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Significant Acidification in Major Chinese Croplands

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Soil acidification is a major problem in soils of intensive Chinese agricultural systems. We used two nationwide surveys, paired comparisons in numerous individual sites, and several long-term monitoring-field data sets to evaluate changes in soil acidity. Soil pH declined significantly ($P < 0.001$) from the 1980s to the 2000s in the major Chinese crop-production areas. Processes related to nitrogen cycling released 20 to 221 kilomoles of hydrogen ion (H^+) per hectare per year, and base cations uptake contributed a further 15 to 20 kilomoles of H^+ per hectare per year to soil acidification in four widespread cropping systems. In comparison, acid deposition (0.4 to 2.0 kilomoles of H^+ per hectare per year) made a small contribution to the acidification of agricultural soils across China.

Acidification can alter the biogeochemistry of ecosystems and adversely affect biota (*1*, *2*). Poorly buffered freshwater systems have been changed substantially by anthropogenic acidification (*3*), mostly by sulfuric and nitric acids, and the surface ocean has acidified measurably from increased carbon dioxide (CO_2) in the atmosphere, raising concerns about marine biodiversity and ecosystem function (*4*–*6*). Anthropogenic acidification of soils has received less attention. Soils are strongly buffered by ion exchange reactions, by the weathering of soil minerals, and (in the acidic range) by interactions with aluminum (Al) and iron (*7*). Soils acidify very slowly under natural conditions over hundreds to millions of years. Old soils and soils in high-rainfall regions tend toward greater acidity (*8*). Naturally acid soils occupy approximately 30% of the world's ice-free land and are commonly associated with phosphorus (P) deficiency, Al toxicity, and reduced biodiversity and productivity (*9*).

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Chinese agriculture has intensified greatly since the early 1980s on a limited land area with large inputs of chemical fertilizers and other resources. Grain production and fertilizer nitrogen (N) consumption reached 502 million and 32.6 million tons nationally in 2007, respectively, increases of 54 and 191% as compared with 1981 (*10*). High levels of N fertilization can drive soil acidification both directly and indirectly (*11*–*13*), and the rates of N applied in some regions are extraordinarily high (*14*) as compared with those of North America and Europe (*15*). These have degraded soils and environmental quality in the North China Plain (*16*) and in the Taihu Lake region in south China (*14*). Here, we investigate whether they also cause significant soil acidification at a national scale.

A national soil survey was conducted during the early 1980s, and pH was determined in all topsoils that were sampled (*17*). For comparison, we collected all published data (*13*) on topsoil pH from 2000 to 2008 and compiled two (unpaired) data sets (1980s versus 2000s) on the basis of six soil groups according to geography and use, with two subgroups per soil group: cereal crops and cash crops (tables S1 and S2 and fig. S1) (*13*). In China, both systems receive very high nutrient inputs as compared with those of other agricultural systems worldwide (*18*), especially the cash crops (such as greenhouse vegetable systems), which have developed rapidly since the 1980s (*19*).

The results reveal significant acidification of all topsoils (average pH declines for the soil groups of 0.13 to 0.80) except in the highest-pH soils, which represent only a small percentage of Chinese cultivated soils (table S1). In all other soil groups, acidification has been greater in cash crop systems (pH decreased by 0.30 to 0.80) than under cereals (0.13 to 0.76) (Table 1). These are substantial changes. The pH scale is logarithmic and a pH decrease of 0.30 corresponds to a doubling in hydrogen ion (H^+) activity.

Soils in group I [for example, leached red soils (*Argi-Udic Ferrosols*) and yellow soils (*Ali-Periudic Argosols*)] are the most acidic in south China and have acidified further since the 1980s, with pH declines of 0.23 and 0.30 ($P < 0.001$) in cereal and cash crop systems, respectively (Table 1). Although net pH decreases for group I soils were small as compared with those of other groups, the impact may be more pronounced because these soils are approaching pH values at which potentially toxic metals such as Al and manganese (Mn) could be mobilized (*20*, *21*).

At the other extreme, soils in group V [mainly fluvo-aquic soils (*Ochri-Aquic Cambosols*), which are widely distributed in north China] are

Table 1. Topsoil pH changes in major Chinese croplands between the 1980s and 2000s. The soil groups are defined in (*13*). NS, not significant; pH range is an average (5 to 95 percentile).

