by the multiple entries and exits and complicated intrafirm and interfirm flows of the given substance.[13] The interfirm flows within the park are also carefully studied.

2. METHODOLOGY AND DATA

Figure 1 presents a six-step schematic diagram of this research. The system boundary is the physical boundary of the 21 km^2 built-up area of SYIA, with 2007 as the reference year.

2.1. Inventory. We divide the carbon metabolism in SYIA into energy-conversion centered carbon metabolism (ECCM) and chemicals production centered carbon metabolism (CPCM).

2.1.1. Energy-Conversion Centered Carbon Metabolism. The carbon inputs of ECCM include coal, diesel, household waste, and calcium carbonate applied for sulfur dioxide scrubber. The carbon outputs include CO_2 emissions into the atmosphere and carbon into slag and flue gas desulfurization gypsum.

Companies in SYIA normally outsource the transportation of their fuel, raw materials, and products, primarily through road and ship transportation, to specialized logistics companies. Fuel consumption in transportation and the associated carbon inputs and outputs are excluded from ECCM. Fuel consumption by companies' own vehicles is neglected due to data unavailability and negligible quantity. The indirect carbon inputs and outputs related to the electricity consumption in SYIA but generated outside SYIA are also not covered.

2.1.2. Chemicals Production Centered Carbon Metabolism. Carbon inputs in CPCM include carbon in reaction materials and auxiliary materials (see SI Figure S1). Reaction materials mainly refer to the reactants that partially form the final products.[16] Auxiliary materials mainly refer to acid, base, solvents, and catalysts, which do not end up in the final products. Carbon outputs include carbon in products and wastes (including gaseous emissions, wastewater, and solid waste). Interfirm carbon metabolism includes carbon flow along vertical integration within SYIA. The material flows among different stakeholders are qualified as interfirm flows. The material flows along the upstream and downstream within a single group is not countered as the interfirm flows.

Figure 2 presents in detail the carbon metabolism along the stepwise waste treatment and disposal. Waste produced in the industrial facilities includes volatile organic chemicals (VOC), solid waste (SW), and wastewater (WW). Recovery of byproducts is also finished in the industrial facility. Hazardous waste (HW) is incinerated and gaseous emissions (GE) emitted into the atmosphere. The general solid waste goes to landfill. Wastewater is first treated by in-house wastewater treatment stations (IWWTS) of individual chemicals producers. It is further treated in a centralized wastewater treatment plant (CWWTP) in SYIA and finally discharged into the Hangzhou Bay (HZB). Waste entering the landfill is partly converted into CO_2 and CH_4, and then released into the atmosphere.

2.2. Data Collection. Data were mainly collected from enterprise-level questionnaire surveys, interviews with stakeholders, environmental impact assessment reports, and cleaner production auditing reports in SYIA. Detailed information on the questionnaire can be found in ref 13. We conducted a questionnaire survey among 100 enterprises each time in 2006, 2008, 2009, 2010, and 2011 to collect data of the previous year. The numbers of returned questionnaires were 56, 71, 70, 19, and 60, respectively. In 2010, we launched an online survey. However, it proved to be less effective than the mail survey. We interviewed more than 60 representatives of different stakeholders and reviewed nearly 70 cleaner production auditing

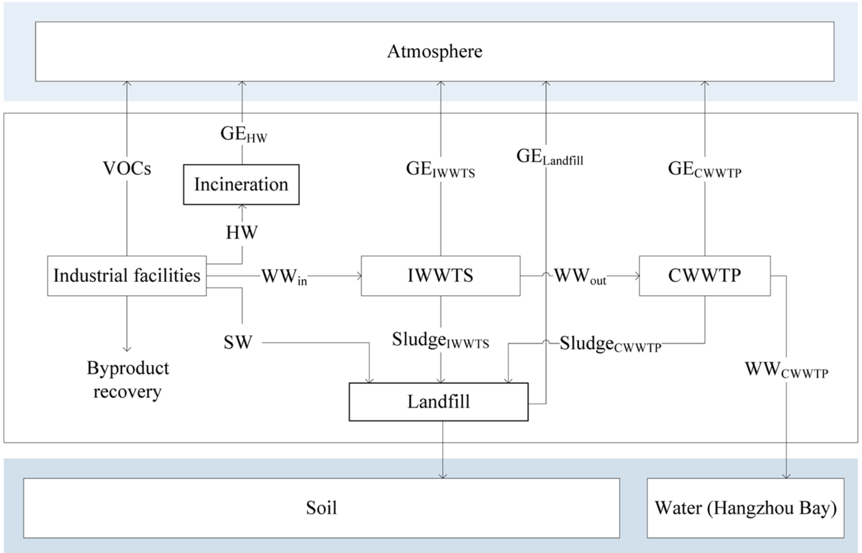

Figure 2. Carbon flow in stepwise waste treatment and disposal.

reports. Since the survey of year 2008 is more complete, we adopted the 2008 questionnaire survey, and a one-year static carbon metabolism is studied at first.

