Coal fly ash is a major carbon flux in the Chang Jiang (Yangtze River) basin

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Edited by Donald E. Canfield, University of Southern Denmark, Odense M., Denmark, and approved March 25, 2021 (received for review December 9, 2019)

Fly ash—the residuum of coal burning—contains a considerable amount of fossilized particulate organic carbon (FOCash) that remains after high-temperature combustion. Fly ash leaks into natural environments and participates in the contemporary carbon cycle, but its reactivity and flux remained poorly understood. We characterized FOCash in the Chang Jiang (Yangtze River) basin, China, and quantified the riverine FOCash fluxes. Using Raman spectral analysis, ramped pyrolysis oxidation, and chemical oxidation, we found that FOCash is highly recyclable and unreactive, whereas shale-derived FOC (FOCrock) was much more labile and easily oxidized. By combining mass balance calculations and other estimates of fly ash input to rivers, we estimated that the flux of FOCash carried by the Chang Jiang was 0.21 to 0.42 Mt C yr−1 in 2007 to 2008—an amount equivalent to 37 to 72% of the total riverine FOC export. We attributed such high flux to the combination of increasing coal combustion that enhances FOCash production and the massive construction of dams in the basin that reduces the flux of FOCrock eroded from upstream mountainous areas. Using global ash data, a first-order estimate suggests that FOCash makes up to 16% of the present-day global riverine FOC flux to the oceans. This reflects a substantial impact of anthropogenic activities on the fluxes and burial of organic carbon that has been made less reactive than the rocks from which it was derived.

coal | fly ash | carbon cycle | Chang Jiang (Yangtze River) | sediment transport

Significance

Coal combustion releases CO2 but also leaves behind solid waste, or fly ash, which contains considerable amounts of carbon. The organic carbon sourced from fly ash resists chemical breakdown, and we find that it now contributes nearly half of the fossil organic carbon exported by the Chang Jiang—the largest river in Asia. The fly ash flux in this basin is similar to the natural sediment flux to the oceans because dam building has reduced sediment transport, while increased coal consumption generates abundant fly ash. Our results show that fly ash is an important component of the present-day carbon load in rivers and illustrates that human-driven carbon cycling can match the pace of the geological carbon cycle at decadal timescales.


The authors declare no competing interest. This article is a PNAS Direct Submission. Published under the PNAS license.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1921544118/-/DCSupplemental.

Published May 17, 2021.
and river sediment through multiple geochemical analyses. We then estimated the CJ-exported FOC_{ash} flux and evaluated how human activities modulated FOC transfer at basin scales. We found that in the CJ basin, coal combustion and dam construction have conspired to boost the FOC_{ash} flux and reduce the FOC_{rock} flux carried by the CJ; as a result, these two fluxes converged over an interval of 60 y.

**The CJ Basin**

The CJ basin is located in central China and has a drainage area of around 1,800,000 km²—nearly 20% of the total terrestrial area of China (30, 31). Originating from the Tibetan Plateau, the CJ drains mountainous areas in its upper reach and alluvial plains in its lower reach, before emptying into the Eastern China Sea (Fig. 1). The regional climate is controlled by the East Asian monsoon with peak precipitation and associated floods occurring from May to September (30, 31). The bedrock geology of the CJ basin is mainly composed of sedimentary rocks, with minor igneous and metamorphic exposures (Fig. 1A) (32, 33).

Over the past 60 y, the CJ basin has undergone significant anthropogenic change including the massive construction of industrial and hydrological infrastructure (e.g., coal-fired power plants and dams) and increased coal combustion (Fig. 1B and C) (34–36). More than 50,000 dams, including the world’s largest—the Three Gorges Dam—have been built in the CJ basin; these dams trap sediment in the resulting reservoirs and have significantly reduced the CJ sediment export to the ocean (Fig. 2) (34, 37). In the process, they profoundly altered the natural transfer of carbon (38, 39). The growth in China’s coal consumption over the past decades has also fundamentally altered the CJ basin, and the annual production of fly ash is, remarkably, now comparable in total mass to the entire CJ sediment flux (Fig. 2). It is not a surprise, then, that fly ash particles and associated black carbon have been observed in recent river and delta sediment in the CJ basin (16, 40–43).