Soil group	1980s		2000s					
			Cereal crop systems*			Cash crop systems†		
	Sample number	pH value	Sample number	pH value	pH change	Sample number	pH value	pH change
I	301	5.37 (4.40–6.60)	505	5.14 (4.17–6.52)	−0.23‡	337	5.07 (3.93–6.44)	−0.30‡
II	1157	6.33 (5.00–8.04)	1101	6.20 (5.00–7.70)	−0.13‡	413	5.98 (4.58–7.49)	−0.35‡
III	297	6.42 (4.50–8.30)	211	5.66 (4.27–8.06)	−0.76‡	98	5.62 (4.27–7.73)	−0.80‡
IV	562	6.32 (5.10–7.89)	537	6.00 (4.84–7.60)	−0.32‡	238	5.60 (4.07–7.42)	−0.72‡
V	995	7.96 (6.39–8.80)	850	7.69 (5.37–8.70)	−0.27‡	520	7.38 (5.69–8.20)	−0.58‡
VI	493	8.16 (7.10–8.80)	250	8.16 (7.49–8.82)	−0.00 (ns)	10	8.17 (7.43–8.93)	0.01 (ns)

*Cereal/fiber crops (such as rice, wheat, maize, and cotton). †High-input cash crops (such as vegetables, fruit trees, and tea). ‡$P < 0.001$.

considered resistant to acidification because of their relatively high $CaCO_3$ content (5 to 10%). However, they have also acidified significantly ($P < 0.001$), with pH decreases averaging 0.27 and 0.58 under cereals and cash crops, respectively. The pH decline in group V is small compared with those of groups III and IV (Table 1) (*13*) but probably resulted in substantial loss of $CaCO_3$. Therefore, soil pH decline might be expected to accelerate in the future.

The broad-scale comparative results are supported by data from 154 agricultural fields, in which strictly paired data were available from the same sites in the 1980s and the 2000s (*13*). Paired *t* tests show that these topsoils were significantly ($P < 0.001$) acidified, with an average pH decline of 0.50 (Fig. 1). Topsoil pH in 53.2% of the sites decreased by over 0.50, 18.2% by 0.30 to 0.50, and 18.9% by 0 to 0.30; only 9.7% of the sites increased in pH. The paired national data strongly support widely occurring soil acidification in Chinese croplands.

We also summarized information from 10 long-term monitoring field (LTMF) sites in which soil pH was measured regularly over an 8- to 25-year period (*13*). Decreases in pH were substantial, from 0.45 to 2.20 (Fig. 2). We found significant soil acidification occurred only in NPK (conventional fertilization) plots ($P < 0.001$), whereas soil pH did not show obvious change in CK (no fertilization) and Fallow (no fertilization and no crop) plots (fig. S2) (*13*).

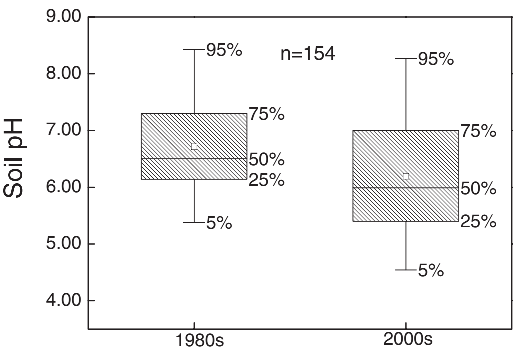

Fig. 1. Topsoil pH changes from 154 paired data over 35 sites in seven Chinese provinces between the 1980s and the 2000s. The line and square within the box represent the median and mean values of all data; the bottom and top edges of the box represent 25 and 75 percentiles of all data, respectively; and the bottom and top bars represent 5 and 95 percentiles, respectively.

