Occurrence and congeners specific of polychlorinated biphenyls in agricultural soils from Southern Jiangsu, China

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Abstract

A total of 198 agricultural soil samples were collected from Zhangjiagang and Changshu in Southern Jiangsu for analysis of 13 polychlorinated biphenyls (PCBs) in order to assess the levels of pollution, sources, area distribution, and potential risk for the environment. All methods were rigorously tested and an adequate quality control was ensured. Only one site had no PCBs residues, and the highest total PCBs concentration in the surface soils was 32.83 ng/g. The average concentration in all the soil samples was 4.13 ng/g, signaling low-level pollution. Tetra-, penta-, and hexa-chlorinated biphenyls were dominant species in soil samples, accounting for more than 75% of $\sum$PCBs in the soil samples. PCB118 was the most abundant congener in all the samples. The PCB118 was about 20% of $\sum$PCBs. The soil organic matter content showed only a weak correlation with the levels of all PCB congeners, in which a better correlation was noted for the more volatile lighter PCB congeners than for the heavier homologues. To a certain extent, the sources and land use seemed to influence the levels of PCBs.

Key words: agriculture soil; polychlorinated biphenyls (PCBs); congeners; distribution

Introduction

Polychlorinated biphenyls (PCBs) are listed along with 11 other organic compounds by Stockholm Convention as the persistent organic pollutants that could seriously threaten the environment and human health. Although their usage has been banned in a lot of countries, they still represent an important class of priority pollutants due to their widespread, long-term persistence, and high toxicity (Yu et al., 2001). PCBs easily dissolve in lipid tissues, so they are deleterious to human health via their distribution and transfer by the food chain (Miao et al., 1996; Ilene et al., 1997). Additionally, as a hormone interferon, PCBs have a great adverse impact on the procreation of both human beings and animals (Nie, 2003).

In China, approximately 10000 t of PCBs were produced from 1965 to 1974 (the production of PCBs was banned in 1974), with 9000 t as trichlorobiphenyl (PCB$_3$, chlorine content is 42%) used primarily as impregnants in power capacitors and 1000 t as pentachlorobiphenyl (PCB$_5$, chlorine content is 54%). PCB$_3$ and PCB$_5$ are similar in compositions to Aroclor 1242 and Aroclor 1254, respectively, used mainly as additives of paint, printing ink, and as lubricants (Jiang et al., 1997; Qin et al., 2003). Moreover, during the 1950s to 1980s, China imported numerous capacitors containing PCBs from Belgium and France (Meng et al., 2000). After mass production and extensive usage, these PCBs entered the soil and adjacent water via waste emissions, oil leakage, volatilization, dry and wet deposition or other means, thus resulting in widespread environmental pollution. Recently, numerous reports have identified various levels of PCB residues in the water, soil, sediment, rice, fish, and birds in the Yangtz Delta industrialized area (Chu et al., 1995; Bi et al., 2001; Nakata et al., 2005).

Soil is usually the source and receptor of environmental pollutants. This study quantified the levels of PCBs in Changshu and Zhangjiagang, which covered certain urban farmlands and farmlands near the factories. This is probably the first comprehensive study to present the PCB-congener levels in the agricultural soils in China, which provides the essential statistics for risk assessments in the Yangtz Delta.

1 Materials and methods

1.1 Materials

Based on the reported abundance and toxicity, the following PCB congeners, identified using the IUPAC numbering system, were targeted for analysis: 18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 170, 180, and 194. In this analysis, 2,4,5,6-tetrachloro-m-xylene and decachlorobiphenyl (PCB209) were used as internal standards and 2,4,5,6-tetrachloro-m-xylene also as a recovery standard. All standards were purchased from Dr. Ehrenstorfer Labo-

ratories, Augsburg, Germany.

All solvents used were distilled-in-glass (AR grade) and were checked for interference prior to use. Granular anhydrous sodium sulfate (AR grade) was heated to 400°C for 4 h prior to use. After being heated at 130°C for 16 h, silica gel (100–200 mesh) was deactivated with 3.3% deionized water of its weight, and then stored in a closed container until use. All glassware was scrupulously cleaned according to the requirement of USEPA and washed with solvents before used.