**Materials and Approaches**

We sampled fly ash, shale, river sediment, and plant debris (leaves of typical plants) in the middle-lower CJ basin and collected samples from a core drilled...
thermograms and translated to spectra of activation energies ($E_0$) (56). In the thermograms, FOCash has a higher fraction of carbon decomposed and more CO$_2$ released at high temperatures ($T > 700$ °C) than FOCrock (Fig. 5E). Converting the thermograms to the spectra of activation energies, we found that fly ash featured much higher $E_0$ than the shale (Fig. 3C) and other FOCash-dominated river sediment samples (9, 56), revealing a high thermal stability and an extremely refractory phase of FOCash ($E_0 > 220$ kJ/mol). The chemical oxidation experiments employed sodium persulfate (Na$_2$S$_2$O$_8$)—a chemical with a very high oxidation potential (standard oxidation-reduction potential is $E^\circ = -2.01$V) comparable to O$_2$ ($E^\circ = -2.07$V) and much higher than O$_3$ ($E^\circ = -1.23$V) (57). This agent has been used in soil studies to simulate oxidation in natural environments (58). The results from oxidation experiments are reported as $f_{ox}$, the mass fraction of OC that gets oxidized in the experiments. A low $f_{ox}$ value means the sample was difficult to oxidize and contains a high proportion of OC that is recalcitrant. For the fly ash samples, $f_{ox}$ is low (0 to 0.25), as expected since FOCash has undergone pedogenesis, petrogenesis, and high-temperature incineration, leaving behind the most refractory OC class (14). For shale samples, $f_{ox}$ values were much higher (0.4 to 0.85), implying that a significant portion of FOCrock is reactive and labile, which is consistent with field observations of substantial loss of FOCrock in soils and sediment routing systems (5, 59, 60). Expectedly, the plant samples were highly labile, with a high $f_{ox}$ of 0.9 to 1.0.

Although current methods cannot delineate the microscale (nanometer to micrometer) characteristics of FOCash and directly quantify all the different carbon forms in fly ash (SI Appendix, section S2), our Raman and RPO results together provided constraints on the carbon species composing FOCash in our samples—and this compositional information helped explain results from the oxidation experiments. First, the Raman data indicated the presence of multiple different carbon species, including the dominance of mineral-associated carbon. Second, considering that graphitic carbon is thermally decomposed at temperatures of 700 to 800 °C, the RPO thermograms designated that 20 to 50% of FOCash is composed of graphitic carbon (SI Appendix, Fig. S4) (61). Altogether, these results of our fly ash samples reveal that graphitic carbon is the major constituent in FOCash and nongraphitic carbon occurs mostly in association with minerals. These two forms of carbon—graphitic and mineral-associated—hinted at two plausible mechanisms for preserving FOCash during high-temperature combustion: selective preservation as stable graphitic carbon and mineral protection (62, 63). Nongraphitic carbon is less recalcitrant than graphitic carbon (5, 47). Thus, the relative proportions of graphitic versus nongraphitic carbon may also explain the natural variation in $f_{ox}$ observed in our fly ash samples (Fig. 3 and SI Appendix, Figs. S2 and S3). In any case, the low $f_{ox}$ of FOCash underscores its recalcitrance; simply put, it is a less reactive component in the surficial carbon cycle than rock-derived FOC.