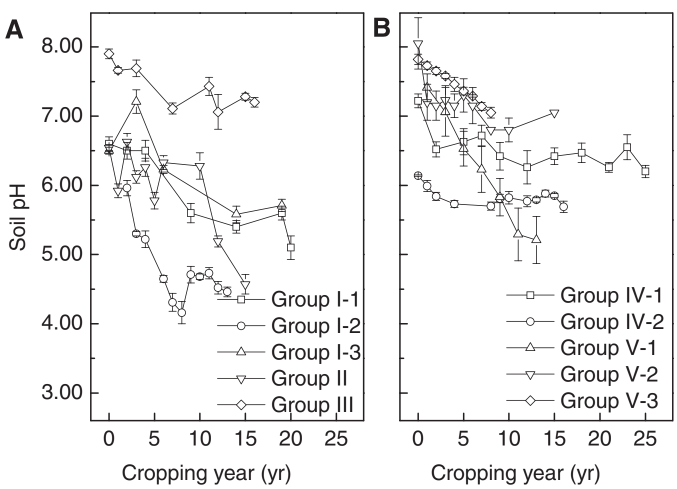

Fig. 2. Long-term changes in topsoil pH in some typical Chinese soils. (**A**) Groups I to III. (**B**) Groups IV and V received conventional rates of NPK fertilizers for 8 to 25 years. Soil groups are described in (*13*). Data are means ± SD.

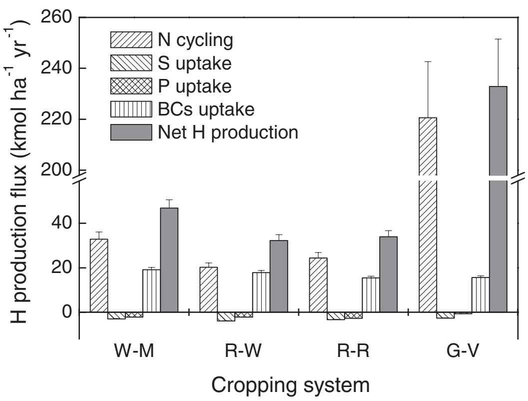

Fig. 3. H^+ production budget of main factors in four typical Chinese cropping systems. W-M, wheat-maize; R-W, rice-wheat; R-R, rice-rice; and G-V, greenhouse vegetables. N cycling, S uptake, and P uptake denote the H produced by N cycling and S and P uptake processes. BCs uptake indicates H released by BCs uptake. Net H production is the algebraic sum of H resulting from N cycling and P, S, and BCs uptake. Data are means ± SD.

Further analysis shows that recent soil acidification in China has resulted mainly from high-N fertilizer inputs and the uptake and removal of base cations (BCs) by plants. In the three major Chinese double-cropping cereal systems (wheat-maize, rice-wheat, and rice-rice), annual N fertilizer rates are usually above 500 kg N ha^{-1} with N use efficiencies of only 30 to 50% (table S3). Calculations based on inputs and outputs of ammonium and nitrate N indicate that N loading contributes 20 to 33 kmol H^+ ha^{-1} $year^{-1}$ of proton generation in these systems (Fig. 3 and table S3). Greenhouse vegetable systems, the major cash crops, receive even higher N fertilizer inputs; in Shandong province, N fertilizer rates above 4000 kg N ha^{-1} $year^{-1}$ are common with N use efficiencies below 10% (*22*, *23*). Under this management, about 220 kmol H^+ ha^{-1} $year^{-1}$ of potential acidity accumulates in each hectare of soil (Fig. 3 and table S3). The proton generation related to N cycling (20 to 221 kmol H^+ ha^{-1} $year^{-1}$) in China is extremely high as compared with values (1.4 to 11.5 kmol H^+ ha^{-1} $year^{-1}$) at lower N fertilizer rates in other regions (*24*).

Plant uptake of BCs together with removal of economic yields and crop residues from fields is another driver of soil acidification because the net removal of excess cations over anions leaves behind equivalent H^+ released to the soil. At current fertilization levels, approximately 25 tons of dry biomass (grain and stalk) (table S4) is harvested annually in the three double-cropping systems, leading to an estimated H^+ production rate by BCs uptake of 15 to 20 kmol H^+ ha^{-1} $year^{-1}$ (Fig. 3 and table S3). In greenhouse vegetable systems, the importance of BCs uptake varies greatly with plant species and yield but overall appears similar to the cereal systems.