1.2 Sample collection

A total of 198 surface soil samples were collected from Zhangjiagang and Changshu in Southern Jiangsu in 2004. The locations of the sampling stations are shown in Fig.1. Throughout the survey, a global positioning system (GPS) was used to locate the sampling sites. The sampling sites were those used mainly for agricultural purposes and certain sites were close to factories, such as chemical plants, electroplate plants, metalwork plants, printing and dyeing plants, and so on. All samples were dried at room temperature, stones and vegetation were removed, sieved (100 mesh), and stored in closed vessels until further analysis.
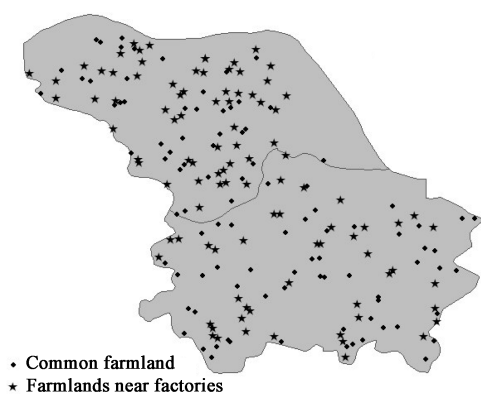

• Common farmland
★ Farmlands near factories

Fig. 1 Sampling map of soils in Zhangjiagang and Changshu of Jiangsu, China.

1.3 Sample extraction and clean up

For determination of PCBs in soils, about 15 g of soil was homogenized with anhydrous sodium sulfate (Na_2SO_4) in a glass centrifugal tube until a free flowing powder appeared. Approximately 1 g of copper powder was added to remove the sulfur. Before extraction, surrogates containing tetrachloro-m-xylene and decachlorobiphenyl were added to the samples. The sample was then extracted with 3×20 ml hexane/acetone (1/1, v/v) by ultrasonication (20 min) and separated by centrifugation. The extract was then concentrated to approximately 1 ml for further purification.

Fractionation was done with anhydrous sodium sulfate modified silica gel chromatography column (3 g of silica gel, with 2 cm anhydrous sodium sulfate added on the upper layer). After the sample was transferred onto the column, PCBs were eluted from the column with hexane in the first 25 ml fraction. The fraction was concentrated under a gentle stream of nitrogen to 1 ml.

1.4 Instrumental analysis

The extracts were injected into a Hewlett Packard 6890 GC-ECD equipped with auto-injector. An HP-5 fused silica capillary column (30 m length, 0.32 mm i.d., 0.25 μm film thickness) coated with 5% phenyl 95% methylpolysiloxane was used for the analysis. The oven temperature started at 90°C (holding time 1 min), increased to 140°C at 20°C/min, to 240°C at 3°C/min (holding time 5 min) and finally to 300°C at 10°C/min (holding time 10 min). Injector and detector temperatures were 280°C and 310°C, respectively. Nitrogen was used as the carrier and make-up-gase. A 1-μl solution was injected in splitless mode.

1.5 Quality control and quality assurance (QA/QC) and quantification

The detection limit of PCBs in samples was designed to be thrice the values of procedural blanks. The PCB detection limit is 0.01–0.015 ng/g. The average recoveries for PCBs through the analytical procedures (laboratory treatment) was 65%–114% as determined by spiking PCBs mixtures in the soil samples, and the relative standard deviation (RSD) was 10%. They all meet the requirement of USEPA (Recovery: 70%–130%, RSD is <30%).

Calibration curves (detector response vs. amount injected) were performed for every compound to be quantified. The range of linearity of the detector was evaluated from the curves generated by plotting the detector signal/amount injected versus the amount injected. All measurements were performed in the linear range for each compound. The quantitative data were corrected for surrogate recoveries.