With careful verification, we retained 58 valid questionnaires as the fundamental data source. Some data are drawn from cleaner production auditing reports to triangulate the survey data and fill the remaining data gaps. In 2011 and 2012, we took samples of wastewater and solid waste from more than five enterprises to have laboratory test, such as total organic carbon (TOC), chemical oxygen demand (COD), moisture, and organic contents to verify the prior data set.

2.3. Carbon Metabolism Analysis. All the parameters and equations are listed in the Supporting Information (Table S1–S4). We only describe the key equations as follows.

2.3.1. Energy Conversion Centered Carbon Metabolism. The carbon inputs and outputs of ECCM (see Figure 2) are calculated as follows. Carbon inputs in fuel are derived from multiplying the quantity of fuel inputs and their respective carbon content. Carbon inputs in calcium carbonate are calculated by the mass and purity of calcium carbonate.

Most of the carbon in the fuel ends up in the form of CO_2 emitted into the atmosphere, while the remaining turns into solid waste. The first parts are derived from the carbon inputs in the fuel and the oxidation rate of carbon during combustion.

Sulfur in coal is transformed into sulfur dioxide during combustion. SYIA has constructed two combined heat and power plants (CHPs) since 2005, which had equipped sulfur dioxide scrubber with furnace limestone injection technology. The CHPs produces additional CO_2 during desulfurization process, and the mass is calculated by eq 1:

$$C_{CaCO_3\text{-Gas}}^{SO_2\text{-scrubber}} = \text{fuel}_{\text{input}} \times S\% \times \eta_{\text{fuel}}^{S} \times \varphi_{CaCO_3}^{SO_2} \times \frac{12}{32} \qquad (1)$$

where $C_{CaCO3-gas}^{SO_2\text{-scrubber}}$ is the quantity of carbon in the form of CO_2 produced during desulfurization process, S% is the sulfur content in fuel, sulfur content of diesel is neglected, η_{fuel}^{S} is the sulfur dioxide release coefficient during coal combustion, φ_{CaCO3}^{SO2} is the efficiency of desulfurization process. Calcium carbonate is generally overdosed, and the excessed part is ended into solid waste together with flue gas desulfurization gypsum.

2.3.2. Chemicals Production Centered Carbon Metabolism. A mass-balance method is used to analyze the carbon metabolism in chemicals production, the details of which can be found in ref.[13,17] Carbon inputs in raw materials and outputs in products can be formulated in eq 2 and 3:

$$C_{RM} = \sum_{j}^{m} \text{cap}_{\text{output}}^{j} \times \left(\sum_{i}^{n} RM_{\text{input}}^{i} \times p_{RM}^{i} \times N_C^i \times \frac{12}{MW_i} \right) \qquad (2)$$

where C_{RM} is the quantity of carbon in raw material, $\text{cap}_{\text{output}}^{j}$ is the production capacity of product j in 2007, RM_{input}^{i} is the quantity of raw material i consumed for producing each unit of the product j, p_{RM}^{i} is the purity of raw material i, N_C^i is the number of carbon atom in the formula of raw material i, and MW_i is the molecular weight of raw material i.

$$C_{\text{prod}} = \sum_{j}^{m} \text{cap}_{\text{output}}^{j} \times p_{\text{prod}}^{j} \times N_C^j \times \frac{12}{MW_j} \qquad (3)$$

where C_{Prod} is the quantity of carbon in products, p_{prod}^{j} is the purity of product j, N_C^j is the number of carbon atom in the formula of product j, and MW_j is the molecular weight of the product j.

The interfirm carbon flow within SYIA is calculated in ways similar to eq 2 and 3. The methods of identifying interfirm flow is the same for the sulfur metabolism research.[13]

2.3.3. Carbon Metabolism during Stepwise Wastewater Treatment. Wastewater produced by each producer is treated in an IWWTS at first to reach the standard that the COD should be less than 1000 mg/L. The effluent from IWWTS is further treated in CWWTP to meet the discharge standard, and finally emitted into the Hangzhou Bay. The quantity of carbon in effluent is calculated by eq 4:

$$C_{\text{effluent}}^{HZB} = (Q_{CWWTP}^{in} \text{-cap}_{\text{slud}}^{CWWTP} \times \theta_{\text{slud}}^{CWWTP}) \times COD_{HZB} \times \delta_{TOC/COD}^{HZB} \qquad (4)$$

where $C_{\text{effluent}}^{HZB}$ is the quantity of carbon in the effluent from CWWTP into Hangzhou Bay, Q_{CWWTP}^{in} is the total amount of wastewater discharged into CWWTP, $\text{cap}_{\text{slud}}^{CWWTP}$ is the quantity

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of sludge from CWWTP, θ_{slud}^{CWWTP} is the moisture in sludge from CWWTP, COD_{HZB} is the annual average concentration of COD in the effluent of CWWTP, and $\delta_{TOC/COD}^{HZB}$ is the ratio of the concentration of total organic carbon and the COD in the effluent of CWWTP.