OC in the CJ River Sediments. Chemical oxidation procedures, in conjunction with radiocarbon analyses, also helped resolve the bulk composition of riverine OC. OC in river sediment represents a mixture of radiocarbon-enriched bioclastic OC and radiocarbon-dead FOC (11, 64). In $f_{ox}$-OC space, CJ suspended sediment sits on a mixing trend between a bioclastic OC end member and a radiocarbon-dead FOC end member (Fig. 3D and SI Appendix, section S7). This study also used flush-out procedures to confirm that CJ river FOC could not be oxidized by the chemical treatment method and made up 85% of the residual OC after oxidation (38). The $f_{ox}$ of the core sediment samples from the CJ estuary had a range similar to the CJ suspended sediment samples (0.5 to 0.8). Those samples came from floodplain and fluvial sedimentary facies (65), representing ash-uncontaminated, preindustrial CJ sediment. If we assumed a behavior of FOC in those preindustrial samples similar to that found during the oxidation experiment (i.e., riverine FOC cannot be oxidized and makes up 85% of the residual OC after oxidation), we estimated a FOC$_{preindustrial}$ Content of 0.15 ± 0.02%—a value 6 to 30 times lower than [FOC]$_{ash}$. We treated this estimate as an approximation of rock-derived FOC in the modern CJ sediment (FOC$_{ash}$) without FOC$_{preindustrial}$ contamination. Note that FOC$_{ash}$ represents the final product of FOCash after alteration during erosion and transfer before entering the sedimentary OC pool, thus it is not necessarily equivalent to the fresh FOCash derived from rocks within the CJ basin. To validate our estimate of FOC$_{preindustrial}$ we defined a similar OC mixing trend for preindustrial CJ sediment using our inferred FOC end member ($f_{ox}$ = 0 and [FOC] = 0.15 ± 0.02%) and the bioclastic OC end member (Fig. 3D). The Holocene sediment samples fit this mixing trend (Fig. 3D), suggesting our estimate of FOC$_{preindustrial}$ is robust.

Examining the geochemical data, we also identified hydrologic and sediment transport controls on the degree of mixing observed between FOCash and FOC$_{ash}$. When separating the CJ sediment samples by river discharge (flood versus dry season) (38), distinct trends emerged (Fig. 3E and SI Appendix, Fig. S3).
uncontaminated sediment, we calculated the flux of FOCash:

\[ \text{Flux of FOCash} = (0.15 \pm 0.02) \text{ Mt C} \]

This represents the riverine-transported FOCash flux. It is unclear how much of the wasted fly ash in the basin (Fig. 4A).

Second, we referred to a prior study that estimated a 37±4% of the unutilized fly ash in the basin (Fig. 4A).

Third, we noticed that the FOC content (0.45 ± 0.10%) in our sediment samples from the lower reach of CJ was typically lower than in the samples (0.10 to 0.20%) from regions upstream of the Three Gorges Dam and areas of intense coal consumption (39, 67). This discrepancy can be explained because the mass balance calculations assume FOCash is the only anthropogenic FOC input to the CJ FOC pool. As there may be other anthropogenic sources of fossil carbon, e.g., from petrochemicals (68–70), our approach may not accurately quantify FOCash in all cases. Further studies are needed to refine these estimates.

**Fly-Ash-Sourced OC Flux.**

During 2007 to 2008, around 130 Mt of fly ash was produced in the CJ basin (36% of the total fly ash production in China; SI Appendix). Taking a ash utilization rate of 67% estimated for China (28), 40 Mt of fly ash was released to the environment in the CJ basin; this is a remarkable flux given that the total CJ sediment flux is around 130 Mt y\(^{-1}\). There is currently no systematic treatment of the unutilized ash, suggesting much of this may be released into the environment. From the budget of production alone, it is unclear how much of the wasted fly ash and FOCash enters rivers, but we can use three lines of evidence to constrain the riverine-transferred FOCash flux.