2 Results and discussion

2.1 Pollutant levels of agricultural soil samples

The results are summarized in Table 1. Only one site showed no PCBs residues. The mean and the highest

Table 1 Concentrations of PCB congeners in soil (ng/g dw)[a]

PCB	Maximum	Minimum	Mean	SD	Frequency (%)
18	nd	nd	0.00	0.00	0.00
28*+31	6.96	nd	0.10	0.56	11.60
52*	6.26	nd	0.65	0.69	93.40
44	26.37	nd	0.49	2.00	77.27
101*	5.11	nd	0.58	0.57	87.88
149	1.38	nd	0.02	0.13	0.02
118*	8.46	nd	0.86	0.93	89.39
153*	5.48	nd	0.45	0.74	82.83
138*	9.24	nd	0.73	1.15	74.75
180*	5.58	nd	0.13	0.44	37.37
170	6.43	nd	0.12	0.51	51.01
194	2.25	nd	0.02	0.17	0.03
Total	32.83	nd	4.13	4.32	

[a]Mean, SD, maximum, minimum were calculated assuming not detected (nd) measurements were equal to zero; *seven indicator PCBs in the European criteria; frequency: frequency of determination.

∑PCBs (the sum of 13 PCB congeners) were 4.13 ng/g, and the maximum was 32.83 ng/g, which showed that the pollutants were at low levels. PCB118 has the highest concentration of 0.86 ng/g, PCB18 was not detectable, and concentrations of PCB28, 31, 149 were extremely low.

In China, PCB concentrations and distribution in soils have been reported more frequently in recent years, but most environmental monitoring provided total concentrations of PCB mixtures (Dong *et al.*, 2002). Average ∑PCBs in agricultural soils in Wentai area was 788 ng/g (Chu *et al.*, 1995). The residue levels in Shanghai paddy field soil, Nanjing paddy field soil, Kunshan farmland soil, Lanzhou pesticide plant soil, and Shanghai farmland soil were 2.5, 5.0, 7.6, 79.9, 0.62 ng/g, respectively (Nakata *et al.*, 2005). Since the determination methods for PCBs varied with the published reports and only 13 congeners were determined in this study, there is a low comparability between the data from different area. Relative to the wider ∑PCBs range of null to 32.83 ng/g in Zhangjiagang, the ∑PCBs in Changshu ranged from 0.24 ng/g to 13.63 ng/g. There was no significant difference between the residue levels in these two areas through statistic analysis. This research indicated that the pollution level of PCBs in this region of North Jiangsu was comparatively low.

2.2 Distribution character and toxicity assessment of PCB congeners

The survey on PCB contamination was conducted earlier in foreign countries than in China, and the PCB assessment criteria varied in different countries. For example, in the health risk assessment, Belgium and Holland used 7-congener indicators of PCB28, 52, 101, 118, 138, 153, 180 to identify the composition of PCBs, while PCB28, 52, 101, 138, 153, 180 were selected in Germany (Kim *et al.*, 2004). Rein and Bittens (2001) pointed out that 51–77 PCB congeners were of environmental concern for their potential toxicity, environment occurrence, mobility, and transport potential.

According to the toxicity and behavioral character of PCB congeners, this study selected 13 PCB congeners as references for assessment (Table 2), in which PCB28, 52, 101, 118, 138, 153, 180 were chosen as indicators in Europe and were present in most PCB-mixtures and in the

environmental samples (Chu *et al.*, 1995; Bi *et al.*, 2001; Huang, *et al.*, 2000; Kim *et al.*, 2004; Atuma *et al.*, 1996; Meijer *et al.*, 2003). Besides, these 13 PCB congeners comprise tri-chlorinated to hepta-chlorinated biphenyls, including lighter and heavier homologues. So the research of these 13 PCB congeners can generally represent the contamination condition and congener difference. Five of the above-mentioned seven reference PCBs, that is, except PCB28 and PCB180, were found in more than 75% of the soil samples. As noted previously, PCB153 is the most abundant congener in the sediment, especially in the human blood and organism medium (Atuma *et al.*, 1996; Frignani *et al.*, 2001; Chou *et al.*, 2004; Kim *et al.*, 2005); the statistical data of the global background soils also show PCB138 to have the highest concentration in all congeners (Meijer *et al.*, 2003). However, this study showed that PCB118 comprises about 20% of all congeners, which is followed by PCB138, 52, and 101.