2.3.4. Carbon in Gaseous Emissions. (1). Carbon in VOCs. Carbon in VOCs is triangulated by two methods. The first one is formulated as eq 5:

$$C_{VOC} = \sum_{j}^{m} cap_{output}^{j} \times \overline{q_{VOC}} \tag{5}$$

where C_{VOC} is the carbon in VOCs produced in the industrial facilities of chemicals producers, Cap_{output}^{j} is the production capacity of product j in 2007, q_{VOC} is the carbon in VOC per unit of product j output, $\overline{q_{VOC}}$, the weighted average of q_{VOC}, is calculated by eq 6:

$$\overline{q_{VOC}} = \left(\sum chem_{VOC}^{i} \times N_{C}^{i} \times \frac{12}{MW_i}\right) / \sum_{j}^{m} cap_{output}^{j} \tag{6}$$

where $Chem_{VOC}^{i}$ is the quantity of chemical i in the VOC emissions for producing product j, N_C^i is the number of carbon atom in the chemical i, and MW_i is the molecular weight of the chemical i.

The second method is based on a box-model with SYIA simplified as a point source. Details on the calculation and location of the eight atmospheric sampling sites can be found in the Supporting Information (see Table S5−S8 and Figure S2). In this study, $\overline{q_{VOC}}$ is calculated based on the onsite testing of six major enterprises in SYIA.

(2). Carbon in Gaseous Emissions from Stepwise Wastewater Treatment. Carbon in gaseous emissions from stepwise wastewater treatment is the sum of emissions from IWWTS (C_{GE}^{IWWTS}) and CWWTP (C_{GE}^{CWWTP}), which is formulated in eq 7 and 8.

$$C_{GE}^{IWWTS} = \sum Q_{WW\text{-}in}^{IWWTS} \times (\overline{COD_{IWWTS}^{in}} \times \delta_{TOC/COD}^{in\text{-}IWWTS} - \overline{COD_{IWWTS}^{out}} \times \delta_{TOC/COD}^{out\text{-}IWWTS}) \times \varepsilon_{solid}^{gas} \tag{7}$$

where $\sum Q_{WW\text{-}in}^{IWWTS}$ is the total amount of wastewater treated in IWWTS, $\overline{COD_{IWWTS}^{in}}$ is the average concentration of COD for wastewater discharged into IWWTS, $\delta_{TOC/COD}^{in\text{-}IWWTS}$ is the ratio of centration of TOC with that of COD in the wastewater inlet IWWTS, $\overline{COD_{IWWTS}^{out}}$ is the average concentration of COD for wastewater outlet IWWTS, $\delta_{TOC/COD}^{out\text{-}IWWTS}$ is the ratio of centration of TOC with that of COD in the wastewater outlet IWWTS, $\varepsilon_{solid}^{gas}$ is the distribution coefficient between gaseous and solid of carbon removed in IWWTS or CWWTP.

$$C_{GE}^{CWWTP} = Q_{CWWTP}^{in} \times (\overline{COD_{CWWTP}^{in}} \times \delta_{TOC/COD}^{in\text{-}CWWTP} - \overline{COD_{CWWTP}^{out}} \times \delta_{TOC/COD}^{out\text{-}CWWTP}) \times \varepsilon_{solid}^{gas} \tag{8}$$

where Q_{CWWTP}^{in} is the total amount of wastewater treated in CWWTP, $\overline{COD_{CWWTP}^{in}}$ is the average concentration of COD for wastewater discharged into CWWTP, $\delta_{TOC/COD}^{in\text{-}CWWTP}$ is the ratio of centration of TOC with that of COD in the wastewater into CWWTP, $\overline{COD_{CWWTP}^{out}}$ is the average concentration of COD for wastewater out of CWWTP, $\delta_{TOC/COD}^{out\text{-}CWWTP}$ is the ratio of concentration of TOC and the COD in the wastewater out of CWWTP.

The farthest length of wastewater pipeline in SYIA is within 7 km, leakage in wastewater pipeline system is neglected. It is assumed that the total amount of wastewater discharged out of IWWTS ($\sum Q_{WW\text{-}out}^{IWWTS}$) is equal to Q_{CWWTP}^{in}. The total amount of wastewater can be formulated in eq 9:

$$\sum Q_{WW\text{-}in}^{IWWTS} = \sum Q_{WW\text{-}out}^{IWWTS} + \sum Cap_{Slud}^{IWWTS} \times \theta_{Slud}^{IWWTS} \tag{9}$$

where cap_{Slud}^{IWWTS} is the amount of sludge produced in IWWTS, θ_{slud}^{IWWTS} is the average moisture content of the sludge produced in IWWTS.