Increasing N fertilizer applications has been a major management technique driving high crop yields, which in turn increase the removal of BCs. These factors combined have produced potential acidity equivalent to 30 to 50 kmol H^+ ha^{-1} $year^{-1}$ in double-cropping cereal systems and ~230 kmol H^+ ha^{-1} $year^{-1}$ in greenhouse vegetable systems (Fig. 3). Although acid deposition is an important regional environmental problem in China, strongly affected areas with a precipitation pH of 4.00 to 5.60 (*25*) receive 0.4 to 2.0 kmol H^+ ha^{-1} $year^{-1}$, much of which is buffered by other depositional or soil processes. Overall, anthropogenic acidification driven by N fertilization is at least 10 to 100 times greater than that associated with acid rain (*13*, Fig. 3). In other regions, serious acidification was found in the long-term $(NH_4)_2SO_4$–treated Park Grass soils at Rothamsted in England when no lime was applied to buffer soil acidity (*26*), and Wallace (*27*) reported soil acidification from routine fertilization practices for crop production.

Anthropogenic acidification of Chinese agricultural soils will be difficult to correct as long as excessive levels of N fertilization continue. Goulding and Annis (*28*) found that each 50 kg ha^{-1} of added ammonium-N generates ~4 kmol H^+ ha^{-1} $year^{-1}$ and requires ~500 kg $CaCO_3$ ha^{-1} $year^{-1}$ to neutralize in their field conditions. Similar theoretical calculations show that each kg of applied NH_4-N leached as NO_3-N demands 7.2 kg of $CaCO_3$ to neutralize the acidity generated (*29*, *30*). Adding appropriate amounts of lime in China would be arduous; intensive double-cropping systems that generate 30 to 50 kmol H^+ ha^{-1} $year^{-1}$ would theoretically require 1.5 to 2.5 tons $CaCO_3$ ha^{-1} $year^{-1}$ to counteract soil acidification—and greenhouse vegetable systems would require ten times this amount.

Overuse of N fertilizer contributes substantially to regional soil acidification in China. Since 1980, crop production has increased with rapidly increasing N fertilizer consumption (fig. S5). Decreasing N use efficiency (fig. S5) indicates that more fertilizer N is being lost to the environment (*31*), causing further negative environmental impacts. Optimal nutrient-management strategies can significantly reduce N fertilizer rates without decreasing crop yields (*14*, *32*, *33*), with multiple benefits to agriculture and the environment (*15*), including the slowing of dangerous rates of anthropogenic acidification. Fertilization based on comprehensive, knowledge-based N management practices has become one of the most urgent requirements for sustainable agriculture in China and in other rapidly developing regions worldwide.

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Supporting Online Material

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Materials and Methods
SOM Text
Figs. S1 to S5
Tables S1 to S4
References and Notes

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Peptidomimetic Antibiotics Target Outer-Membrane Biogenesis in *Pseudomonas aeruginosa*

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Antibiotics with new mechanisms of action are urgently required to combat the growing health threat posed by resistant pathogenic microorganisms. We synthesized a family of peptidomimetic antibiotics based on the antimicrobial peptide protegrin I. Several rounds of optimization gave a lead compound that was active in the nanomolar range against Gram-negative *Pseudomonas* spp., but was largely inactive against other Gram-negative and Gram-positive bacteria. Biochemical and genetic studies showed that the peptidomimetics had a non–membrane-lytic mechanism of action and identified a homolog of the β-barrel protein LptD (Imp/OstA), which functions in outer-membrane biogenesis, as a cellular target. The peptidomimetic showed potent antimicrobial activity in a mouse septicemia infection model. Drug-resistant strains of *Pseudomonas* are a serious health problem, so this family of antibiotics may have important therapeutic applications.

Naturally occurring peptides and proteins make interesting starting points for the design and synthesis of biologically active peptidomimetics. We previously synthesized libraries of β-hairpin–shaped peptidomimetics (*1*, *2*) based on the membranolytic host-defense peptide protegrin I (PG-I) (*3*). These mimetics contain loop sequences related to that in PG-I, but linked to a D-proline–L-proline template, which helps to stabilize β-hairpin conformations within the macrocycle (*4*, *5*) (Fig. 1A). One sequence variant, L8-1, had broad-spectrum antimicrobial activity like that of PG-I, but with a reduced hemolytic activity on human red blood cells (*2*). To optimize this lead, we performed iterative cycles of peptidomimetic library synthesis and screening for improved antimicrobial activity. The optimal hit from each library was used as a starting point for the synthesis and testing of variations in a subsequent library. This structure-activity trail led sequentially to mimetics L19-45, L26-19, and L27-11 (Fig. 1). L27-11

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