The PCB-congener distribution is governed mainly by the congener properties and the industrial usage. Commonly, the vapor pressure, water solubility, and biodegradation probability of PCBs decrease with increasing degree of chlorination, while the lipid-water partition coefficient and particle appetency are opposite to it. After entering the environment, PCB compositions will change significantly under various environmental processes and reactions, including volatilization, solubilization, leaching, bioconcentration, biodegradation, and other physical transports (e.g., runoff and soil erosion). In short, the heavier homologues have larger tendency to be retained by the soil than the lighter ones. Fig.2 shows the PCB-congener profile in the soil samples. This result indicates that tetra-, penta-, and hexa-chlorinated biphenyls were dominant species, followed by tri-, hepta-chlorinated biphenyls, which may result from the use of highly chlorinated PCB products, such as PCB5, in this area (Nakata *et al.*, 2005).

PCBs are strongly retained in soils and sediments despite being subjected to a lot of loss processes and reactions. Doick *et al.* (2005) determined the half-lives of PCB28 and PCB52 in soil to be 10.9 and 11.2 years, respectively. Anders *et al.* (2003) suggested the mean residence times of PCB153 and PCB180 were on the order of 110 and 70 years, respectively, by estimating the global

Table 2 Toxicity and present ratios of the 13 indicator PCB congeners

PCB	Structure		Abduction type[a]	Potential toxicity[b]	TEFs[c]	Frequency[b]
PCB18	Trichloro-biphenyl	2,2',3		Null	-	⩾ 5%
PCB28		2,2',5		Null	-	⩾ 5%
PCB31		2,4',5		Null	-	⩾ 5%
PCB52	Tetrachloro-biphenl	2,2',5,5'	Wk PB	Low	-	⩾ 0.5%
PCB44		2,2',3,5'		Null	-	⩾ 5%
PCB101	Pentachloro-biphenyl	2,2',4,5,5'	PB	mh	-	⩾ 0.5%
PCB118		2,3',4,4',5	Mixed	eh	0.0001	⩾ 0.5%
PCB149	Hexachloro-biphenyl	2,2',3,4',5,6		Null	-	⩾ 5%
PCB153		2,2',4,4',5,5'	PB	mh	-	⩾ 0.5%
PCB138		2,2',3,4,4',5'	Mixed	eh	-	⩾ 0.5%
PCB180	Heptachloro-biphenyl	2,2',3,4,4',5,5'	PB	mh	-	⩾ 0.5%
PCB170		2,2',3,3',4,4',5	Mixed	eh	-	⩾ 0.5%
PCB194	Octachloro-biphenyl	2,2',3,3',4,4',5,5'	PB	mh	-	⩾ 0.5%

Wk PB: weak PB inducers; mixed: mixed-type MFO inducers; PB: PB inducers; TEFs: toxic equivalency factors for risk assessment of human and mammal health; mh: mid-high; eh: extremely high; [a] McFarland and Clarke, 1989; Chu *et al.*, 1995; [b] Rein and Bittens, 2001; [c] Van *et al.*, 1998.
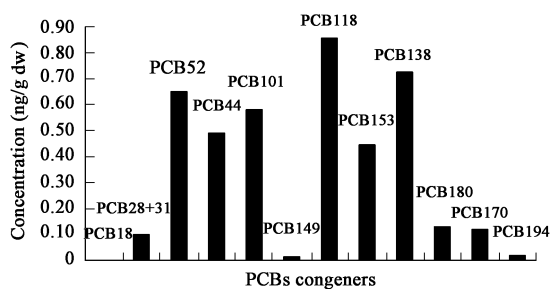
Fig. 2 PCB-congener profile in soil.

inventory and burial fluxes of PCBs in continental shelf sediments. As shown in Tables 1 and 2, PCB118, a mono-ortho congener and the most abundant congener in this study, has the highest potential toxicity among the 13 congeners, with its toxic equivalency factors as 0.0001 recommended by the WHO. Although the residual levels of PCBs in soil are low, their health risks warrant consideration, due to their high bioaccumulation and environmental persistence. To determine the risk level thoroughly in this area, it is necessary to investigate the exposure of foodstuff and human body to existing PCBs.