Most of the IWWTS in SYIA carried out aerobic biological treatment technology. It is assumed that the carbon removed in IWWTS was released into the atmosphere in the form of CO_2. CWWTP carried out anaerobic−aerobic biological treatment technology. The carbon removed in CWWTP was mainly in the form of CO_2 and CH_4, and the ratio of the two parts is formulated in eq 10:

$$\theta_{GE\text{-}CH_4}^{CWWTP} = \frac{\overline{COD_{CWWTP\text{-}in}} \times \delta_{TOC/COD}^{in\text{-}CWWTP} - \overline{COD_{CWWTP\text{-}A\text{-}O}} \times \delta_{TOC/COD}^{A\text{-}O\text{-}CWWTP}}{\overline{COD_{CWWTP\text{-}in}} \times \delta_{TOC/COD}^{in\text{-}CWWTP} - \overline{COD_{CWWTP\text{-}out}} \times \delta_{TOC/COD}^{out\text{-}CWWTP}} \tag{10}$$

where $\theta_{GE\text{-}CH_4}^{CWWTP}$ is the ratio of CH_4 in gaseous emissions of CWWTP, $\overline{COD_{CWWTP\text{-}A\text{-}O}}$ is the average concentration of COD for wastewater out of anaerobic biological treatment apparatus in CWWTP, $\delta_{TOC/COD}^{A\text{-}O\text{-}CWWTP}$ is the ratio of centration of TOC with that of COD in the wastewater.

The ratio of CO_2 in gaseous emissions of CWWTP ($\theta_{GE\text{-}CO_2}^{CWWTP}$) is the result of one minus $\theta_{GE\text{-}CH_4}^{CWWTP}$.

(3). Carbon in Gaseous Emissions from Hazardous Waste Incineration. SYIA constructed a hazardous waste incineration plant, which incinerates rectification residue, waste active carbon, and other hazardous waste. It is assumed that all the carbon in the hazardous waste is converted into CO_2 emitted into the atmosphere through incineration. It can be calculated by the quantity of hazardous waste incinerated (cap_{HWI}) and the carbon content of hazardous waste (C_{HWI}).

The compositions of hazardous waste from different enterprises vary widely. It is calorific value rather than carbon contents of hazardous waste that undergoes regular test for the purpose of more thorough incineration. We use the weighted average of carbon content both of raw materials and products to represent the carbon content of hazardous waste (see Supporting Information).

2.3.5. Carbon Metabolism with Solid Waste Treatment and Disposal. Sludge from IWWTS and CWWTP, and part of general solid waste are landfilled in SYIA. The carbon in landfilled solid waste is calculated by eq 11:

$$C_{landfill} = cap_{landfill}^{CWWTP} \times org_{landfill}^{CWWTP} \times C_{org_{landfill}}^{CWWTP} + \sum_{landfill}^{ent} cap \times org_{landfill}^{ent} \times C_{org_{landfill}}^{ent} \tag{11}$$

where $C_{landfill}$ is the quantity of carbon in solid waste landfilled, $cap_{landfill}^{CWWTP}$ is the quantity of sludge from CWWTP, $org_{landfill}^{CWWTP}$ is the content of organic matter in sludge from CWWTP, $C_{org_{landfill}}^{CWWTP}$ is the carbon content in the organic matter of sludge, $cap_{landfill}^{ent}$ is the quantity of landfilled solid waste generated from enterprises, $org^{ent}_{landfill}$ is the average content of organic matter in solid waste from enterprises, and $C^{ent}_{org_{landfill}}$ is the average carbon content in the organic matter of solid waste from enterprises. We took samples of solid waste from four enterprises and CWWTP to measure the organic matter and other parameter.

The gaseous emissions from the landfill consist of CH_4 and CO_2.The amount of carbon in CH_4 is formulated in eq 12 according to guideline of IPCC:[18]

$$C_{CH_4} = C_{landfill} \times r \times 0.5. \quad (12)$$

where r is the degradation efficiency of organic carbon in landfill,[19] 0.5 is the ratio of carbon in CH_4 to total carbon in gaseous emissions from the landfill.[18] The amount of carbon in CO_2 is equal to that in CH_4. The remaining carbon in the landfill is the nonbiodegradable and left intact.

2.4. Assessment of Carbon Metabolism. Carbon efficiency, C factor, and E factor, are applied to assess the performance of carbon metabolism of SYIA. The three kinds of chemicals, pharmaceuticals, dyes, and other fine chemicals, and the chemical industrial park as a whole are considered, respectively, and also compared with the similar industrial area.

Carbon efficiency is defined as the percentage of carbon in the reactants that remain in the final product,[16] and calculated by the mass ratio of carbon in a products to the sum of carbon in raw materials consumed for producing the target product.[15,16] The ideal carbon efficiency is 100%.