First, we conducted mass balance calculations using the pre-industrial [FOC] (0.15 ± 0.02%) as an approximation of the [FOC] of ash-free sediment. As an approximation of the [FOC] of fly ash, we took 2.25±1.63/1.18% for [FOC]\(_{\text{ash}}\), 0.15 ± 0.02% for [FOC]\(_{\text{CJ}}\), and 0.45 ± 0.10% for [FOC]\(_{\text{CJ}}\) (38), to resolve \( f_{\text{ash}} \) and the fraction of FOCash in the CJ-exported FOC, \( f_{\text{OC-ash}} \). We then employed Monte Carlo random sampling techniques to propagate errors and propagate uncertainties [SI Appendix], reported as medians and the 16th to 84th percentiles of the sampling results. We obtained a \( f_{\text{OC-ash}} \) of 72±19%/12%, with a FOCash riverine flux of 0.42±1.19 Mt C, whereas the total CJ-exported FOC flux is 0.58 ± 0.13 Mt C y\(^{-1}\) (38). We also estimated a \( f_{\text{ash}} \) of 13±7%/12%, which is 13±7%/12% of the total produced fly ash and 39±7%/12% of the ash wasted in the basin (Fig. 4A).

**Fig. 3.** Geochemical characteristics of CJ sediment and fly-ash samples. (A) Histogram of OC content in CJ fly-ash samples with a box-and-whisker plot showing the 5th, 16th, 50th, 84th, and 95th percentiles and mean of OC content for fly-ash samples. (B) Selected Raman spectra of CJ fly-ash samples showing a mix of organic and inorganic mineral phases with mineral and graphitic carbon peaks (D and G bands) denoted (for more data see SI Appendix, Figs. S2 and S3). (C) Probability density of activation energy (E\(_A\)) of a fly-ash sample and a shale sample derived from RPO results, indicating a higher modal E\(_A\) of the fly ash sample than the shale sample. (D) Oxidation fraction \( f_{\text{ox}} \) versus 1/[OC] (reciprocal of OC content) for studied samples, with two dashed lines indicating mixing trends between the fossil OC and biogenic OC end members. (E) Mixing relationships for the CJ sediment collected in the dry season (yellow) versus in the flood season (blue), defined by least-squares linear regression.
2008 (28), leaving transfer in this basin (Fig. 2), the same is not true globally. The globally available mass flux of fly ash in the CJ now matches the scale of natural sediment and thus may partially explain why the CJ FOCash content is lower than estimated from mass balance calculations and from changes in MS of CJ sediment, respectively. The released FOCash flux is estimated from this study as the product of the released fly ash flux and the FOCash content. The 2007 to 2008 riverine FOC flux is estimated in ref. 35. and the silicate weathering flux (2006) is from ref. 25. The riverine FOCash flux (2007 to 2008) and the riverine FOC flux (1950s) are quantified from this study.

Fig. 4. Fluxes of FOC, fly ash, and sediment in the CJ basin. (A) $f_{\text{FOC-ash}}$ (fraction of fly ash-sourced fossil OC in the total flux of fossil OC exported by CJ) as a function of $f_{\text{sed-ash}}$ (mass fraction of fly ash in the total sediment flux) (curves with uncertainty bands determined from Monte Carlo simulations; SI Appendix), with the mix between FOCash and FOC-J (FOC in ash-free sediment), fly-ash release (dashed line, difference between produced and utilized fly ash), and estimates of $f_{\text{sed-ash}}$ (red line from changes in MS of the CJ sediment, and black line and gray range from mass balance calculations). (B) Different types of carbon flux in the CJ basin where "1" and "2" denote riverine FOCash flux estimated from mass balance calculations and from changes in MS of CJ sediment, respectively. The released FOCash flux is estimated from this study as the product of the released fly ash flux and the FOCash content. The 2007 to 2008 riverine FOC flux is estimated in ref. 35, and the silicate weathering flux (2006) is from ref. 25. The riverine FOCash flux (2007 to 2008) and the riverine FOC flux (1950s) are quantified from this study. (C) Changes of riverine FOCash flux versus released (produced – utilized) FOCash flux in 1950 to 2010. (D) Sediment flux and fly-ash flux in the CJ basin in 1950 to 1970 (pre-damming) and 2004 to 2010 (post-damming).