2.3 Spatial distribution of PCBs and influencing factors

Soil PCB concentrations were strongly influenced by proximity to the source and the soil organic matter (SOM) content. Most (>80%) of the estimated soil PCB burden remains in the "global source region" of the Northern Hemisphere (NH) temperate latitudes (30–60°N) or in the OM-rich soils (Meijer *et al.*, 2003). The SOM content has been shown to influence soil PCB concentrations at the local, regional, and global scale (Meijer *et al.*, 2002, 2003), but it seems too simplistic to consider it as the most important factor (Meijer *et al.*, 2003; Edgar *et al.*, 2003). The transportation and spatial distribution of PCBs is a complex process. The land use/vegetative cover presumably influences the rate and processes of air-surface exchange and the dynamics of PCBs within the soil in different ecosystems.

Total PCB concentrations are here regressed against the SOM content. All data are natural log transformed to reduce the data scatter and to allow for linear fits. The R^2 is only 0.0737, implying low correlation. Furthermore, the levels of lighter PCB congeners having a higher volatility show a better correlation with the OM content than do the heavier congeners, which are consistent with the earlier reports (Frignani *et al.*, 2001; Meijer *et al.*, 2003). This implies that the atmospheric transport and air-surface exchange are important factors influencing the soil PCB levels.

In the sampling area, there were two types of sampling sites, the common farmlands (101 sampling sites) and farmlands near factories (97 sampling sites). Through the nonparametric test of ∑PCBs and OM content between the two kinds of sampling sites, small differences were noted in respective low significant levels of 0.184 and 0.283, with $P>0.05$. However, when the relation between ∑PCBs and OM% was analyzed, soil samples near factories exhibited

a higher correlation, reflecting probably the more intimate impact of the pollution source on the concentration distribution.

Three types of land use (vegetable field, paddy field, dry field) were selected for analysis with the nonparametric Kruskal-Wallis H test method. The significance of differences between paddy field and dry field was 0.005, with $P⩽0.05$. On the whole, ∑PCBs in the paddy field was higher than that in the dry field. That ∑PCBs varied with different land use and is probably related to the difference in planting patterns and soil conditions.

3 Conclusions

After determination of 198 samples of surface soil from Changshu and Zhangjiagang, the highest PCB concentration in the surface soils was 32.83 ng/g. The average concentrations in Changshu and Zhangjiagang were 4.957 ng/g and 3.307 ng/g, respectively, indicating low pollution levels. There was a significant variation among the levels of PCB congeners, with null residue of dichlorobiphenyl, wide distribution and high levels of tetra-, penta-, and hexa-chlorinated biphenyls, which account for 75% of the total PCB congeners; the tri-, hepta-chlorinated biphenyls were found at low levels. This pattern may result from the use of highly chlorinated PCB product, such as PCB_5, in or near this area. PCB118 has the highest level of about 20% in all PCBs congeners. The organic matter content showed a weak correlation with the levels of all PCB congeners, and the strength of this relationship was more evident for the more volatile PCB congeners than for the heavier homologues. This finding suggests a potential impact of air transportation and air-soil deposition on the soil pollution. Correlation between ∑PCBs in soils and soil OM contents is higher for farmlands near factories than for common farmlands, suggesting that the proximity to the PCB source is the main factor on the PCB distribution. Further, the land use is also noted to influence the pollution level, in which the paddy fields showed higher ∑PCBs than the dry fields.

References

Anders J, Orjan G, Johan A *et al.*, 2003. Global accounting of PCBs in the continental shelf sediments[J]. Environ Sci Technol, 37: 245–255.

Atuma S S, Linder C E, Andersson O *et al.*, 1996. CB153 as indicator for congener specific determination of PCBs in diverse fish species from Swedish waters[J]. Chemosphere, 33(8): 1459–1464.

Bi X H, Chu S G, Xu X B, 2001. Transport of PCBs in contaminated paddy fields[J]. Acta Scientiae Circumstantiae, 21(4): 454–458.

Chen W Q, Hong H S, Zhang L P *et al.*, 2004. Persistent organochlorine pollutants in surface sediments and suspended particulate matter of Zhujiang River Estuary[J]. Journal of Xiamen University (Natural Science), 43(B08): 230–235.

Chou C C, Chen Y N, Li C S, 2004. Congener-specific polychlorinated biphenyls in cetaceans from Taiwan waters[J]. Arch Environ Contam Toxicol, 47: 551–560.

Chu S G, Yang C, Xu X B *et al.*, 1995. Polychlorinated biphenyl congener residues in sediment and soil from pollution area[J]. China Environmental Science, 15(3): 199–203.