C factor is defined as a parameter to evaluate the CO_2-burden of a product. The C factor contains information of the total amount of CO_2 emitted in order to produce a product, and thus enables a direct comparison of different processes from a CO_2 aspect.[20]

E factor, defined as the mass ratio of waste to desired product, is one of the most widely accepted metrics for assessing waste emissions in chemical industry.[21,22] The E factor for bulk chemicals, fine chemicals, and pharmaceutical industry are generally <1−5, 5−50, and 25→100, respectively.[23] By plus one to E factor, another key and high-level metric, named process mass intensity (PMI, the total mass of materials per mass of product), was gotten, which was chosen by the American Chemical Society Green Chemistry Institute's Pharmaceutical Roundtable for evaluating and benchmarking process toward more sustainable manufacturing.[24] The role of E factor is to help drive the reduction of waste, that is, waste minimization, and to improve mass efficiency as far as possible. The ideal E factor for a chemical production is zero.

Statistical analysis of carbon efficiency and E factor of individual product is conducted using SPSS v. 18. The results shown in the box plots (Supporting Information Figure S3 and S4) present the values of the "5−95 percentiles" samples (referring to the bottom line and the top line, respectively). Furthermore, "25−75 percentiles" samples (referring to the bottom and top of the box, respectively) are applied to represent the general distribution scope of carbon efficiency, and the "50 percentile" value (also called the statistical median value, the bold line in the box) is applied to represent the carbon efficiency. The weighted average of carbon efficiency, C factor, and E factor of pharmaceuticals, dyes, other fine chemicals, and entire SYIA was also analyzed. The weighted average, exemplified with carbon efficiency, is defined as the ratio of the sum of carbon in products to the sum of carbon in raw materials.

3. RESULTS AND DISCUSSIONS

3.1. Overview of the Carbon Metabolism in SYIA. Figure 3 summarizes the overall carbon metabolism of SYIA in 2007.

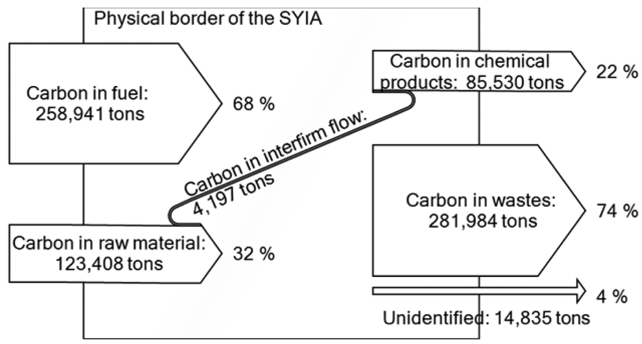

Figure 3. Overview of the carbon metabolism in SYIA. Note: The diagram is drawn by the software e! Sankey 2.0 of *ifu Hamburg GmbH*. The widths of indicated flows represent their magnitude in the unit of tons of elemental carbon, and similarly hereinafter.

The collective carbon inputs were 382 349 tons, of which 258 941 tons (i.e., 68%) were energy conversion related, and the remaining 123 408 tons (i.e., 32%) were chemicals production related. As to the total carbon outputs, 22% were in the products (85 530 tons), 74% in waste (281 984 tons), and the remaining 4% (14 835 tons) was unaccounted for.

SYIA has built up some vertical integration in fine chemicals production. The ratio of the quantity of interfirm flow with the carbon inputs of raw chemicals for chemicals production can indicate the degree of association among stakeholders within SYIA. Higher the ratio is, greater the degree of association is. The interfirm carbon flow has a quantity of 4197 tons, accounting for 3.4% of the carbon inputs in raw materials. In our former study on sulfur metabolism in SYIA, the interfirm sulfur flow accounts for 3.6% of the total elemental sulfur inputs.[13] The proportion of interfirm flow in SYIA is still very small.

3.2. Carbon Metabolism in Energy Conversion. In 2007, the total carbon inputs related with energy conversion were 258 941 tons, among which coal, diesel, household waste, and calcium carbonate account for 93.6%, 0.5%, 5.1%, and 0.8%, respectively (Figure 4).

As for the outputs, calculated in the form of carbon atoms, 244 936 tons were in CO_2, making up 94.6% of the carbon inputs related with energy conversion. The mass of CO_2 was about 900 000 tons. The carbon in the solid waste from CHPs accounted for 5.4% (i.e., 14 005 tons), which is used to produce building materials.

3.3. Carbon Metabolism in Chemicals Production and Waste Treatment. Figure 5 indicates the breakdown of the carbon in products and waste generated from chemicals production, based on analysis of 380 raw chemicals and 130 products.

The raw chemicals had a total mass of about 544 976 tons, among which carbon was 123 408 tons. The outputs of fine chemical products amount to 208 990 tons, among which carbon was 85 530 tons, comprising 69% of the total carbon inputs in raw chemicals. In other words, the average carbon efficiency of SYIA for fine chemicals production is 69% (See Supporting Information Table S2). The remaining 31% of carbon in raw chemicals entered the waste streams.