Fossil Carbon Flux Perturbed by Human Activities. Globally, the total fly ash production during the 2000s was around 750 Mt yr$^{-1}$ (28, 71), with annual global river sediment export estimated at 17,800 Mt yr$^{-1}$ (72). Thus, while the mass flux of fly ash in the CJ now matches the scale of natural sediment transfer in this basin (Fig. 2), the same is not true globally. The overall averaged utilization rate of fly ash is not well determined, but the major coal consumers (China, United States, and India, accounting for 70% of the total consumption) reported an average utilization rate of ~50% during 2007 to 2008 (28), leaving ~375 Mt yr$^{-1}$ of fly ash that was not utilized. A global-average FOCash content is challenging to estimate accurately, because FOCash depends on a range of factors including coal types and combustion conditions (see expanded discussion in SI Appendix, section S6) (23, 24, 45, 51)—conditions that likely vary from region to region. For a first-order constraint, we compiled data on FOCash content for 247 samples from different regions and found an FOCash content of 4.70$^{+0.89}_{-1.69}$% (median and 16th to 84th percentiles; SI Appendix, section S5 and Fig. 56), which was on the same order of magnitude as the FOCash content (2.25$^{+0.84}_{-1.18}$%) measured in our CJ fly-ash samples. Note that most global ash FOC content data were estimated via the loss on ignition—a method that can overestimate the true FOC content and thus may partially explain why the CJ FOCash content is lower than estimated globally (see more discussion in SI Appendix, section S7). Considering the global data compilation, the CJ FOCash content likely represents a conservative estimate of the actual carbon content in fly ash. Notably, FOCash contents we measured in CJ ash samples and those from the compiled global dataset were similar to the industrial standards of FOCash content of 5 to 10% in different countries and regions (SI Appendix, section S6) (23, 24, 26, 27), lending confidence to the overall estimates of the FOCash flux. If [FOC]ash found in the CJ samples is typical, a global FOCash yield of 8.43$^{+1.11}_{-1.46}$ Mt yr$^{-1}$ can be expected. Assuming 20% of the utilized fly ash is transported by rivers (we found that this number was 13 to 27% for the CJ basin), the global riverine FOCash flux to the oceans is then 1.69$^{+0.25}_{-0.49}$ Mt yr$^{-1}$, making up 3.9$^{+1.6}_{-1.3}$% of the modern-day riverine FOC flux (43$^{+61}_{-21}$% Mt yr$^{-1}$) (44). Note that this estimate of global FOCash flux carries large uncertainties, and further studies of FOCash contents and ash supply to rivers in different regions will be required to improve upon it. Nonetheless, our first-order estimate of the global-average FOCash of ~4% is lower than the CJ case (37 to 72%), meaning that the CJ basin likely represents an upper end member in the distribution of FOCash production and export. So why does the CJ basin have such a high $f_{\text{FOC-ash}}$, and such a dominant overall flux of fly ash? We attributed this to two of the major anthropogenic modifications of the CJ basin: increasing coal consumption and dam construction.

First, coal consumption in China has substantially increased over the past 60 y, boosting fly ash production (Figs. 2 and 4C). Hosting China’s most economically developed and populated areas, the CJ basin has witnessed intense construction of coal-fired power and steel plants (Fig. 1C), providing a major source of FOCash, especially in its middle and lower reaches (35, 70, 73). In the 2000s, China’s consumption increased to more than 50% of the global coal consumption. Alone, all the provinces in the CJ basin comprise 36% of China’s coal consumption—a value equivalent to 18% of the global coal consumption. Thus, the CJ basin represents a major locus of fly ash production. Second, the continued construction of dams and reservoirs in the CJ basin has decreased fluxes of sediment and FOCash. After the impoundment of the Three Gorges Reservoir in 2003, the CJ sediment export has reduced to ~100
Mt. y \textsuperscript{-1} from ~500 Mt y \textsuperscript{-1} before the dams were emplaced (Fig. 4 C and D) (34), contributing <1% to the global riverine sediment flux to the oceans (72). FOC\textsubscript{rock} is mainly eroded from upstream areas and scales with sediment flux (38, 44), a significant proportion of FOC\textsubscript{rock} is being sequestered in the reservoirs, leading to a reduction in the riverine-carried FOC\textsubscript{rock} flux in the lower CJ reach where many large-scale power and steel plants, the major sources of FOC\textsubscript{ash}, are located (Fig. 1c).