Doick K J, Klingelmann E, Burauel P *et al.*, 2005. Long-term fate of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in an agricultural soil[J]. Environ Sci Technol, 39: 3663–3670.

Dong L, Feng Y P, Peng H J *et al.*, 2002. Analysis of PCBs in environmental samples[J]. Environmental Monitoring in China, 18(1): 35–38.

Edgar P J, Hursthouse A S, Mattews J E *et al.*, 2003. An investigation of geochemical factors controlling the distribution of PCBs in intertidal sediments at a contamination hot spot, the Clyde Estuary, UK[J]. Applied Geochemistry, 18: 327–338.

Frignani M, Bellucci L G, Carraro C *et al.*, 2001. Polychlorinated biphenyls in sediments of the Venice Lagoon[J]. Chemosphere, 43: 567–575.

Huang Y R, Shi J H, Tang L, 2000. Analysis of polychlorobiphenyl in environmental sample by GC-MS[J]. Journal of Chinese Mass Spectrometry Society, 21(4): 45–46.

Ilene R D, William M L, Gordon W N *et al.*, 1997. Position paper of the american council on science and health: public health concerns about environmental polychlorinated biphenyls (PCBs)[J]. Ecotoxicology and Environmental Safety, 38: 71–84.

Jiang K, Li L, Chen Y *et al.*, 1997. Determination of PCDD/Fs and dioxin-like PCBs in Chinese commercial PCBs and emission from a testing PCB incinerator[J]. Chemosphere, 34: 941–950.

Kim M, Kim S, Yun S *et al.*, 2004. Comparison of seven indicator PCBs and three coplanar PCBs in beef, pork, and chicken fat[J]. Chemosphere, 54(10): 1533–1538.

Kim B H, Ikonomou M G, Lee S J *et al.*, 2005. Concentrations of polybrominated diphenyl ethers, polychlorinated dibenzo-*p*-dioxins and dibenzofurans, and polychlorinated biphenyls in human blood samples from Korea[J]. Science of the Total Environment, 336: 45–56.

McFarland V A, Clarke J U, 1989. Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: considerations for a congener-specific analysis[J]. Environmental Health Perspectives, 81: 225–239.

Meng Q Y, Chu S G, Xu X B, 2000. Advances of PCBs environmental adsorption behavior research[J]. Chinese Science Bulletin, 45(15): 1572–1583.

Meijer S N, Steinnes E, Ockenden W A *et al.*, 2002. Influence of environmental variables on the spatial distribution of PCBs in Norwegian and U.K. soils: implications for global cycling[J]. Environ Sci Technol, 36: 2146–2153.

Meijer S N, Ockenden M A, Sweetman A *et al.*, 2003. Global distribution and budget of PCBs and HCB in background surface soils: Implications for sources and environmental processes[J]. Environ Sci Technol, 37: 667–672.

Miao X S, Chu S G, Xu X B, 1996. Advances in the research of structure-activity relationships for polychlorinated biphenyls[J]. Progress In Chemistry, 8(4): 293–300.

Nie X P, 2003. The advance in environmental eco-toxicology of polychlorinated biphenyls[J]. Ecologic Science, 22(2): 171–176.

Nakata H, Hirakawa Y, Kawazoe M *et al.*, 2005. Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai City region, China[J]. Environmental Pollution, 13: 415–429.

Qin Z F, Zhou J M, Chu S G *et al.*, 2003. Effects of Chinese domestic polychlorinated biphenyls (PCBs) on gonadal differentiation in *Xenopus laevis*[J]. Environmental Health Perspectives, 111: 553–556.

Rein A, Bittens M, 2001. Identification of environmentally relevant PCB-congeners–Considerations for a multimedia environmental risk assessment[EB/OL]. http://www.uni-tuebingen.de/sowa/sites/presentations.html.

Van den Berg M, Birnbaum L, Bosveld A T C *et al.*, 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife[J]. Environmental Health Perspectives, 160(12): 775–792.

Yu G, Huang J, Zhang P Y, 2001. Persistent organic pollutants: one of the important global environmental problems[J]. Environmental Viewpoint, 4: 34–39.