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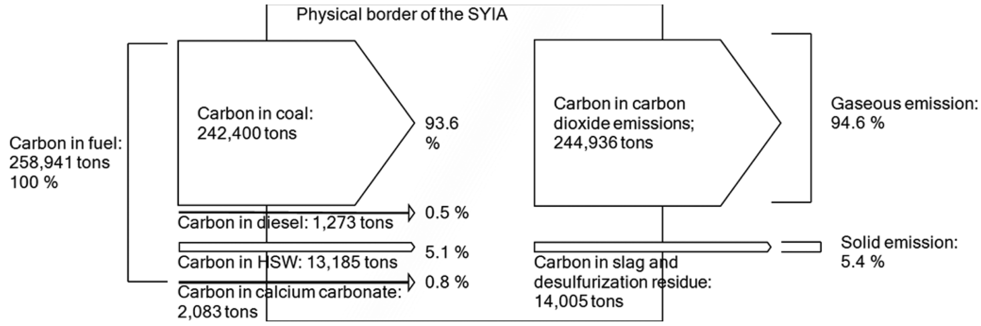

Figure 4. Carbon metabolisms in energy conversion.

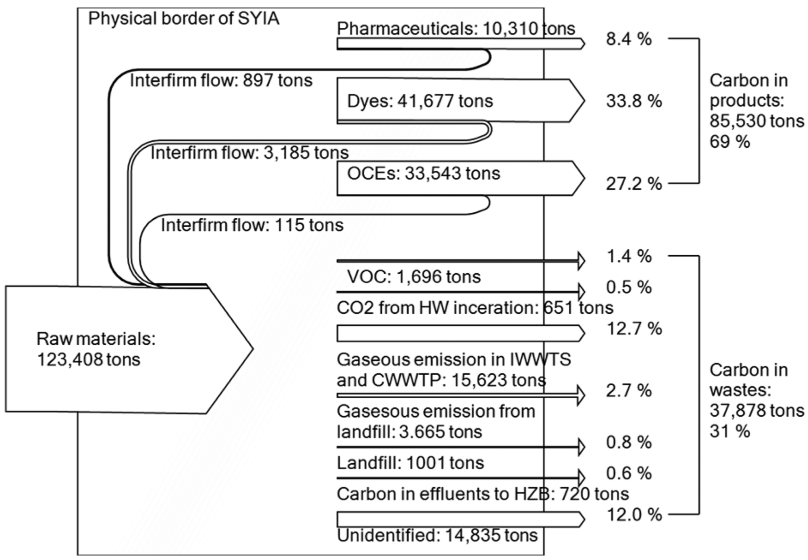

Figure 5. Carbon metabolisms in chemical production and waste treatment and disposal.

The interfirm carbon flows are broken down as follows: 897 tons for pharmaceuticals, 3185 tons for dyes, and 115 tons for other fine chemicals. The interfirm flows of the three industries account for 8.3%, 6.5%, and 0.3% of the carbon in each kind of products, respectively. SYIA has established varying levels of vertical integrations among 10 producers for fluoroquinoline antibiotic production, the products of one company served as the raw materials of another company.[5] SYIA has formed an anchor-tenor cooperation centered by *Group L* and *Group R*, two leading dye producers in China, in dye production.[13] Pharmaceuticals and dyes production dominates the interfirm carbon flow.

SYIA has suffered three major environmental concerns, that is, odor, organic pollutant from effluent discharge, and solid waste. VOCs are the major source of odor in SYIA. Organic raw materials, which are not transformed into products, result in pollutants in effluent. Sludge from IWWTS and CWWTP is the second largest source of solid waste only after calcium sulfate produced in dye production.[13] Carbon metabolism is closely related with the above three concerns. Figure 5 shows that carbon in VOCs, effluents to Hanzhou Bay, and solid waste landfill only represent 1.4% (1696 tons), 0.6% (720 tons), and 0.8% (1001 tons) of total carbon inputs in raw materials, respectively. However their local impact is overwhelming. In chemicals manufacturing, emission sources and contents of VOCs are both enormous, which make the prevention and treatment of VOCs intractable. In this research, we triangulated the amount of VOC emissions in SYIA with two different methods, which yielded similar results, 1696 and 1842 tons, respectively. SYIA had made great efforts to reduce VOC emissions. The three-foot centrifuges, which are operated in an open manner and difficult to capture VOCs, have started to be phased out since 2007. The anaerobic facilities in IWWTS have been covered, and the gaseous emissions were collected and treated by rinsing and active carbon absorption successively before emitting into the atmosphere. In 2011, a producer with gigantic VOC emissions constructed a 1 km long pipeline to pump VOC-contained waste gas to CHP for incineration.[14]

In this case, pursuing local environmental goals (i.e., abatement of odor, COD, and solid waste) results in greater CO_2 emissions, which runs against protection of the global environment. Most of the organic pollutants in wastewater are transformed into CO_2 and methane. The carbon in gaseous emissions from IWWTS and CWWTP accounts for 12.7% (i.e., 15 623 tons) of carbon inputs in raw chemicals, among which CO_2 and CH_4 account for 80.5% and 19.5%, respectively. In 2011, SYIA built up a facility to incinerate sludge from the CWWTP with a capacity of 750 tons per day, which will consume 50% of the sludge landfilled previously. Hazardous waste incineration emitted 651 tons of carbon into the atmosphere, accounting for 0.5% of carbon inputs in raw chemicals. The capacity of the hazardous waste incineration plant is also enlarged from 12 tons a day to 30 tons a day. In general, CO_2 and CH_4 emissions account for at least 16% of the carbon inputs in raw materials, and they are still not listed as the key environmental issues in SYIA.