Transport and Fate of Fossil OC. Our analysis revealed that FOC\textsubscript{ash} and FOC\textsubscript{rock} have systematically distinct reactivities. When compared overall to biogenic carbon, the low \textit{f}_{\text{SO}} and high \textit{E}_{\text{SO}} values we observed indicated that FOC\textsubscript{ash} is expected to be significantly more recalcitrant and conserved during transport and storage compared to FOC\textsubscript{rock}. These differences will affect their fates during fluvial transport and storage, leading to different impacts on the carbon cycle. For FOC\textsubscript{ash}, the graphic component is less reactive and is expected to be more conserved as it transits the landscape, whereas the nongraphic carbon is more reactive and thus more likely to interact with active carbon-cycle processes in surface and subsurface environments (5, 47).

The fate of FOC\textsubscript{rock}, as it becomes exposed to surface processes depends on its chemical properties and the geomorphic setting. We saw that FOC\textsubscript{rock} in the CJ basin contains a large fraction that is labile and prone to oxidation (Fig. 3), whereas FOC in river sediments is comparatively recalcitrant (38). This suggested the preferential loss of the labile component during denudation, fluvial transport, and sediment storage in the CJ system—a pattern consistent with prior observations of significant oxidation of FOC\textsubscript{rock} in large fluvial systems (e.g., Amazon) (59). Although laboratory experiments have intimated slow reaction kinetics of FOC\textsubscript{rock} oxidation (e.g., first-order kinetic coefficients on the order of 10\textsuperscript{-4} to 10\textsuperscript{-5} y\textsuperscript{-1}) (74), the long-term transport of OC and sediment (e.g., \textsim 10\textsuperscript{3} to 10\textsuperscript{5} y) in large fluvial systems (75, 76) matches or exceeds the characteristic reaction timescales of FOC\textsubscript{rock} and thus would allow sufficient reaction time for FOC\textsubscript{rock} oxidation. In contrast, FOC\textsubscript{rock} oxidation might be kinetically limited in river systems with smaller catchment sizes and shorter transit timescales such as the rivers in mountainous islands (8). Overall, we hypothesized that the differences in the reactivity of FOC\textsubscript{ash} and FOC\textsubscript{rock} translate into the differences in their fates most profoundly in large alluvial systems (e.g., CJ and Amazon) with long transit times, and such differences are expected to be dampened in smaller catchments with shorter transit times.

Dam building in the CJ basin has probably influenced the fate of FOC\textsubscript{rock} during fluvial transit as well. Previous studies suggested that the high sedimentation rate in the reservoirs would limit oxygen exposure time of carbon-bearing particles and promote their preservation (11, 38, 39, 64). Thus, the reservoirs in the CJ basin might be expected to help sequester and preserve FOC\textsubscript{rock} from upstream CJ, buffering its oxidation in downstream floodplains and estuaries (38). In addition, although there has been an increased supply of FOC from coal ash in the middle-lower CJ basin; one prior study hypothesized that the emplacement of the Three Gorges Dam in 2003 would lead to younger and fresher OC export by the CJ (39). We do not have upstream samples during our study time interval to delineate the downstream changes of riverine OC in 2007 and 2008. However, we noticed that the average proportion of FOC\textsubscript{ash} in our riverine samples in 2007 to 2008 sediment (--25%) was higher than the FOC proportion in the middle-to-lower CJ sediment samples (--10%) collected 1 to 2 y later after our sampling time. This difference suggested a temporal shift toward a lower proportion of FOC in the CJ-exported OC—a trend consistent with the proposed change toward a younger and fresher riverine OC flux after the impoundment of the Three Gorges Reservoir. Nonetheless, continued monitoring and systematic sampling of the whole CJ fluvial network are needed for a more detailed picture of how hydraulic engineering impacts carbon cycling in this system (38, 39).