Table 1. Summary of Carbon Metabolism in SYIA

index	unit	SYIA	pharma-ceuticals production	dyes production	other fine chemicals production	comparison with ref.
carbon efficiency[a]	%	69 (69)	53 (44)	78 (70)	68 (83)	ideal is 100 32–96[b] [16]
C factor[c]	kg-CO_2/kg product	3.2	20.8	2.2	0.9	0.4[d] [20]
E factor	kg/kg	1.7 (1.6)	2.2 (4.3)	1.2 (1.9)	1.6 (0.9)	ideal is zero 5–50[e] [21,22]

[a]Fist line is the statistical median, second line in parentheses is the weighted average value, and similarly hereinafter. [b]It is the carbon efficiency of different chemical reactions. [c]C factor of individual product is not singled out, because the energy consumption of each product manufacturing is not documented separately. [d]It is for ethylene, acetic acid, methanol, and ethanol. [e]It is for fine chemicals.

After the above accounting, 14 835 tons of carbon in waste remains unaccounted for, which was mainly in the form of solvents and byproducts recovered through pretreatment of the high-strength organic wastewater generated in the chemicals production. One of the aims of the pretreatment of the in situ wastes in the industrial facilities before discharged into IWWTS is to reduce the loading of organic materials in wastewater and to prevent negatively impacting the biological systems in IWWTS. Based on interviews in eight typical enterprises in 2008, some of the in situ wastes, such as crystallized solution and aqueous solution after solvent extraction, had a COD concentration of about 50 000–160 000 mg/L. After pretreatment, such as distillation and evaporation, the concentration of COD decreased to about 5000–10 000 mg/L and was then mixed with other dilute wastewater and discharged into IWWTS. Pretreatment of the in situ waste differs greatly, and the data on destination of the recovered material thereof is inaccessible. We were told that some of the recovered material had been privately traded outside SYIA. From the view of extended producer responsibility, both the chemicals producers and SYIA should enhance the administration and reuse of recovered byproducts.

3.4. Performance of Carbon Metabolism in SYIA. Table 1 summarizes the findings of carbon metabolism in SYIA. Carbon efficiency, C factor, and E factor of SYIA will be further discussed in detail as follows.

3.4.1. Carbon Efficiency. The carbon efficiency of 59 pharmaceuticals had a statistical distribution of 30% and 75%, and a statistical median value of 53%. For the 47 kinds of dyes, the scope was 52–88%, and the statistical median value was 78%. For the 21 kinds of other fine chemicals, the scope was 45–86%, and the statistical median value was 68%. The weighted average of carbon efficiencies of pharmaceuticals production, dyes production, other fine chemicals production, and SYIA as a whole were 44%, 70%, 83%, and 69%, respectively.

We thoroughly examined the synthetic reactions of all the products. For pharmaceuticals, carbon–carbon bond formation is the core. However, carbon–carbon bond formation has long been acknowledged as the most challenging field of organic synthesis. For dyes, the bond formation of carbon-heteroatom is more popular, such as creations of the carbon–nitrogen, carbon-chlorine, and carbon–oxygen bonds. Carbon–heteroatom bond formation is less difficult than carbon–carbon bond formation in most cases. Such a difference is a more decisive factor that affects the carbon efficiency of chemicals production.

Based on the SPSS analysis of all the products, 35 products located in the "25% region" with lowest carbon efficiency had a scope of carbon efficiency of 8–44%, and the weighted average efficiency was 23%. The rest "75% region" of products had a scope of carbon efficiency of 45–99%, and the weighted average efficiency was 80%. As for the 35 products with lowest carbon efficiency, 24 of them are pharmaceuticals. If the "25% region" products can improve the carbon efficiency to the average level of 69%, the carbon emissions released into the environment can be reduced by more than 10 000 tons.

3.4.2. C Factor. The total amount of CO_2 produced in the 130 chemicals production was 669 757 tons (see Supporting Information Table S9). The volume of chemicals production was 208 990 tons. Thus the C factor of SYIA in 2007 was 3.2 kg-CO_2/kg products. The C factor of pharmaceuticals, dyes, and other fine chemicals production were 20.8, 2.2, and 0.9 kg-CO_2/kg products, respectively. Voss et al. calculated the C factor of ethylene (oil resource), acetic acid (NG resource), methyl alcohol (NG resource) and ethanol (oil resource), all getting a C factor of 0.4 kg CO_2/kg product.[20] The C factor of fine chemicals in SYIA is much higher than that of bulk organic chemicals.

3.4.3. E Factor. The weighted average E factor of pharmaceuticals, dyes, other fine chemicals, and SYIA as a whole were 4.3, 1.9, 0.9, and 1.6 kg/kg, respectively. The E factor of the 59 pharmaceuticals had a distribution of 1.2–5.3 kg/kg and a statistical median value of 2.2 kg/kg. For the 47 kinds of dyes, the scope was 0.6–3.0 kg/kg, and the statistical median value was 1.2 kg/kg, respectively. For the 21 kinds of other fine chemicals, the range was 0.5–4.3 kg/kg, and the statistical median value was 1.6 kg/kg, respectively (see SI Figure S4).

The sequence of C factor and E factor is the same for pharmaceuticals, dyes, and other fine chemicals, but opposite to that of carbon efficiency. Higher the carbon efficiency is, lower the E and C factors are. Pharmaceuticals have the highest E and C factors, and the lowest carbon efficiency.

Pharmaceuticals and their intermediates have strict standards for purity. Thus, the workup process is very important and always elaborately designed to purify the product. As a result, the yield of pharmaceuticals production is generally low. Therefore, the E factor is high. On the contrary, finding high dye purity is not as difficult for pharmaceuticals. The commercial dye is normally a mixture of dyes, additives and surfactants calibrated to reach the standard of staining intensity for different commercial dyes. The mixing process, named finishing, is one of the most important workup processes of dye production after the synthesis of dye molecule. Due to the great difference of pharmaceuticals and dyes workup process, the performance of dye production is much better than pharmaceuticals with respect to E factor and carbon efficiency. The other fine chemicals also have special requirement for purity but are less stringent than that of pharmaceuticals.

4. OPTIONS TO IMPROVE CARBON EFFICIENCY

The direct carbon inputs related to energy conversion took up 68% of total direct carbon inputs in SYIA. Thus, one of the major initiatives in lowering the C factor of SYIA is to decrease the ratio of coal consumption by replacing with low carbon energy.[20] Energy-saving and improvement of energy-efficiency are also effective in lowering the CO_2 burden of chemicals production in SYIA.[14]

In this study, we focused on the following three options to improve carbon efficiency during chemicals production.

First, the most effective way is to develop more efficient synthetic and workup processes, according to the 24 principles of green chemistry and green engineering PRODUCTIVELY and IMPROVEMENTS.[25] Synthetic process innovation can significantly improve the yields of products and efficiency of carbon, whereas material consumption and waste production per unit of product output can also be reduced. Optimization of workup process can also make great contribution to energy saving during fine chemicals production.

Choosing an appropriate synthetic alternative entails a multicriteria decision analysis process.[15,16,26] We proposed a method to assess the greenness of commercial-scale synthetic alternatives by coupling mass balance analysis and multicriteria ranking.[17] During our investigation, we were informed of many good commercialized examples of green chemistry and green engineering implementation. Such examples include continuous nitration, catalytic hydrogenation, high-efficiency rectification, organic solvents replacement, and synthetic steps shortening.

Second, strengthening environmental regulation is also very crucial in improving the carbon efficiency. According to China's Cleaner Production Promotion Law launched on January 1, 2003, fine chemicals producers must carry out cleaner production auditing. Most of the chemicals producers in SYIA have conducted cleaner production audits. The results have shown that cleaner production is very effective in reducing waste generation. (See Supporting Information Table S10).

SYIA has made a great effort to control both the volume of wastewater discharge and the quantity of organic pollutant emissions since 2005. SYIA has gradually raised the standards of wastewater discharge from IWWTS into CWWTP, which cut the maximum COD concentration from 1000 mg/L in 2007 to 800 mg/L in 2008, and further to 500 mg/L in 2010. The standard of discharging effluent from CWWTP into the Hangzhou Bay has also been heightened, from 200 mg/L to 100 mg/L. In 2009, Shangyu city government launched an emission trading scheme covering such pollutants as COD. The policies had stimulated enterprises to spend more on R&D to develop green chemistry and green technologies to improve carbon efficiency.

Third, on the park level, uncovering and fostering industrial symbiosis [26] is also beneficial. Industrial symbiosis has been proved to be effective on improving the collective performance of colocated firms.[27] SYIA has established more than 30 bilateral physical exchanges of chemicals, which will be discussed later.

Carbon metabolism is very closely related with GHG aspects. In this study, the GHG emission in SYIA is yet to be thoroughly examined. In further study, we will carry out a dynamic assessment of GHG emissions and mitigation potentials in SYIA. A linkage between GHG emissions and value chain analysis will also be conducted.

■ ASSOCIATED CONTENT

Supporting Information

Supporting Information with this article includes (1) Fundamental data, equations, and parameters for carbon metabolism, (2) Box-model, parameters, and space location of monitoring sites in VOC emission calculation, and (3) Statistical distribution diagram on carbon efficiency and E factor.This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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