FOC\textsubscript{ash} and FOC\textsubscript{rock} are also carried by particles of different sizes, which can affect their fate via transport processes. FOC\textsubscript{ash} is mostly encapsulated in micrometer-sized fly ash particles, whereas FOC\textsubscript{rock} is bound to coarser (e.g., sand-sized) grains. Thus, FOC\textsubscript{ash} could more easily bypass dams during flow release, whereas FOC\textsubscript{rock} is likely to be sequestered in reservoirs. When delivered to the CJ estuary and the East China Sea margin where hydraulic conditions and sediment transport and storage processes are complex, the fine-grain-carried FOC\textsubscript{ash} may have more dynamic behavior (e.g., flocculation settling, suspension, and dispersion) and may be spread over a larger depositional area than FOC\textsubscript{rock} (77). The fine particle sizes that carry FOC\textsubscript{ash} can also be more efficiently transported by aeolian processes, which can deliver FOC\textsubscript{ash} to remote areas beyond riverine transport within a given catchment (78). The aeolian flux of FOC\textsubscript{ash} both within and outside of the CJ basin requires further assessment, but we anticipated that these fluxes are minor compared to the riverine flux, considering the dominance of the wet, monsoonal climate in the basin that limits ash transport by aeolian processes (79, 80). In northern China where a drier climate dominates, aeolian processes may well play a more important role transporting FOC\textsubscript{ash} (80, 81).

Conclusions and Implications

The CJ basin illustrates how human activities have significantly altered the carbon cycle at continental scales. In the CJ basin, fly ash contributes a remarkable 37 to 72% of the riverine fossil OC exported to the oceans. Driven by the human pursuit of energy, the riverine-carried FOC\textsubscript{ash} flux has increased while the riverine FOC\textsubscript{rock} flux decreased—and as a result, these two fluxes have converged over an interval of 60 y to amplify the concentration of FOC\textsubscript{ash} on the landscape. This serves as an example of how the pace of the human-induced alteration of the carbon cycle can catch up with nature-sourced carbon at decadal timescales and demarcates another dimension of the human imprint on the short-term carbon cycle beyond that directly associated with CO\textsubscript{2} emission during fossil fuel combustion (19, 82).

Our results showed that not all fossil OC is made equal: FOC\textsubscript{rock} has a significant fraction that is labile and can be oxidized during transport, whereas FOC\textsubscript{ash} is highly recalcitrant (i.e., unreactive) and can be conserved during transport. While coal burning is a leaky process with respect to OC, the way that carbon is transformed by incomplete combustion means that the FOC\textsubscript{ash} that escapes this process is much less likely to end up as CO\textsubscript{2} compared to the FOC\textsubscript{rock} naturally derived from erosion. Furthermore, its fossil origin means FOC\textsubscript{ash} is radiocarbon-dead (7, 11). With increasing coal consumption and ash production (19), FOC\textsubscript{ash} is expected to increase and to contribute to a greater proportion of the total riverine FOC flux to the oceans. With this growing human-induced carbon flux, caution will need to be taken when interpreting radiocarbon-based material flux as well as records from recent offshore sediments. With this observation in mind, given that the magnitude of fly ash release can match natural sediment fluxes at regional scales (e.g., in the CJ basin), the unique properties of FOC\textsubscript{ash} make it a useful tracer of anthropogenic impacts on the OC cycle. By reflecting the history of coal consumption, FOC\textsubscript{ash} in sedimentary cores and other archives could provide a distinct marker of the Anthropocene (78, 83).

Data Availability. All study data are included in the article and/or supporting information.

Acknowledgments. This project was funded by the National Key R&D Program of China (Grant 2017YFD0800004). G.K.L. acknowledges support from a California Institute of Technology Geology Option Postdoctoral Fellowship and a National Ocean Sciences Accelerator Mass Spectrometry Laboratory Graduate Intern Fellowship. W.W.F. and M.P.L. acknowledge support from Foster and Cocoa Stantack, California Institute of Technology's Terrestrial Hazard Observation and Reporting Center, and the Resnick Sustainability Institute. We thank Yuliang Chen for help with data compilation.